THE UNIVERSITY OF ALBERTA

THE RADIOLYSIS OF CYCLOPENTANE

BY

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "The Radiolysis of Cyclopentane" submitted by Leonard G. Walker in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

The gamma radiolysis of cyclopentane in the liquid phase at room temperature was investigated. Four major products were observed: hydrogen ($G_o = 5.35$), pentene-1 ($G_o = 0.74$), cyclopentene ($G_o = 2.97$), and cyclopentylcyclopentane ($G_o = 1.29$).

A kinetic model for the scavenging of ions produced in pairs is presented. Application of the model to electron scavenging by sulfur hexafluoride and octafluorocyclobutane suggests that the ion pair population is distributed over separation distances, y, in a manner well approximated by a $y^{-\frac{5}{2}}$ function. With this distribution function the scavenging model predicts a region of scavenging efficiency dependent on the square root of the scavenger concentration. The hydrogen yields from fully scavenged cyclopentane solutions of octafluorocyclobutane indicate that the G value for hydrogen that has ionic precursors is 3.4.

The isotopic forms of hydrogen from cyclopentane solutions of ND_3 show that a hydrocarbon ion intermediate acts as a Brønsted acid toward ND_3 to form ND_3H^+ ions. The decomposition of isotopically mixed ammonium ions has an isotope effect greater than about 2 for the cleavage of an N-H bond compared to an N-D bond.

Hydrogen yields from cyclopentane solutions of benzene show at least two distinct intermediates for this product. Below about 1% benzene hydrogen inhibition may involve predominantly the scavenging of cyclopentane positive ions. Above 1% other hydrogen precursors are inhibited; these may be "hot" or thermal hydrogen atoms or neutral excited cyclopentane molecules capable of activation transfer to benzene.

ACKNOWLEDGEMENTS

The author would like to express his appreciation to his research director, Dr. G. R. Freeman and to Dr. R. Crawford and Dr. W. F. Allen for valuable discussions during the course of the work.

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INTRODUCTION

A. RADIATION CHEMISTRY

1. Definition of Radiation Chemistry.

Radiation chemistry may be defined as the study of the chemical effects produced by the absorption of high energy radiation through multiple interaction processes. Radiation chemistry is distinguishable from photochemistry. In photochemistry photons are completely absorbed by an electronic system in a single interaction which may result in either discrete, continuum, or ionized final states. Radiations producing radiation chemical effects include high energy photons(X rays and gamma rays), nucleons, positrons, negatrons, α particles, and other stripped or partially stripped fast nuclei such as deuterons, fission fragments, etc. Such radiations transfer their energy to the medium along their paths in numerous stochastic interactions and consequently inhomogeneously for sufficiently large systems and for times short compared to molecular motion.

In addition to excitation, the penetration of high energy radiations in a medium results in ion formation at the primary stage. For this reason they are frequently called ionizing radiations. Radiolysis is that aspect of radiation chemistry concerning the chemical transformations induced by these ionizing radiations. This report will be concerned almost exclusively with the gamma radiolysis of hydrocarbons, especially liquid cyclopentane.

2. General History

Fundamental discoveries in physics and chemistry at the close of the nineteenth century, such as X rays by Roentgen (1) in 1895, radioactivity in uranium by Becquerel (2) in 1896, and polonium (3) and radium (4) by the Curies and Bemont in 1898, had immediate implications for chemists. The newly discovered penetrating radiations and emanations associated with radioactivity were found to produce profound changes in exposed materials. Some of the effects noticed included the ionization of gases, the formation a photographic latent image, the decomposition of water and aqueous solutions, and the coloration of some minerals.

W.H. Bragg (5) [1907], using the quantitative data of Ramsay and Soddy (6) [1903] for the chemical decomposition of water by the α particles from radon, calculated that the number of water molecules decomposed was approximately the same as the number of ions that would have been produced in air for the same radiation exposure. He referred to these facts as a "curious parallelism in numbers ...." As ionization in gases was easily measured, quantitative work on the radiation chemistry of gases progressed rapidly. The ionic yield (M/N), the ratio of the number of molecules undergoing change (M) to the number of ion pairs formed (N) served as a useful indicator of radiation sensitivity. S.C. Lind (7) used this concept as early as 1912. It was realized that for some gases the ionic yield greatly exceeded unity. Independently, S.C. Lind and W.A. Mund developed "ion cluster" theories to explain the large ionic yields. The basis of these theories was the condensation of neutral molecules on an ion by polarization forces, followed by reaction on charge neutralization.

Almost simultaneously with the discovery and development of the nuclear aspects of chemistry another fundamental chemical advance occurred when M. Gomberg (8) [1900] resurrected and placed on a firm basis the concept of a free radical. The first good evidence that aliphatic free radicals had at least a transitory existence in thermal decompositions came from the work of Paneth and Hofeditz (9) [1929]. However, neutral reactive intermediates had been postulated earlier to explain the kinetics of some gas reactions (Bone and Coward (10)[1908], Langmuir (11)[1912], Christainsen (12)[1919]). Using the Paneth mirror removal technique Rice and coworkers (13) showed that many first order thermal decompositions of organic molecules had chain mechanisms involving aliphatic free radicals. Of historical importance is Debierne's (14)[1914] suggestion that the radiolysis of water involved neutral radicals, contrary to the generally held opinion that only ionic species were the reaction intermediates.

Applying mass spectroscopic and thermochemical data with quantum mechanical calculations, Eyring, Hirschfelder, and Taylor (15)[1936] showed that for the radiation induced ortho-to-para conversion of hydrogen, large clusters around an ion were of low probability and that the products of neutralization of ions may be neutral fragments which could initiate a chain reaction with a large ionic yield. These workers also pointed out the following facts which have important implications in radiation chemistry:

a) Primary ions have a free radical character.

b) Primary ions may undergo secondary ion molecule reactions to generate a neutral radical.

c) The energy required to produce an ion pair, W, in a pure gas is about twice the first ionization potential. Nearly as much energy is partitioned among excitation, dissociation to neutral fragments, and increased thermal energy, as is expended in causing ionization.

In a series of studies beginning in 1938 Essex and coworkers (16) developed a technique suitable for distinguishing the contributions of different processes to radiolysis yields in gases. The method consists of measuring the ionic yield as a function of the electric field strength. They suggested that it was possible to determine the fraction of the decomposition which, in the absence of a field, is consequent on the recombination of ions. Essex has summarized the results of these studies in 1954 (17). However, to date, the technique has had little application in condensed phase radiolysis.

Radiation chemistry received its greatest impetus with the nuclear reactor programs starting in Canada and the United States in about 1942. The effects of high energy radiations on matter in the condensed phase then assumed a very practical importance. Although much empirical knowledge of radiation damage to engineering structural materials and to biological systems was quickly obtained it is clear that a complete understanding of radiolytic mechanisms is still to be achieved. Only through a study of the simplest chemical systems such as water, aqueous solutions, and simple organic compounds can fundamental advances be made. Radiolytic yields in condensed phases are now commonly expressed as G values, the number of molecules destroyed or product molecules formed for each 100 ev of energy absorbed by the medium.

The work of Eyring, Hirschfelder and Taylor showed that the available data on the radiation induced ortho-to-para conversion in hydrogen could be understood in terms of a neutral radical chain reaction. Thompson and Schaeffer (18) examined radiation induced exchange in highly purified equimolar mixtures of H_2 and D_2, with and without added rare gases. They showed that in this system ionic chain processes were 10^2 times as important as neutral radical processes in causing exchange. The potential effect of impurities in a radiolytic system was forcefully illustrated. It was shown that when 4 parts of xenon per million was present in the H_2 - D_2 mixture the exchange rate decreased one hundred fold (19).

B. THE PHYSICAL INTERACTION OF GAMMA RADIATION WITH MATTER

1. The Radioactive Decay of ^{60}Co

The experimental work to be presented later in this report has used exclusively the gamma radiation resulting from the events contingent on the radioactive decay of ^{60}Co. Appreciable concentrations of the latter nuclide can be produced through neutron capture by natural cobalt stored in an intense neutron flux such as that occurring in a critical nuclear reactor. The gamma radiation depends on the emission, in cascade, from nuclear excited states of ^{60}Ni. The pertinent data are shown in Figure I-1 (20). The rate controlling process is the β^- decay of ^{60}Co as shown in equation I-1. The half-life for this process is

$$^{60}Co \longrightarrow {}^{60}Ni + \beta^- + \bar{\nu} \text{ (antineutrino)} \qquad \text{(I-1)}$$

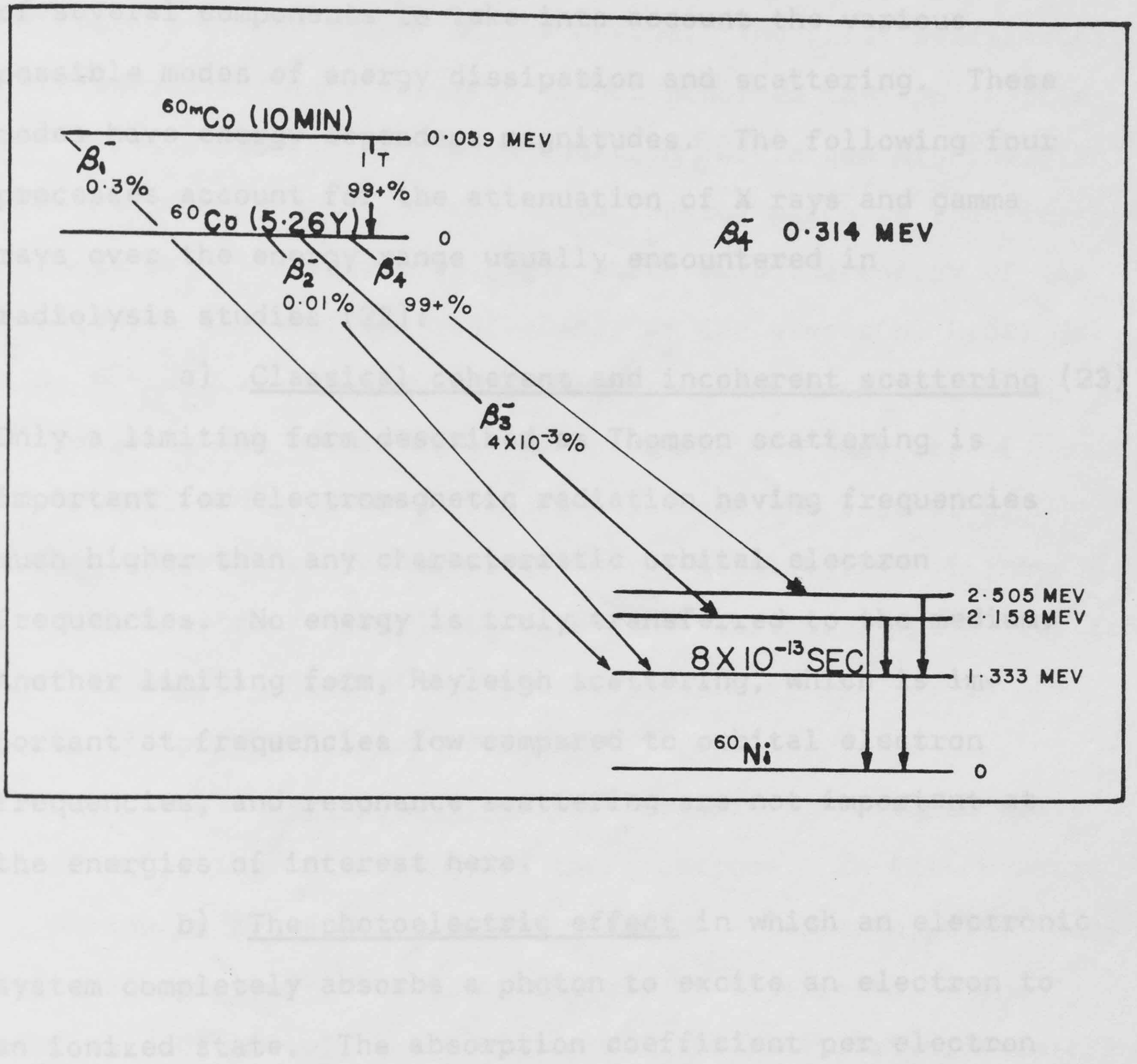
5.26 years (21). For all practical chemical purposes the β^- decay of ^{60}Co ultimately gives two gamma rays one of 1.17 Mev and another of 1.33 Mev. The β^- radiation itself, having a maximum energy of 0.314 Mev. is of no consequence using the techniques reported in the present work because of their short range (in metal and glass) compared to the wall thicknesses of irradiation vessels.

2. Attenuation of High Energy Electromagnetic Radiation

The attenuation of a monoenergetic beam of electromagnetic radiation occurs exponentially on traversing

FIGURE I - 1

Decay Scheme for ^{60}Co



60mCo (10 MIN)
0·059 MEV
IT
99+%
β1−
0·3%
60Co (5·26Y)
0
β2−
0·01%
β4−
99+%
β4− 0·314 MEV
β3−
4 X 10−3%
2·505 MEV
2·158 MEV
8 X 10−13 SEC
1·333 MEV
60Ni
0

an increasing thickness of an absorbing medium. The absorption coefficient defining this attenuation is composed of several components to take into account the various possible modes of energy dissipation and scattering. These modes have energy dependent magnitudes. The following four processes account for the attenuation of X rays and gamma rays over the energy range usually encountered in radiolysis studies (22):

a) Classical coherent and incoherent scattering (23) Only a limiting form described as Thomson scattering is important for electromagnetic radiation having frequencies much higher than any characteristic orbital electron frequencies. No energy is truly transferred to the medium. Another limiting form, Rayleigh scattering, which is important at frequencies low compared to orbital electron frequencies, and resonance scattering are not important at the energies of interest here.

b) The photoelectric effect in which an electronic system completely absorbs a photon to excite an electron to an ionized state. The absorption coefficient per electron is dependent on an average binding energy and consequently is a function of the effective atomic number of the medium.

c) The Compton process in which a photon can interact with an electron, as if free, to partially transfer momentum and energy. Only the energy transferred to the electron may be truly absorbed by the system. For photon energies large compared to electronic binding energies the Compton absorption coefficient per electron is independent of the effective atomic number of the medium. The first satisfactory treatment of this scattering effect required the application of Dirac's relativistic wave equation [Klein and Nishina, (24)]. The maximum fraction of the photon energy which is transferable to the recoil electron is $\frac{2\alpha}{1+2\alpha}$ where α is the energy of the photon in units of the rest energy of the electron, 0.511 Mev., ie. $\alpha = \frac{h\nu}{M_e C^2}$. For the two kinds of photons resulting from ^{60}Co decay the recoil electrons have maximum energies of 0.96 Mev. and 1.12 Mev. Figure I-2 shows the results of calculations* for the complete energy distribution of these recoil electrons giving the number of intitial Compton electrons per ev energy interval for the absorption of 10^{12} ev in one gram of "polymethylene", $(CH_2)x$.

d) Pair production which occurs at energies above 1.02 Mev., the rest energy of two electrons. In this process a photon is transformed into a positron - negatron pair. Some of the energy of these electrons may be dissipated in the medium. Ultimately the positron will be annihilated, resulting in an emission of photons with total energy of 1.02 Mev.

Between 0.01 Mev. and 10 Mev. the true total electronic absorption coefficient for photons, $_e\mu$, can be written as

$$_e\mu = {_e\tau} + {_e\sigma_a} + {_e\kappa} \qquad \text{(I-2)}$$

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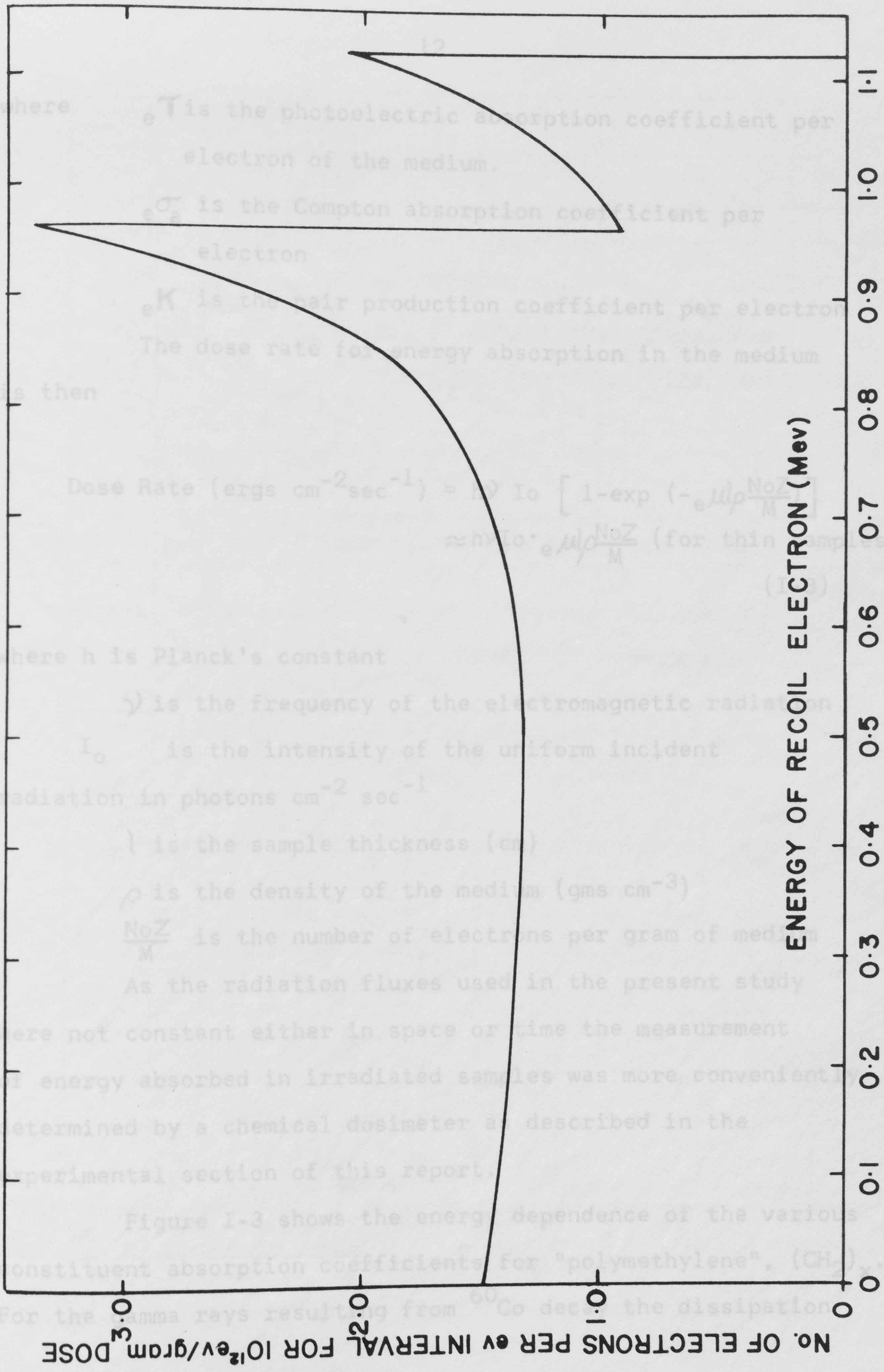
* Use was made of equation 26.7 in the article by R.D. Evans in Handbuch der Physik, 34, 267, (1958).

FIGURE I-2

Distribution of Compton Electrons from ^{60}Co Gamma Radiation


ENERGY OF RECOIL ELECTRON (Mev)
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
1·1
No. OF ELECTRONS PER ev INTERVAL FOR 10¹² ev/gram DOSE
1·0
2·0
3·0

where $_e\tau$ is the photoelectric absorption coefficient per electron of the medium.

$_e\sigma_a$ is the Compton absorption coefficient per electron

$_e\kappa$ is the pair production coefficient per electron

The dose rate for energy absorption in the medium is then

$$\text{Dose Rate (ergs cm}^{-2}\text{sec}^{-1}) = h\nu\, I_o \left[1-\exp\left(-{}_e\mu l \rho \frac{N_oZ}{M}\right)\right]$$
$$\approx h\nu I_o \cdot {}_e\mu l \rho \frac{N_oZ}{M} \text{ (for thin samples)} \tag{I-3}$$

where h is Planck's constant

ν is the frequency of the electromagnetic radiation

I_o is the intensity of the uniform incident radiation in photons cm^{-2} sec^{-1}

l is the sample thickness (cm)

ρ is the density of the medium (gms cm^{-3})

$\frac{N_oZ}{M}$ is the number of electrons per gram of medium

As the radiation fluxes used in the present study were not constant either in space or time the measurement of energy absorbed in irradiated samples was more conveniently determined by a chemical dosimeter as described in the experimental section of this report.

Figure I-3 shows the energy dependence of the various constituent absorption coefficients for "polymethylene", $(CH_2)_x$. For the gamma rays resulting from ^{60}Co decay the dissipation

FIGURE I-3

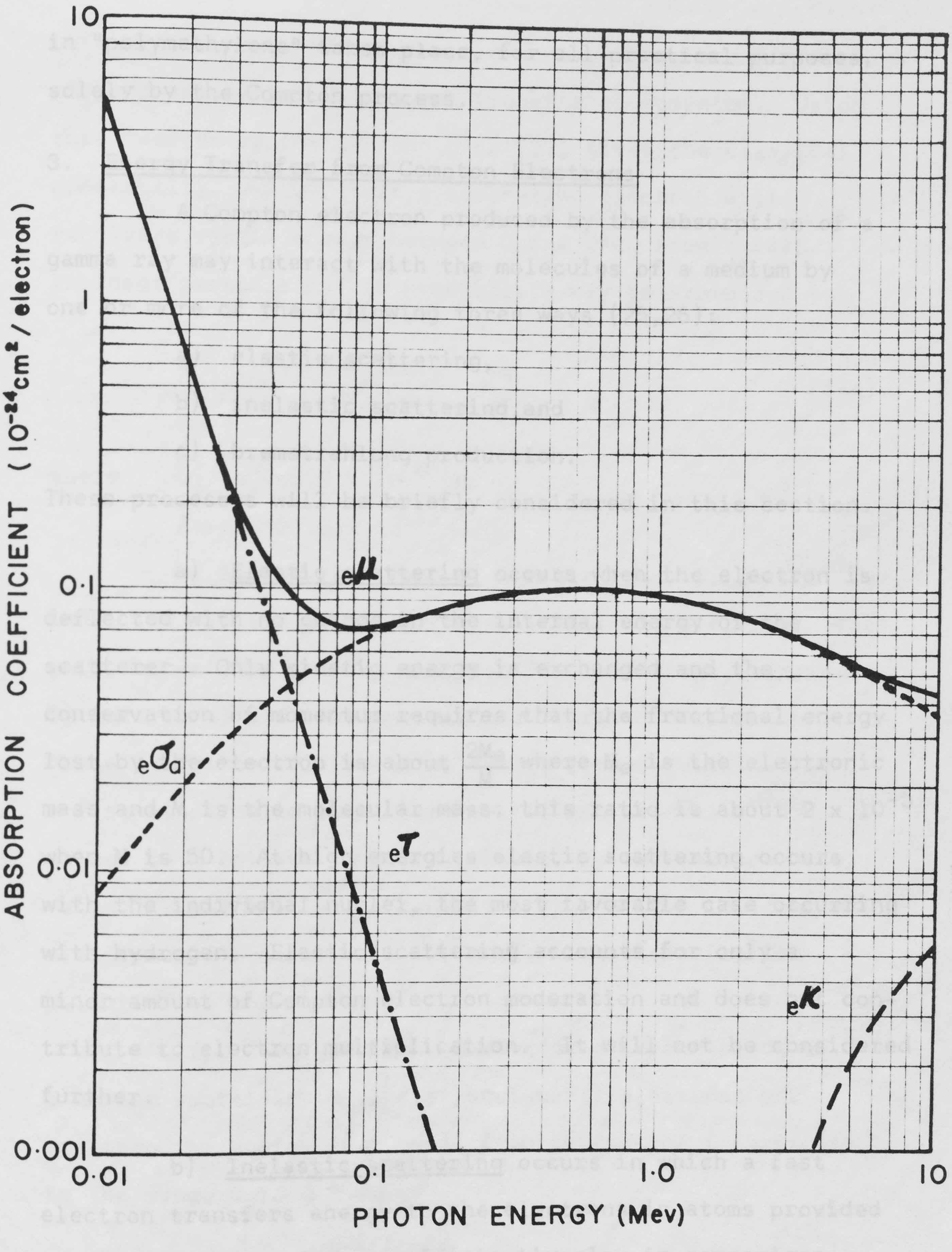
Absorption Coefficient of Polymethylene, $(CH_2)_x$, for Various Photon Energies.

${}_e\mu$ is the total absorption coefficient per electron

${}_e\tau$ is the photoelectric absorption coefficient per electron

${}_e\sigma_a$ is the Compton absorption coefficient per electron

${}_e\kappa$ is the pair production coefficient per electron


ABSORPTION COEFFICIENT (10^{-24}cm^2 / electron)
10
1
0·1
0·01
0·001
0·01
0·1
1·0
10
PHOTON ENERGY (Mev)
$_e\mu$
$_e\sigma_a$
$_e\tau$
$_e\kappa$

in "polymethylene" takes place, for all practical purposes, solely by the Compton process.

3. Energy Transfer from Compton Electrons

A Compton electron produced by the absorption of a gamma ray may interact with the molecules of a medium by one or more of the following three ways (25,26):

a) elastic scattering,
b) inelastic scattering, and
c) bremstrahlung production.

These processes will be briefly considered in this section.

a) Elastic scattering occurs when the electron is deflected with no change in the internal energy of the scatterer. Only kinetic energy is exchanged and the conservation of momentum requires that the fractional energy lost by the electron is about $\frac{2M_e}{M}$ where M_e is the electronic mass and M is the molecular mass; this ratio is about 2×10^{-5} when M is 50. At high energies elastic scattering occurs with the individual nuclei, the most favorable case occurring with hydrogen. Elastic scattering accounts for only a minor amount of Compton electron moderation and does not contribute to electron multiplication. It will not be considered further.

b) Inelastic scattering occurs in which a fast electron transfers energy to the electrons in atoms provided their orbital speeds are sufficiently slow in comparison to that of the incident particle. Otherwise, bound electrons respond adiabatically without transfer of momentum. Using this "sudden approximation" Bohr (27) gives the classical probability, P(Q), that a scattering electron will receive a recoil energy between Q and Q+dQ from a fast incident particle. This probability may be expressed as

$$P(Q)dQ = \frac{8\pi a_o^2 (R\infty)^2}{m_e v^2} \frac{dQ}{Q^2} \qquad \text{(I-4)}$$

where a_o is 0.529×10^{-8} cm,

$R\infty$ is 2.18×10^{-11} erg,

m_e is the rest mass of the electron, 9.10×10^{-28} gm,

and v is the speed of the fast incident electron. The units of $P(Q)dQ$ are cm^2 electron^{-1}. Collisions described by Eqt. (I-4) are sometimes called "hard" or "knock-on". These calculated differential energy losses sustained by a fast electron in such "hard" collisions are valid for values of Q between some lower limit, H, and extends to a value T/2 where T is the kinetic energy of the incident electron. H must be well above the highest excitation potential of the medium.

If a fast electron penetrates a thickness ds of a medium containing N_m indistinguishable electrons per cm^3 then the energy lost, -dT, from the incident particle in the range Q to Q + dQ is

$$-dT(Q) = N_m \cdot \frac{8\pi a_o^2 (R\infty)^2}{m_e v^2} \cdot \frac{dQ}{Q^2} \cdot Q ds \qquad \text{(I-5)}$$

The total linear loss from the incident electron will then be

$$-\left(\frac{dT}{ds}\right)_{\text{hard}} = N_m \frac{8\pi a_0^2 (R\infty)^2}{m_e v^2} \int_H^{T/2} \frac{dQ}{Q} \qquad \text{(I-6)}$$

Bethe (28), in a quantum-theoretical treatment for energy transfers in "soft" collisions to the quantized states (also the continuum) of hydrogen and hydrogen-like atoms, gives the general result for linear energy loss applicable to "soft" collisions ($Q_{\min} \leqslant Q \leqslant S$). It may be expressed as

$$-\left(\frac{dT}{ds}\right)_{\text{soft}} = N_m \frac{8\pi a_0^2 (R\infty)^2}{m_e v^2} \left[\sum_j \epsilon_j \ln \frac{2 m_e v^2 S}{I_j^2 (1-\beta^2)} - \beta^2\right]$$

(I-7)

S is the maximum energy transferable to a state such that the oscillator strengths for transitions to all higher lying states are negligibly small. ϵ_j is the fraction of electrons in the medium of a particular class, for example, inner shell electrons of carbon. I_j is the mean excitation potential of the j class of electrons. β is vc^{-1} where c is the velocity of light in vacuum. The mean excitation potential of a molecular medium $\bar{I}$ is given by:

$$\sum_j \epsilon_j \ln I_j = \ln \bar{I} \qquad \text{(I-8)}$$

Using published values of I_j for individual atoms (29), the mean excitation potential of $(CH_2)_x$ is 51.2 ev. The assumption is made in deriving Eqt. (I-7) that the incident electron has a higher speed than any bound electron in the scattering medium.

The total collisional linear energy loss for an incident electron with an instantaneous kinetic energy T is $-\left(\frac{dT}{ds}\right)_{coll}$. This quantity is given by the sum of the expressions representing "hard" and "soft" collisions:

$$-\left(\frac{dT}{ds}\right)_{coll} = -\left(\frac{dT}{ds}\right)_{hard} -\left(\frac{dT}{ds}\right)_{soft} \qquad \text{(I-9)}$$

Bethe (30) gives this total linear energy loss for electrons in the non-relativistic region as (in our symbols)

$$-\left(\frac{dT}{ds}\right)_{coll} = N_m \frac{16\pi a_o^2 (R\infty)^2}{m_e v^2} \ln\left[\frac{T}{\bar{I}}\sqrt{\frac{e}{2}}\right] \qquad \text{(I-10)}$$

where e is the natural number 2.718.... This result is accurate to only a few per cent since the majority of electrons generated by Compton scattering of ^{60}Co rays have speeds in the relativistic region. For relativistic electrons

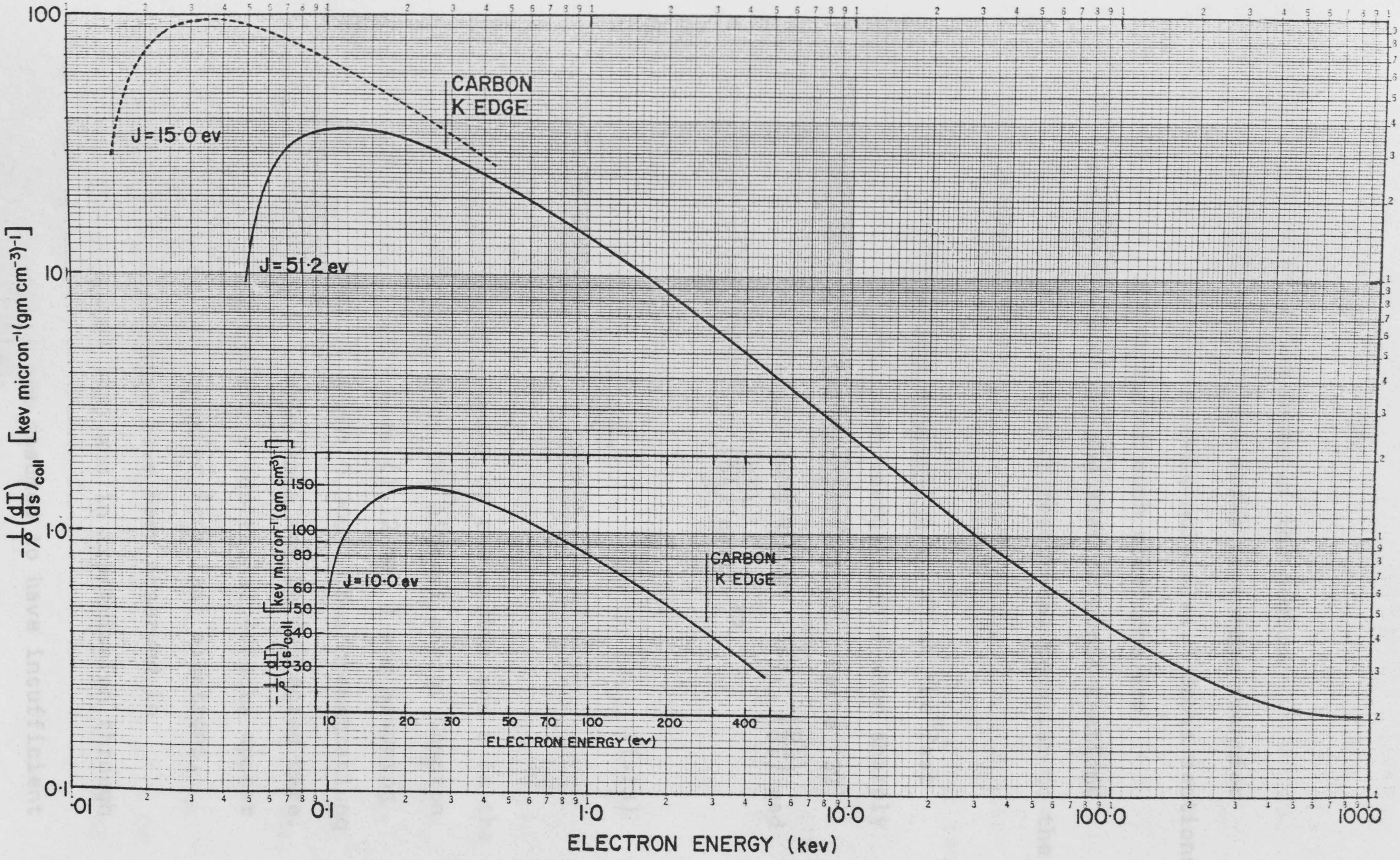
$$-\left(\frac{dT}{ds}\right)_{coll} = N_m \frac{8\pi a_o^2 (R\infty)^2}{m_e v^2} B \qquad \text{(I-11)}$$

$$\text{where } B = \ln\left(\frac{m_e v^2 T}{2\bar{I}^2(1-\beta^2)}\right) - \left[2(1-\beta^2)^{1/2} - 1 + \beta^2\right]\ln 2 + 1-\beta^2 + \frac{1}{8}\left[1-(1-\beta^2)^{1/2}\right]^{1/2} \qquad \text{(I-12)}$$

The speed of incident electrons with energies of approximately 300 ev is comparable to the speed of inner shell electrons in hydrocarbons. Equation (I-11) does not apply below this energy. There is no satisfactory theory at this time for treating energy losses from such low energy electrons. As the energetic electron slows down, the K shell electrons of carbon atoms in the medium become less efficient in the transfer of energy from the fast particle. Below 284 ev the K shell electrons in carbon atoms cannot contribute to the inelastic energy losses described by Eqt. (I-11). Furthermore, electrons with energies below the first electronic excitation potential of the hydrocarbon medium (about 10 ev) cannot lose energy through inelastic electronic collisions. On the other hand, the decrease in the effective number of electrons in the medium which contribute to the stopping power may be compensated to some extent by a smaller mean excitation potential. This follows from the fact that valence shell electrons have relatively low excitation and ionization potentials compared to those for inner shell electrons. Figure I-4 shows calculated values of $-\frac{1}{\rho}\left(\frac{dT}{ds}\right)_{coll}$ for electrons of energy E kev in $(CH_2)_x$. ρ is the density of the medium in gm cm^{-3}. Equation (I-11) was used in these calculations. When using a value of $\bar{I} = 51.2$ ev, all electrons contributed to the stopping power. When $\bar{I}$ was taken as 10.0 ev or 15.0 ev, only 75% of the electrons, viz., only the valence shell electrons were considered to

FIGURE I-4

Collisional Energy Losses, $-\frac{1}{\rho}\left(\frac{dT}{ds}\right)_{coll}$, in $(CH_2)_x$ for Electrons. J denotes the mean excitation potential of the medium.

100
10
1·0
0·1
·01
0·1
1·0
10·0
100·0
1000
ELECTRON ENERGY (kev)
$-\frac{1}{\rho}\left(\frac{dT}{ds}\right)_{coll}$ [kev micron⁻¹(gm cm⁻³)⁻¹]
J=15·0 ev
J=51·2 ev
CARBON
K EDGE
150
100
80
60
50
40
30
$-\frac{1}{\rho}\left(\frac{dT}{ds}\right)_{coll}$ [kev micron⁻¹(gm cm⁻³)⁻¹]
J=10·0 ev
CARBON
K EDGE
10
20
30
50
70
100
200
400
ELECTRON ENERGY (ev)

contribute to the stopping power of the medium.

Little is known of the modes of energy transfer from slow electrons* to polyatomic molecules. Cross sections for the inelastic scattering of such electrons are generally a small fraction of the elastic cross sections (26) and they show characteristic resonances peculiar to the individual molecule (31).

c) Bremstrahlung production in which the fast Compton electrons may emit high energy quanta when sharply deflected, especially in nuclear collisions. Bethe (32) gives the ratio of the bremstahlung energy loss, $-\left(\frac{dT}{ds}\right)_{rad}$ to that for collisional loss, $-\left(\frac{dT}{ds}\right)_{coll}$, as

$$\frac{-\left(\frac{dT}{ds}\right)_{rad}}{-\left(\frac{dT}{ds}\right)_{coll}} = \frac{TZ}{1600 m_e c^2} \qquad \text{(I-13)}$$

Z is the effective atomic number of the medium and c is the speed of light in vacuum. For the highest energy Compton electrons expected in this work (1.12 Mev) and assuming Z to be 4.8 this ratio is about 0.006. Thus bremstrahlung production as a mode of energy loss may be neglected here.

In the condensed phase additional effects appear to be involved in energy transfer from fast electrons. Characteristic energy losses have been observed in scattering from surfaces (33) and in transmission through

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* Here, slow electrons are assumed to have insufficient energy to cause ionization.

thin films (34). The effect was treated by, among others, Bohm and Pines (35), on the basis of collective energy losses to an electron plasma. However, the effect is not limited to electronic conductors since it has also been observed with ionic (36) and covalent (37) solids. The use of experimentally determined mean excitation potentials, I_j, may alleviate to some extent the neglect of the characteristic energy losses in the present work, at least for fast electrons.

When electron penetration takes place in a dense medium, electronic polarization of the absorber takes place at distant scatterers. This affects energy losses in the "soft" collisions. This effect has been treated by Sternheimer (38). A comparison of collisional energy losses with and without corrections for this effect shows that for polystyrene the correction lowers $-\left(\frac{dT}{ds}\right)_{coll}$ by about 3% (39). The correction, however, will be neglected here.

The emission of Čerenkov radiation will be a mode of energy loss for those electrons having a speed greater than that of light in the medium. In the near ultraviolet region of the spectrum and extending to longer wavelengths, the refractive index of a liquid alkane is greater than unity. For example, η_D for cyclopentane is 1.40 showing that the velocity of sodium D light is only 2.24×10^{10} cm sec^{-1} in the medium. The kinetic energy of electrons with this velocity is 0.220 Mev. From Figure I-2 it is apparent that a large fraction of the initial Compton electrons have velocities in excess of 2.24×10^{10} cm sec^{-1}. However, for these Compton electrons Čerenkov losses only amount to about 0.1% of the collisional losses (40) and they will be ignored.

4. Degradation Spectrum of Secondary Electrons

Recent radiolytic studies with liquid alkanes show that it is possible to interfere with the geminate recombination of parent positive ions and their counter electrons through the addition of suitable reagents (41, 42). A quantitative treatment of such competitive participation of ion scavengers in the recombination process requires information on the number of ionic intermediates produced by a given amount of absorbed energy, and their lifetimes. Equation (I-4) shows that the low energy loss events are dominant for the fast secondary and Compton electrons. If the lifetime of an ion depends on the separation between it and a counter ion then the range of these low energy electrons will be of paramount importance in a kinetic analysis. The range of an electron, R, may be calculated from the total linear energy loss, $-\left(\frac{dT}{ds}\right)_{\mathrm{tot}}$, if this is known, by the following integration:

$$R = \int_{T_o}^{\mathrm{Thermal}} \left[-\left(\frac{dT}{ds}\right)_{\mathrm{tot}}\right]^{-1} dT \qquad \text{(I-14)}$$

T_o is the initial energy of the electron. The total linear energy loss, $-\left(\frac{dT}{ds}\right)_{tot}$, consists of several energy dependent components which are associated with elastic scattering, inelastic collisional losses, radiation losses, etc. For the present purposes, $-\left(\frac{dT}{ds}\right)_{tot}$ may be approximated by two components:

$$-\left(\frac{dT}{ds}\right)_{tot} \approx -\left(\frac{dT}{ds}\right)_{l} \; -\left(\frac{dT}{ds}\right)_{coll} \qquad \text{(I-15)}$$

where $-\left(\frac{dT}{ds}\right)_{l}$ is the linear energy loss to the medium through processes other than electronic excitation or ionization (or bremstrahlung). Excitation of vibrational and rotational states contribute to $-\left(\frac{dT}{ds}\right)_{l}$, for example. For electrons with energy less than the minimum mean electronic excitation potential of the medium*, $\bar{I}_{min}$, the total linear energy loss is $-\left(\frac{dT}{ds}\right)_{l}$. $-\left(\frac{dT}{ds}\right)_{coll}$ describes the electronic collisional energy losses as expressed, for example, by the Bethe equation (I-11). Above $\bar{I}_{min}$, the total linear energy loss is largely due to $-\left(\frac{dT}{ds}\right)_{coll}$.

Samuel and Magee (43) developed an expression for $-\left(\frac{dT}{ds}\right)_{l}$ and applied it to electron thermalization in liquid water. They estimated that a 15 ev electron is thermalized in about 3×10^{-14} sec with a root mean square separation from the parent positive ion of 18 Å if the fractional energy loss per collision is 2.5% or 12 Å if 4%. A maximum recapture time of about 2×10^{-13} sec

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* Such electrons will hence forth be designated subexcitation electrons.

was also calculated. They assumed liquid water behaved as highly compressed water vapor in applying experimental data on both the fractional energy loss per collision and the electron mean free path. Platzman has questioned the validity of applying the gas phase data to liquid water; he has outlined a different approach to calculating $-\left(\frac{dT}{ds}\right)_l$ (44). Platzman estimated the root mean square separation of the thermalized electron and its counter ion in liquid water to be about 50 Å for an electron initially having about 10 ev. There is no theory at the present time that is suitable for treating the behavior of subexcitation electrons in liquid alkanes. However, some experimental results have been reported on the ranges of low energy electrons in organic materials. Fleisher (45) determined the mean penetration distance of electrons with initial energies of approximately 10 ev to be about 50 Å in an absorbed film of a liquid, long chain alkyl-phosphorus compound. Seiler and Stärk (46) found that the secondary electrons generated by a 20 kev electron have a mean free path of 95±20 Å in a polymeric hydrocarbon film.

Much use has been made of the electron ranges in water as tabulated by Lea (47). Lea's results were obtained by integrating the range relation (I-14) using only $-\left(\frac{dT}{ds}\right)_{coll}$. The range of an electron having an energy of 100 ev, for which the Bethe equation gives an estimate of $-\left(\frac{dT}{ds}\right)_{coll}$ to be 33.23 kev per micron (47), was arbitrarily taken as 0.0031μ, ie.,

$$\text{range of 100 ev electron} = \frac{100\ \text{ev}}{33.23\ \text{kev per}\,\mu}.$$

No consideration was given to a range-energy relation for subexcitation electrons. From their study of radiation induced conductance of n-hexane, Hummel et al (48) have suggested a range-energy relation which gives optimum agreement with their data. Fig I-5 shows some estimated and measured penetration ranges* for electrons of various energies.

A knowledge of the fraction of ion pairs, N(y), having separation distances between y and y + dy on thermalization is a quantity of importance in a quantitative treatment of ion scavenging. The distribution, N(y), is not directly determined although chemical scavenging results give some information on its "shape". In principle, N(y) can be determined by combining information on the range of electrons having energy E with information on the fraction of ionization events in which electrons are ejected with energy between E and E + dE, ie., an N(E). However at the present time there is no experimental data on N(E) for hydrocarbons. Birkhoff and coworkers have measured "slowing down spectra", ie., N(E), by using radioactive β-particle emitters imbedded homogeneously in several metallic media. The spectral distribution of electron flux for ^{64}Cu (β^+ and β^- have maximum energies of 657 kev and 571 kev, respectively) imbedded in natural copper was determined over the energy range of 11 ev to

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* The total range, R, of an electron corresponds to the complete sinuous path of the decelerated electron and may be 1.4 times as large as the penetration range (49).

FIGURE I-5

Some Estimated and Measured Penetration Ranges of Electrons with Various Energies

A. Estimated ranges given as full curves:

a) A. Hummel et al (48) best fit with irradiation induced conductance data for n-hexane.

b) Lea's (47) calculated ranges in water divided by 1.4.

c) Integration of $-\left(\frac{dT}{ds}\right)_{coll}$ of Figure (I-4) for $(CH_2)_x$; $-\left(\frac{dT}{ds}\right)_{coll}$ calculated by starting $\bar{I}$ at $\bar{I}_{min}$, viz., 10.0 ev, and increasing $\bar{I}$ to 51.2 ev as T increases from 30 ev to energies above the K shell energy. The results plotted are

$$\frac{1}{1.40}\int_{T}^{\bar{I}_{min}}\left[-\left(\frac{dT}{ds}\right)_{coll}\right]^{-1} dT$$

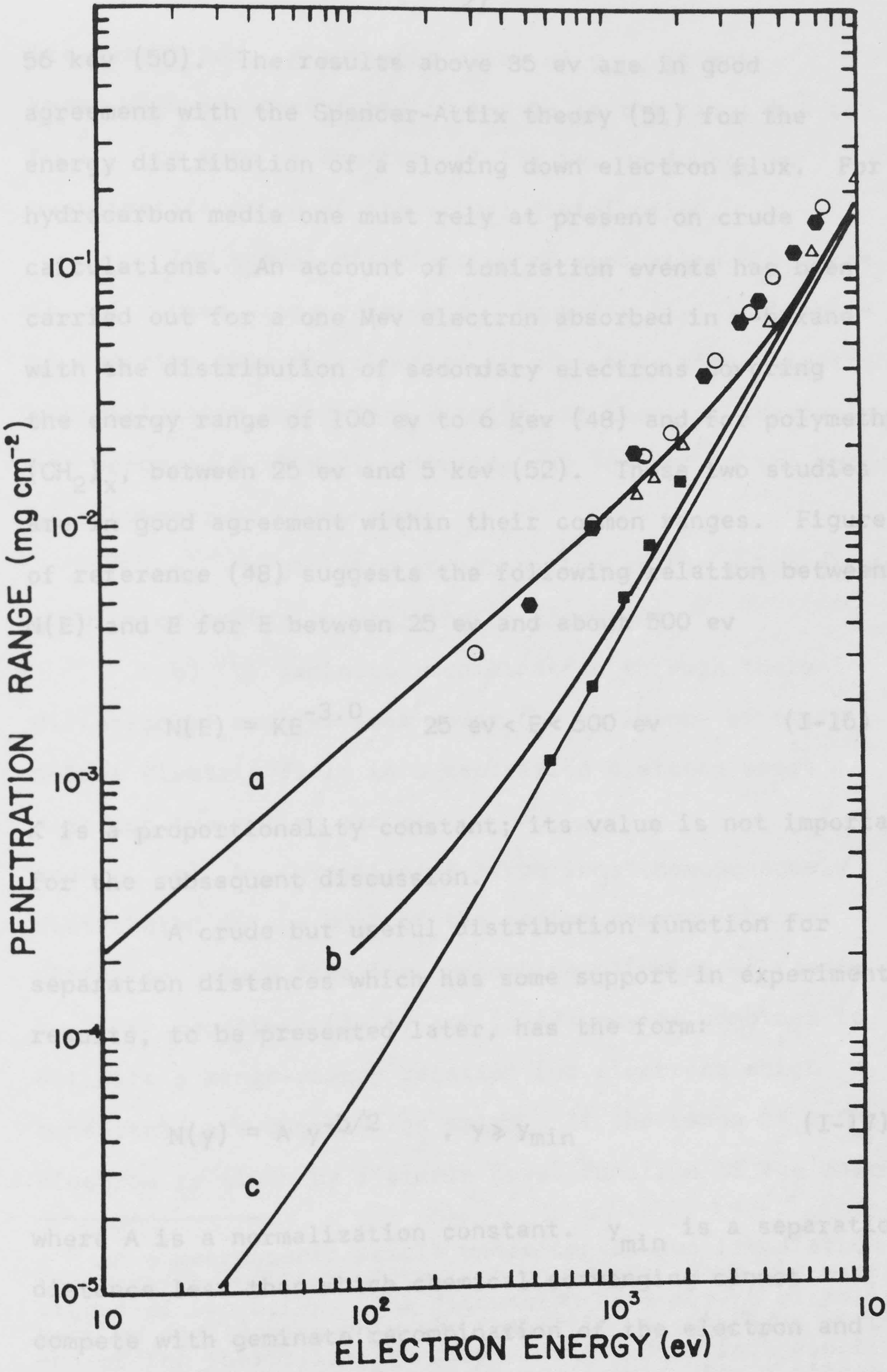
B. Experimental Ranges given by following symbols:

○ Young (53), penetration ranges in Al_2O_3 films

● Young (53), penetration ranges in Al films

△ Morbitzer and Scharman (54), penetration ranges in LiF films

▨ Davis (55), deactivation of molecular layers of invertase enzyme


PENETRATION RANGE (mg cm^{-2})
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
a
b
c
10
10^{2}
10^{3}
10^{4}
ELECTRON ENERGY (ev)

56 kev (50). The results above 35 ev are in good agreement with the Spencer-Attix theory (51) for the energy distribution of a slowing down electron flux. For hydrocarbon media one must rely at present on crude calculations. An account of ionization events has been carried out for a one Mev electron absorbed in n-hexane with the distribution of secondary electrons covering the energy range of 100 ev to 6 kev (48) and for polymethylene, $(CH_2)_x$, between 25 ev and 5 kev (52). These two studies are in good agreement within their common ranges. Figure 4 of reference (48) suggests the following relation between N(E) and E for E between 25 ev and about 500 ev

$$N(E) = KE^{-3.0} \qquad 25\text{ ev} < E < 500\text{ ev} \qquad \text{(I-16)}$$

K is a proportionality constant; its value is not important for the subsequent discussion.

A crude but useful distribution function for separation distances which has some support in experimental results, to be presented later, has the form:

$$N(y) = A\,y^{-5/2} \quad , y \geqslant y_{min} \qquad \text{(I-17)}$$

where A is a normalization constant. y_{min} is a separation distance less than which chemical scavenging cannot compete with geminate recombination of the electron and its parent ion. A suitable value of y_{min} is not known with any certainty; it may be in the range 5 Å to 50 Å. The form of Equation (I-17) is, no doubt, an oversimplification of the actual distribution.

The actual distribution of separation distances is, of course, time dependent. Equation (I-17) attempts to describe this distribution at some time after electron thermalization but before significant chemical scavenging has occurred.* The distribution may "decay" in the absence of scavenger in three ways:

a) by geminate recombination of ion pairs through quantum mechanical tunnelling of electrons,

b) by geminate recombination through thermal diffusion of counter ions under the influence of their mutual electric field to a separation distance where electron tunnelling occurs,

and c) by formation of "free ions" homogeneously distributed in the bulk of the medium through thermal diffusion. Such free ions recombine pairwise at random.

Equations (I-16) and (I-17) may be combined to estimate a range-energy relation for electrons which constitute scavengable ion pairs. If the range of an electron is given by a simple power function of the energy,

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* In a macroscopic sample under continuous irradiation the total population of ionization events shows all possible stages of evolution. The discussion here may be visualized best by considering only the ionization events just at the end of the thermalization stage for a single fast electron or, possibly in the case of macroscopic sample, for a single instantaneous pulse of radiation.

$$y = CE^{n} \qquad \text{(I-18)}$$

where C is a constant of proportionality and n is an exponent to be determined, then

$$dE = \frac{1}{nC} E^{1-n} dy \qquad \text{(I-19)}$$

$$= \frac{1}{nC} \frac{y}{C}^{\frac{1-n}{n}} dy \qquad \text{(I-20)}$$

Equation (I-16) may be transformed to a distribution over separation distances by substitution $(y/C)^{\frac{1}{n}}$ for E and converting the unit energy interval to a unit separation distance. Using Equations (I-18) and (I-20) in Equation (I-16), N(E) becomes:

$$N(y) = K\left(\frac{y}{C}\right)^{\frac{-3}{n}} \cdot \frac{1}{nC} \left(\frac{y}{C}\right)^{\frac{1-n}{n}} \qquad \text{(I-21)}$$

$$= Ay^{-5/2} \quad , \; y \geqslant y_{min} \qquad \text{(I-17)}$$

or $$y^{-\left(\frac{n-z}{n}\right)} = y^{-5/2}$$

and $n = \frac{4}{3} = 1.3$.

This value of n is in agreement with those found experimentally with low energy electrons (500 ev to 10 kev) penetrating, for example, aluminum and aluminum oxide (53) and alkali metal halide films (54). Some results on deactiving layers of the enzyme invertase by low energy electrons (55) gives a range-energy relation with the exponent n close to 1.8, near the value expected for an integration of $-\left[\left(\frac{dT}{ds}\right)_{coll}\right]^{-1}$ based on the Bethe Equation.

A view taken in the present study is that data on chemical scavenging of ions as reflected in the yields of radiolysis products from scavenger solutions will give information on the distribution of separations for ion pairs. It may well be that an accumulation of radiolysis data will help form a basis for a satisfactory theory of energy loss from low energy electrons in nonpolar media.

C. CHEMICAL ASPECTS OF GAMMA RADIATION ABSORPTION

1. Temporal Sequence of Radiation Induced Transformations

The complex series of events following the absorption of a gamma ray represents the tendency of a perturbed system to relax to a new state of thermodynamic equilibrium. The various relaxation processes which occur have characteristic times. These allow the approach to equilibrium to be partitioned into several stages. These stages are not clearly demarcated since events classified in a particular stage of track evolution may have a broad range of possible characteristic times. During continuous irradiations all stages of evolution will be present simultaneously in a macroscopic sample. The following three stages will be taken as comprising the normal development of radiation induced transformations in condensed phases (56):

a) Physical stage involving the highly inhomogeneous dissipation of energy from the fast Compton and secondary electrons. This stage, discussed in Section B-3 of this chapter, has a duration of approximately 10^{-15} second. During this period any molecular motion of the medium is effectively "frozen".

b) Thermalization stage, lasting about 10^{-12} second. During this period excess kinetic and internal energy has some chance of being dissipated into the many degrees of freedom in the medium. Excited molecules and ions may undergo bond breakage and rearrangement. There is little firm information on the nature and distribution of reactive species at this stage. Many aspects of other specialized fields are pertinent here as, for example, the chemistry of excited molecules and the unimolecular decomposition of excited ions. The chemistry of excited states has been treated by Laidler (57) and Reid (58). The application of a theory of unimolecular decomposition to some excited hydrocarbon ions is discussed with regard to radiolytic action by Vestal et al. (59). During this stage electrons from ionization events will be moderated to thermal energies. The behavior of these slow electrons is a problem which has not been settled satisfactorily at this time. Samuel and Magee (43) calculated that the time required for an electron with energy of 15 ev to be captured by the positive parent ion in water (with a high frequency dielectric constant of 3) is about 2×10^{-13} second. A different treatment for water (44) suggested that thermalization of the electron in the dipolar medium required about 10^{-12} second. Within this time polarization forces were predicted to effectively trap the electron. Recombination would then involve a relatively slowly diffusing negative entity. The hydrated electron has now been observed (60) directly in water through its absorption spectrum, measured by a pulse radiolysis technique.

c) <u>Chemical stage</u> which becomes important at times greater than 10^{-12} second after the track formation.

During this stage some of the final stable products are formed through the diffusion and reaction of intermediate radicals and possibly ions and electrons. For example, the solvated electron in water has a sufficient lifetime [$t_{1/2}$ is ca. 1.1 milliseconds at 25°C in water (61)] so that its reaction rate with many common oxidants has now been measured (62). In solid systems the duration of this stage may amount to hours or even days.

2. Reactive Intermediates in Alkane Radiolysis

The initial effect of the absorption of energy from a high energy photon or charged particle is a Franck-Condon transition to an electronic state which may be discrete, predissociative, or ionized. Electrical conductivity of irradiated gases is easily observed and one can safely assume that numerous ionization events occur in condensed phases as well. Although they are not as easily detected, excited neutral molecules are produced during the primary absorption stage. During the thermalization stage of track evolution a heterogeneous population of excited and charged parent molecules and fragments will exist in a highly inhomogeneous spacial distribution. In general the constituents of this population may be classified as neutral excited molecules, free radicals, positive and possibly negative ions, and electrons. The discussion here will be limited where possible to the species related to the current cyclopentane radiolysis study.

a) Excited molecules may be formed either directly during the absorption of ionizing radiation or at a later stage through ion neutralization. With respect to alkane radiolysis Dyne (63) states,

> "Ion-electron recombination leads to the formation of excited molecules which have similar properties to those formed initially; all subsequent decomposition proceeds through these excited molecules."

Many of the electronically excited states of alkanes are expected to be dissociative (64). Excited alkane molecules are important free radical sources as well as precursors of "molecular" products (ie., molecular products formed directly from the alkane and not through any freely diffusing intermediate). For example, in the radiolysis of cyclopentane a fraction of the cyclopentene is believed to have such a "molecular" origin.

$$c\text{-}C_5H_{10} \rightsquigarrow c\text{-}C_5H_{10}^{*} \longrightarrow c\text{-}C_5H_8 + H_2(\text{or } 2H\cdot) \qquad [I\text{-}1]$$

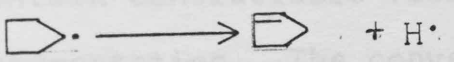
Excited molecules may rearrange. An example is the mercury photo-sensitized formation of vinylcyclopropane from cyclopentene (65).

b) Free Radicals. The cyclopentyl radical has been directly observed in the radiolysis of liquid cyclopentane at -80°C by its electron paramagnetic resonance (ESR) spectrum (66). If the cyclopentyl radicals arise in part from the homolytic cleavage of a C-H bond in cyclopentane, a complementary yield of hydrogen atoms would be expected. However, ESR spectroscopy (66) gave no evidence for their presence. There is no direct evidence for the presence of hydrogen atoms in the radiolysis of cyclopentane. The mutual reactions of the cyclopentyl radical were studied by Stock and Gunning (67). It was found that the ratio of the rate of reaction [I-2] to that of [I-3] was 1.0 over the temperature range 26°C to 250°C.

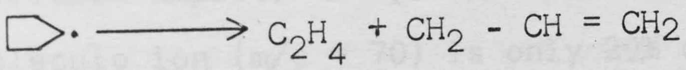
$$2\ c\text{-}C_5H_9\cdot \longrightarrow C_{10}H_{18}\text{(cyclopentylcyclopentane)} \qquad [\text{I-2}]$$

$$2\ c\text{-}C_5H_9\cdot \longrightarrow c\text{-}C_5H_{10} + c\text{-}C_5H_8 \qquad [\text{I-3}]$$

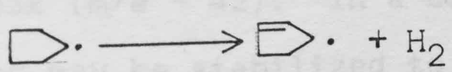
Above 250°C the cyclopentyl radical is unstable (68). Three modes have been postulated for this thermal decomposition (69):



[I-4]

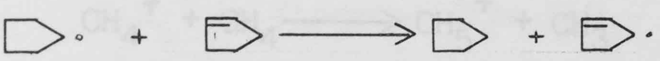


[I-5]

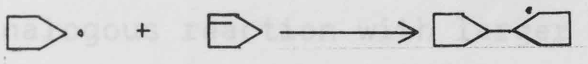


[I-6]

The activation energy of reaction [I-5] has been measured as 36.9 ± 0.1 kcal (69). Reaction [I-4] has an activation energy greater than 36.0 kcal (69). Even at 700°C less than 2% of the cyclopentyl radicals decompose by reaction [I-6]. The isomerization of the cyclopentyl radical to an open chain pentenyl radical has not been studied. When prolonged radiolysis leads to the build-up of appreciable concentrations of stable products then secondary reactions involving these and the reactive intermediates may become important. For example, cyclopentyl radicals may be consumed in reactions with cyclopentene, a major radiolysis product of cyclopentane. Two possible reactions are:



[I-8]



[I-9]

c) <u>Positive ions</u>. Electron impact ionization follows the Franck-Condon principle (70). In such "vertical" transitions from the ground state the resulting ion may contain considerable vibrational energy which could lead to fragmentation. The conventional mass spectrum (70 ev electron impact) of cyclopentane (71) shows that the parent molecule ion (m/e = 70) is only 29% of the most abundant peak (m/e = 42). In a condensed phase the parent molecule ion may be stabilized to some extent through dissipation of vibrational energy. However, hydrocarbon ions show extremely high reactivity and the increased collision frequency would be conducive to ion-molecule reactions. The reactions of positive hydrocarbon ions and their energetics have been discussed by Lampe et al. (72), and Kevan and Libby (73). Since their reactions occur at near collision frequencies, ion-molecule reactions are best studied by the methods of mass spectometry. Although the ion-molecule reactions of the cyclopentane positive ion have been little studied the results from other alkanes may have some validity for cyclopentane.

A remarkable reaction occurs between the methane ion and methane (74):

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \qquad [I\text{-}10]$$

The analogous reaction with larger alkanes becomes insignificant in comparison to other ion-molecule reactions, at least in the mass spectrometer at low pressures (75).

In cyclohexane radiolysis, ions of unknown identity are suspected of being Brønsted acids. Williams (41) observed a variation in the isotopic composition of the radiolytic hydrogen from cyclohexane containing up to one mole percent of ammonia-d_3. A step involving the protonation of the ammonia was proposed to account for the appearance of HD.

$$RH \rightsquigarrow Y^+ + e^- \qquad [I\text{-}11]$$

$$Y^+ + ND_3 \longrightarrow Y(-H) + ND_3H^+ \qquad [I\text{-}12]$$

$$ND_3H^+ + e^- \longrightarrow D\cdot \text{ or } H\cdot + ND_2H \text{ or } ND_3 \qquad [I\text{-}13]$$

$$D\cdot + RH \longrightarrow HD + R\cdot \qquad [I\text{-}14]$$

Y^+ in cyclohexane may be $C_6H_{12}^+$, $C_6H_{13}^+$, or possibly a fragment ion.

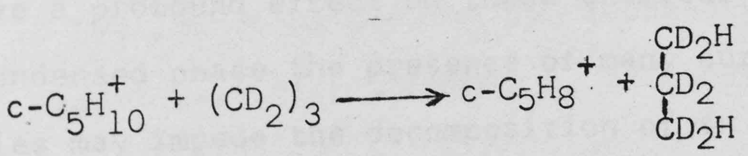
Some fragment ions from hydrocarbon molecules are potential hydride ion acceptors. The following reaction occurs in neopentane (76):

$$C_3H_5^+ \text{ (a fragment from } C_5H_{12}^+\text{)} + C_5H_{12} \longrightarrow C_5H_{11}^+ + C_3H_6. \qquad [I\text{-}15]$$

Some fragment ions may undergo condensation reactions, an example being (77):

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \qquad [I\text{-}16]$$

Ausloos and Lias (78) discovered a significant H_2-transfer reaction between gaseous alkane ions (cyclo-C_6H_{12}, cyclo-C_5H_{10}, and n-C_5H_{12}) and several unsaturated hydrocarbons or cyclopropane. For example, the following reaction was observed in gamma radiolysed gaseous cyclo-C_5H_{10} containing up to 5% cyclo-C_3H_6:



$$c\text{-}C_5H_{10}^+ + (CD_2)_3 \longrightarrow c\text{-}C_5H_8^+ + CD_2H\text{-}CD_2\text{-}CD_2H \qquad [I\text{-}17]$$

Reaction [I-17] is exothermic by about 46 kcal. Similar reactions in condensed phase alkane radiolyses were observed by Ausloos and coworkers (79, 80).

Ionic processes in mixed hydrocarbon systems may show* additional reactions such as charge exchange (81, 63) and cationic polymerization of olefins (82).

Charge neutralization limits the lifetime of any positive ion.

d) Negative ions and electrons. Electron capture by alkanes to form stable negative ions has not been observed. The ability to take up thermal electrons occurs, possibly dissociatively in some cases, with a few classes of compounds including some alkyl halides and some aromatic hydrocarbons such as naphthalene (83). A solution of these compounds in an alkane shows radiolytic behavior which may be associated, in part, with such electron attachment (63).

3. Reactivity Transfer

The multitude of stable products in hydrocarbon radiolysis results from the reactions of a conglomeretic population of species generated during electron moderation and by ion pair recombination. The state of the medium may have a profound effect on these chemical processes. In a condensed phase the presence of many surrounding molecules may impede the decomposition of an activated molecule that would normally decompose in the gas phase. However radicals having once escaped this "cage" will

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* This statement does not imply that such reactions are absent in the pure alkane or olefin.

have a reduced chance of undergoing geminate recombination. This "cage effect" (84) will be manifest only if the medium is sufficiently inert. If the constituents of the "cage wall" are not inert but may transfer charge or possibly atoms to the active species, then chemical reactivity may rapidly migrate throughout the medium by a "relay effect".

The following parallels an argument developed by Semenov (85). If the activation for reactivity transfer is E kcal and the liquid phase collision frequency is 10^{13} sec^{-1}, the mean life of the reactive species with respect to "relay" transfer will be approximately $10^{-13} \exp\left(\frac{1000\ E}{RT}\right)$ seconds. If each displacement of the reactive site is 3×10^{-8} cm (about half a molecular diameter) the displacement speed of reactivity transfer will be approximately $3 \times 10^{-8} \cdot 10^{13} \exp \left(- \frac{1000\ E}{RT}\right)$ cm sec^{-1}. The mean molecular diffusion speed of a cyclopentane molecule in the liquid state may be estimated from the diffusion coefficient, D, (86):

$$D = \frac{(\text{root mean square displacement})^2}{6\tau} \qquad \text{(I-22)}$$

where τ is the mean time between two successive displacements. The root mean square displacement, S, is consequently

$$S = \frac{6\ D}{\text{root mean square displacement}} \qquad \text{(I-23)}$$

Arbitrarily taking the root square displacement as 3×10^{-8} cm, or about one half a molecular diameter, and D = 2.6 x 10^{-5} $cm^2 sec^{-1}$ at 20°C [calculated from the Chang and Wilke formula (87)] , S is about 6×10^3 cm sec^{-1}. For transfers having favorable steric factors and no activation energy, "relay" transfer would occur faster than transfer via mass transport by more than an order of magnitude. For a process with E = 5 kcal, which is reasonable for alkyl radical interchange (88), the "relay" displacement speed at 20°C would be about an order of magnitude less than the mass transport speed.

In pure cyclopentane, radical reactivity transfer given by reaction [I-18] does not lead to a new "carrier". It is difficult (if not impossible) to detect the effect of

$$c\text{-}C_5H_9\cdot + c\text{-}C_5H_{10} \longrightarrow c\text{-}C_5H_{10} + c\text{-}C_5H_9\cdot \quad [I\text{-}18]$$

such exchange through product yield analysis. However, in the radiolysis of cyclopentane-cyclohexane mixtures at dose rates below 4×10^{18} ev $gm^{-1}hr^{-1}$, Muccini and Schuler (89) suggested that the observed product yields of the various radical combination products were consistent with the following radical reactivity transfer reactions:

$$c\text{-}C_5H_9\cdot + c\text{-}C_6H_{12} \xrightarrow{k_a} c\text{-}C_5H_{10} + c\text{-}C_6H_{11}\cdot \quad [I\text{-}19]a$$

$$c\text{-}C_6H_{11}\cdot + c\text{-}C_5H_{10} \xrightarrow{k_b} c\text{-}C_5H_9\cdot + c\text{-}C_6H_{12} \quad [I\text{-}19]b$$

The rate constant k_b was found to be greater than k_a. An examination of the congruent olefins in this system lead Toma and Hamill (90) to suggest that charge transfer from cyclopentane ion to cyclohexane also occurred [ionization potentials of cyclopentane and cyclohexane have been measured as 10.51 ± 0.03 ev and 9.88 ± 0.02 ev respectively by photoionization (91)]. Using perdeuterated cyclohexane in cyclopentane, Yang and Marcus (92) suggest that charge transfer in this system is unimportant, the results being explained simply by sufficiently different rates for the two possible modes of the disproportionation reactions involving the cyclopentyl and cyclohexyl radicals. Inefficient charge transfer in alkane mixtures is also suggested by the work of Stone (93) using small amounts of cyclo-C_6D_{12} in the cyclo-C_6H_{12} - cyclo-C_5H_{10} mixtures. However, radical-radical interaction did not account completely for the observed behavior.

Reactivity transfer reactions may have important implications for understanding radiolytic action. Even in the radiolysis of mixtures of isotopically labelled molecules of a compound, exchange reactions would complicate the analysis. Reactivity transfer effects may be important in the radiolysis of hydrocarbon solutions containing suitable solutes able to "trap" reactivity by virtue of low ionization or excitation potentials, high proton or electron affinities, low bond energies, etc. Such "trapped" reactivity may be degraded in a way that little radiolytic decomposition is produced. Inhibition of radiolytic action is observed, for example, in alkane-benzene solutions (94).

D. ALKANE RADIOLYSIS

1. General Features of Alkane Radiolysis

There appears to date to be little agreement on the precise values for the absolute yields of the major products in alkane radiolysis conducted under supposedly similar irradiation conditions. One reason for the disparity of results is easily found : few workers have used materials of sufficient purity in their studies. Often the elimination of olefinic impurities from an alkane was thought sufficient. Little or no regard was given to the possibility that other alkanes may influence yields through reactivity transfer (81, 63).

It is possible to give only some very general results on product yields from an examination of the many surveys on saturated hydrocarbon radiolyis (95,96, 97, 98). Hydrogen is invariably the product produced in largest yield. In the case of n-alkanes this yield increases slightly with chain length reaching a limiting G value of about 6 with liquid polyethylene at 142^{o}C (99). Hydrogen deficient products (relative to the irradiated alkane) occur, such as the congruent (same number of carbon atoms) olefins and species having twice the number of carbon atoms as the parent. Generally the material balance of the measured products has been poor. Fragmentation products also are produced, the yield of which diminish with increasing size. However, for isomeric alkanes, fragmentation increases with increased degree of chain branching. There are small yields of products having molecular weights between that of the parent and that of the "dimer". Products larger than dimers occur but their yields and structures are difficult to determine for parent alkanes with more than four carbon atoms. An accurate determination of these polymeric products is expected to improve the material balances of many alkane radiolyses. G values for the destruction of alkane, G(-alkane), are in the range of 6 to 8. Reactive additives suppress product yields only incompletely.

One of the purposes of radiation chemistry is to suggest plausible mechanisms for the formation of the stable radiolysis products. The yields and identities of these products must be satisfactorily known. This has not always been the case. The majority of suggested mechanisms contain much which is speculative and this aspect of radiolysis is far from clear at the present time. In a few cases direct measurement of identifiable intermediates has been possible (66) but even here useful rate data from decay studies are difficult to obtain. Several techniques have been applied to help elucidate alkane radiolysis mechanisms. They are usually used in combination. Some of these methods are:

a) spectroscopic studies,

b) dose rate studies,

c) phase and temperature effects,

d) chemical scavenging,

and e) use of labeled indicator molecules.

a) Spectroscopic methods for measuring reactive intermediates are among the most powerful developed for studying radiolytic kinetics and mechanism. They often allow one to examine aspects of the early stages of radiolytic action. ESR spectra of steady state radical concentrations in several liquid hydrocarbons during irradiation were measured by Fessenden and Schuler (66). The spectra allowed unequivocal identification of radical species in many cases.

Hamill and co-workers have examined low temperature absorption spectra (UV, visible, and near IR) of irradiated alkane glasses containing various solutes especially reactive to electrons or positive ions [see, for example, reference (100)]. The effects of optical and thermal bleaching of the absorption bands give useful information on the nature and density of trapping sites. The maximum yield of anions of ca. 3 was equated with the yield of electrons in alkane radiolysis (101).

b) Dose rate studies. The rate at which reactive intermediates are produced is directly proportional to the rate of energy absorption by the medium. The primary reactive species may mutually interact or possibly react with the medium or added solutes. If an intermediate is consumed in measurably competitive reactions of different kinetic order (with respect to the concentration of the intermediate) there will be a dose rate dependence of the product yields for the alternate reaction paths. A comprehensive treatment of dose rate effects including the case for inhomogeneous reaction of active radicals is given by Burns and Barker (102). Under the conditions used in the present study, dose rate changes are expected to have little effect on the yields of radiolysis products of pure cyclopentane. However, dose rate effects have been observed for the yields of radical-radical reaction products in cyclopentane containing small amounts of ethylene added as a scavenger (103). Dose rate effects observed in some gas phase alkane radiolyses were attributed to competition between neutralization of the ions in the gas and diffusion of the ions to the wall of the irradiation vessel (104).

Effects somewhat similar to those caused by high dose rates occur when the ionizing radiation has a high rate of linear energy loss (LET). This may occur, for example, in irradiations with protons and α particles. Spurs containing the reactive intermediates may then overlap. There is some evidence for this LET effect in cyclohexane (105).

Closely related to dose rate studies are the intensity and space intermittancy techniques recently applied to radiation chemistry. These methods are extensively applied in photochemical studies for an estimate of the lifetimes of short lived intermediates (106). Using a variable pulsed 2.8 Mev electron beam from a Van de Graaff accelerator and ESR detection, Fessenden (107) determined the rate constant for bimolecular disappearance of $C_2H_5\cdot$ in irradiated liquid ethane to be $1.3 \times 10^{10} \exp\left(-\frac{830}{RT}\right)$ l mole^{-1} sec^{-1} between -140°C and -177°C. A monograph on pulse radiolysis has recently been published (108).

Dyne and Denhartog (109) have applied to radiolysis a novel technique analogous to Noyes' photochemical space intermittancy methods (110). They determine radiolytic product yields from solid cyclo-C_6H_{12} layers of variable thickness (20 Å to 1000 Å) "sandwiched" between other materials which either activate or deactivate the hydrocarbon through energy or reactivity transfer. The yield of a particular product may change rapidly when the cyclo-C_6H_{12} layer thickness becomes comparable to the range of interaction characteristic to the process generating the product. With regard to the processes pertinent to irradiated alkanes they found, for example, with cyclo-C_6H_{12} that

i) its activation by n-C_6H_{14} has a very short range consistent with an ion-molecule reaction between neighboring molecules,

ii) its deactivation by carbon tetrachloride or benzene has a longer range (180 Å or more), and iii) the intermediates in the bimolecular reaction giving HD when using interspersed layers of cyclo-C_6D_{12}, have a short range (less than 100 Å) which they suggest rules out thermal hydrogen atoms as precursors.

c) Phase and Temperature Effects. The fate of an activated molecule may depend critically on whether it is produced in a gas, liquid, or solid. In the gas phase there are no caging effects; a pair of neutral fragments of a given molecule have a negligible chance of recombining or disproportionating with one another. Even electrons ejected by ionization processes have in the gas phase at one atmosphere pressure, a negligible chance of recombining with their parent ions, even assuming the latter preserve their identities (111). In a condensed phase, however, neutral fragments may be produced in a cage or possibly a spur where any back reaction is enhanced. In the condensed state of alkanes the majority of electrons from ionizations appear to recombine with their geminate counter-charge, (112) although the lifetimes of the separated ion pairs in liquid alkanes appear to be sufficient for ion-molecule reactions to compete with parent-ion recapture (41).

A comparison of vapor and liquid phase alkane radiolyses at about 25°C with gamma rays or electrons in n-butane (113, 114, 115), n-pentane (116, 117, 118, 119, 120, 121), n-hexane (122, 123, 124, 125), and cyclohexane (126, 127, 128, results for vapor extrapolated to 25°C) shows that C-C bond cleavage is greater in the gas phase than in the liquid. Total hydrogen yields appear to be similar in both states while congruent olefin and dimer yields are markedly reduced in the vapor phase (except for n-butane, where the congruent olefin and dimer yields seem to be relatively low in both phases). To explain vapor phase radiolysis yields Futrell (129, 130) applied the standard mass spectral "cracking patterns" for n-hexane and n-pentane and used the assumption that all fragment ions reacted with the substrate by hydride ion abstraction. The reaction products were low molecular weight alkanes and the parent hydrocarbon carbonium ions. An excited substrate radical, produced on neutralizing the parent hydrocarbon carbonium ion, was postulated to decompose to the congruent olefin and a hydrogen atom, possibly hot. No account was taken of any energy being degraded in non-ionizing primary events. The predicted and observed product distributions were in good agreement. Some experiments indicate that the substrate carbonium ions are unimportant in liquid or solid n-hexane radiolysis, at least during the chemical stage of evolution (131).

From a study of gaseous ethane, the density of which was varied from 0.001 gm cm^{-3} (at atmospheric pressure) to 0.30 gm cm^{-3}, Wodetzki et al. (132) concluded that there are at least three modes of hydrogen formation in the radiolysis of this alkane. Mixtures of C_2H_6 and C_2D_6 with and without scavengers (ethylene, propylene) were used. Two processes for hydrogen formation, abstraction of hydrogen from the substrate by thermal hydrogen atoms and molecular detachment, decrease in importance with increasing density; the third, a bimolecular reaction uninhibited by a radical scavenger increases in importance with density. The bimolecular reaction may be either an ion-molecule reaction or abstraction by a hot hydrogen atom. Unimolecular hydrogen formation is attributed to the following processes:

$$C_2H_6{}^* \longrightarrow C_2H_4 + H_2 \qquad [I\text{-}20]$$

$$\left(C_2H_6{}^+\right)^* \longrightarrow C_2H_4{}^+ + H_2 \qquad [I\text{-}21]$$

Unscavengable bimolecular hydrogen may arise from one or more of the following reactions:

$$C_2H_6{}^+ + C_2H_6 \longrightarrow C_2H_7{}^+ + C_2H_5\cdot \qquad [I\text{-}22]$$

$$C_2H_7{}^+ + e^- \longrightarrow C_2H_5\cdot + H_2 \qquad [I\text{-}23]$$

$$H^* + C_2H_6 \longrightarrow H_2 + C_2H_5\cdot \qquad [I\text{-}24]$$

where H* represents a hot hydrogen atom. It was concluded that the density effects were a consequence of decreased ion fragmentation and increased parent-ion recapture at high densities in accordance with the theoretical expectations suggested by Stevenson (133), and ElKomoss and Magee (111).

Kevan and Libby in their attempt to simulate the radiolysis of polyethylene, studied liquid n-hexane at 20°C and the solid at -196°C (124). It was found that C-C bond breakage was futher inhibited in the solid compared to the liquid state. However, their results do not allow one to readily distinguish temperature effects from those of phase change. To overcome this problem Falconer and Salovey have examined product yields in irradiated solid and liquid n-hexadecane (134, 135) and n-heptadecane (136, 137) over a small temperature range near their melting points (19°C and 22°C respectively). Cage recombination of scission fragments and crosslinking of radical pairs were enhanced in the solid states of both alkanes. A hot hydrogen atom mechanism and molecular elimination accounted for most of the hydrogen production. Thermal hydrogen atoms contributed a maximum of 20% to the hydrogen production in liquid n-hexadecane and possibly much less in the solid. Differences in crystal structure between the n-C_{16} and n-C_{17} alkanes were invoked to explain variations in the radiolysis of the respective solids.

In their examination of solid n-hexane radiolysis, Kevan and Libby (124) found the dimer distribution resulted from preferential linking of proximate sites. They suggested two ion-molecule reactions for dimerization:

$$\mathrm{RH^{+} + RH \longrightarrow R\cdot + RH_2^{+} \xrightarrow{e^{-}} 2R\cdot(adjacent) + H_2} \qquad [\text{I-25}]$$

$$\mathrm{RH^{+} + RH \longrightarrow RR^{+} + H_2} \qquad [\text{I-26}]$$

Neutralization of the dimer ion is expected to produce some scission. The direct dimerization reaction [I-26] was first suggested by Weiss (138) to explain hydrogen yields and crosslinking in polyethylene.

Temperature variation is expected to have little effect on the primary absorption processes. The Bethe equation (I-11) was derived on the basis of isolated electronic systems. Any temperature dependent molecular motion is usually insignificant compared to the speed of a Compton or secondary electron. Small temperature effects are anticipated for some processes associated with the thermalization stage of energy dissipation.

The mass spectra of polyatomic molecules are slightly temperature dependent, for example, in the range 50°C to 250°C (139). The Gioumousis-Stevenson theory of ion-molecule reactions predicts a rate constant independent of gas temperature (140).

For the most part, the temperature dependence of radiolytic product yields originate in activation controlled reactions of freely diffusing intermediates. Both diffusion of an intermediate in the condensed phase and radical reactions with most substrates or scavengers require some activation energy, although it is small in most cases.

Above about 600°K decomposition of large alkyl radicals may occur to give olefins and small reactive radicals which can then attack parent alkane molecules. A chain reaction is generated (141). Pyrolytic chain decomposition of alkanes is usually unimportant below 800°K (142). Thus chain decomposition of alkanes may be initiated by radiation some 200°C lower than required in normal pyrolysis (143). The effect is apparent in the results of Blachford and Dyne for the radiolysis of cyclohexane vapor at temperatures up to 320°C (128).

Dewhurst found the yield of hydrogen from liquid n-hexane to increase by about 3% for every 10°C between the melting point (-95°C) and 30°C (144). The similarity of the corresponding activation energy of about 3 kcal mole^{-1} to that required in diffusion processes was noted. Temperatures below the melting point down to -196°C had no apparent effect on the hydrogen yield. The congruent olefin yield was unaffected by temperature while the dimer yield was halved in going from 30°C to -196°C. The yields of compounds intermediate to n-hexane and dimer were almost absent in the irradiated solid. The results for n-hexane irradiated at 30°C were interpreted as follows. The G value for molecularly detached hydrogen is 1.5, an unscavengable hydrogen yield from a bimolecular process (possibly ionic) of 2.0, and G(H·) equal to 2.0.

Widmer and Gaumann (125) examined the gamma radiolysis of liquid n-hexane in the temperature range -78°C and +150°C and the solid at -196°C. A thorough product analysis was done. The results could not be explained in terms of radical reactions alone although it was suggested that they were major contributors to product yields. As temperature increased, the product yields indicated that small radicals reacted with the medium to generate hexyl radicals. Product yields at the highest temperatures showed that the less reactive 2-hexyl and 3-hexyl radicals were predominant. The results added support to the concept of reactivity transfer discussed in section C-3 of this chapter.

Hamashima, Reddy, and Burton found little or no temperature effect on $G(H_2)$ in either cyclohexane or neopentane between -60°C and 25°C (145). They also noted that $G(CH_4)$ in neopentane radiolysis increased from about 0.9 at -60°C to about 3.3 at 25°C with most of the increase occuring above the melting point at -20°C. Later work of Taylor, Burton, and Mori (146) reports higher methane yields especially at the lower temperatures and also a minimum in the hydrogen yield curve. The effect of temperature on the hydrogen yield suggested two processes for hydrogen formation; one dominant at low temperatures but becoming insignificant at higher temperatures, the other with opposite temperature characteristics. The process operative at low temperatures was suggested to be

$$H\cdot + H\cdot \longrightarrow H_2 \qquad [I\text{-}27]$$

which becomes less important at intermediate temperatures when H· may be scavenged in a process of relatively low activation energy, eg., addition to radiolytic olefin. At high temperatures the reaction

$$H\cdot + C_5H_{12} \longrightarrow H_2 + C_5H_{11}\cdot \qquad [I\text{-}28]$$

was said to be the new source of H_2.

d) <u>Chemical scavenging</u>. Chemical additives, generically called "scavenger" (in some cases, inhibitors), are often used in radiolysis studies to distinguish between product yields occurring by way of freely diffusing intermediates and those occurring by fast inter- and intramolecular processes. The normal reactions of the intermediates are suppressed by their reaction with the scavenger. It is sometimes possible to identify the reactive species by characterizing the new products formed. In general, however, the mode of action of the scavenger in radiolysis is not directly determined but it is assumed on the basis of its previous behavior in other experiments such as pyrolyses, photolyses, etc. For intermediates which react quickly with the substrate, the activation energy for their reaction with the scavenger must be small or zero (147). For example, since radical-radical reactions appear to have low activation energies, one finds stable free radicals such as gavlinoxyl* having been used as radical scavengers in alkane radiolysis (148). Low concentrations ($< 10^{-3}$ M) of the scavenger are preferred to avoid its direct radiolysis. Scavenging of "hot" intermediates (ie. epithermal or electronically excited species which may react on first collision) and species in spurs will be more difficult than homogeneously distributed thermal radicals and atoms. By increasing the scavenger concentration sufficiently it may be possible to react with at least some species in spurs although other effects may then occur such as direct radiolysis or possibly interaction with excited molecules (150).

Only two examples of chemical scavenging techniques will be described here in any detail. These are homogeneous scavenging of thermal hydrogen atoms and the use of radioactive scavenger radicals generated in situ from a labeled additive.

If a substrate under radiolysis produces a

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*Gavlinoxyl (or Coppinger's radical) is 2,6-di-t-butyl-(3,5-di-t-butyl-p-oxocyclo-hexadiene-1-ylidene)-p-tolyloxy (149).

product which can arise "molecularly" and also by mutual reaction of scavengable intermediates, then only part of the product yield may be diminished by scavenger reactions. Consider the scavenging of hydrogen atoms generated radiolytically along with "molecular" hydrogen. If RH is an alkane susceptible to hydrogen atom abstraction and S is a hydrogen atom scavenger present in low concentration to avoid its direct radiolysis then a simple mechanism describing hydrogen formation and hydrogen atom scavenging may be expressed as follows:

$$RH \rightsquigarrow H\cdot + H_2 \qquad [I\text{-}29]$$

$$H + RH \xrightarrow{k_a} H_2 + R\cdot \qquad [I\text{-}30]$$

$$H + S \xrightarrow{k_s} SH\cdot \qquad [I\text{-}31]$$

If $G(H_2)_o$, $G(H_2)_m$ and $G(H\cdot)$ are respectively the 100 ev yields of hydrogen produced in the absence of scavenger, the "molecular" hydrogen, and atomic hydrogen, then

$$G(H_2)_o = G(H_2)_m + G(H\cdot) \qquad (I\text{-}24)$$

or

$$G(H_2)_m = G(H_2)_o - G(H\cdot) \qquad (I\text{-}25)$$

If the scavenger concentration is sufficiently low so that its direct radiolysis does not occur, then the observable yield of hydrogen, $G(H_2)$, is given by*

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* Equation (I-26) can be improved by taking the electron fraction of the substrate into account. If the pure scavenger has a hydrogen yield an additional amount of hydrogen in proportion to its electron fraction can be added.

$$G(H_2) \approx G(H_2)_o - G(H\cdot) + \frac{k_a [RH]}{k_a [RH] + k_s [S]} G(H\cdot) \qquad \text{(I-26)}$$

or $$G(H_2)_o - G(H_2) \approx G(H\cdot) \left\langle \frac{k_s \cdot [S]}{k_a [RH] + k_s [S]} \right\rangle$$

or $$\frac{1}{G(H_2)_o - G(H_2)} \approx \frac{1}{G(H\cdot)} + \frac{1}{G(H\cdot)} \left(\frac{k_a [RH]}{k_s [S]} \right) \qquad \text{(I-27)}$$

For sufficiently small amounts of scavenger reacting with thermal hydrogen atoms, this mechanism predicts that a linear relation exists between a function of the observable hydrogen yield, $\frac{1}{G(H_2)_o - G(H_2)}$, and the reciprocal of the scavenger concentration. The relation allows one to determine G(H·) from an intercept. When this information is combined with the slope of the linear relation one obtains $\frac{k_a}{k_s}$. Adams, Baxendale, and Sedgwick (151) applied the above mechanism and associated kinetic relation (I-27) to benzoquinone scavenging of H· in cyclohexane. Similarly, Hardwick treated several additives as H· scavengers in an extensive number of liquid alkanes (148). Although the observed behavior agreed with the expected scavenger dependence predicted by the mechanism and often consistent results were obtained for $\frac{k_a}{k_s}$ with many different scavengers in a host of alkanes, the conclusions are of doubtful value. Many of the additives are now known to interfere with ionic intermediates which may be precursors to at least part of the hydrogen yield. The indiscriminate use of Equation (I-27) was discussed by Klots, Raef, and Johnson (152).

Significant improvement in scavenger technique utilizes a radionuclide incorporated in a scavenger. Gevantman and Williams (153) used radioiodine as a scavenger in several C_1 to C_5 alkanes to determine radical yields. These were determined by adding the appropriate inactive alkyl iodide to the irradiated samples as a carrier, fractionating the mixture to recover the alkyl iodide, and measuring its radioactivity. A more recent application of this technique was developed by Holroyd and Klein (154). Their method employs a radioactive labeled solute (usually $^{14}CH_3I$ or $^{14}C_2H_4$) from which labeled radicals may be generated during radiolysis. For example, the following reactions of the additives are assumed to occur:

$$e^- + {}^{14}CH_3I \longrightarrow {}^{14}CH_3\cdot + I^- \qquad [I\text{-}32]$$

and
$$H\cdot + {}^{14}CH_3I \longrightarrow {}^{14}CH_3\cdot + HI \qquad [I\text{-}33]$$

or
$$H\cdot + {}^{14}C_2H_4 \longrightarrow {}^{14}C_2H_5\cdot \qquad [I\text{-}34]$$

High dose rates and/or low temperatures give the most suitable conditions because of the necessary radical-radical reactions dominate radical identity change reactions. For example, dose rates in excess of 5×10^{22} ev ml^{-1} hr^{-1} are required with $^{14}CH_3I$ at 25°C in 2,2,4-trimethylpentane to ensure that less than 10% of the methyl radicals react with the substrate (120, 155).

Under these conditions labeled hydrocarbons (excepting $^{14}CH_4$ and $^{14}C_2H_6$) are formed only by combination reaction. For example, for one radical, R_i, of a set:

$$R_i \cdot + {}^{14}CH_3 \cdot \longrightarrow R_i{}^{14}CH_3 \qquad [I\text{-}35]$$

$^{14}CH_4$ is formed by disproportionation reactions such as

$$R_i \cdot + {}^{14}CH_3 \cdot \longrightarrow R_i(-H) + {}^{14}CH_4 \qquad [I\text{-}36]$$

The yield of the labeled radical is small ($G < 0.2$) and only a small fraction of the radicals, R_i, are scavenged. The normal radical processes are assumed to be negligibly perturbed. It is asserted that the relative yields of labeled hydrocarbons formed, corrected for disproportionation, are proportional to the corresponding radical yields. Chemical analysis is done by the sensitive method of radio gas chromatography (156).

Recent chemical scavenging experiments with liquid alkanes suggest that diffusion controlled ionic reactions with suitable scavengers can compete with electron capture by the parent ion. In liquid cyclohexane, ammonia-d_3 (41) and ethanol-O-d (157) were used to scavenge species acting as Brønsted acids, believed to be alkane positive ions. The proportions of H_2, HD, and D_2 in the radiolytic hydrogen indicated the extent to which deuterated onium ions were neutralized. Meissner and Henglein (158) have done similar experiments with D_2S in n-hexane. Additional compounds were added to the solutions to evaluate the contribution of ionic, radical, and molecular processes to yields of the various isotopic forms of the hydrogen produced. The results were interpreted as showing that D_2S charge exchanged with alkane positive ions as well as reacted with atomic hydrogen. It has been shown (42, 159) that nitrous oxide, a powerful electron scavenger in aqueous systems, markedly affects the hydrogen yields in liquid cyclohexane radiolysis. A marked increase in the yield of cyclohexylcyclohexane in the radiolysis of the same system was observed by Blackburn and Charlesby (160) who outlined the following stages involving ionic intermediates and nitrous oxide:

$$RH \rightsquigarrow \overset{+}{RH} + e^- \tag*{[I-37]}$$

$$RH^+ + e^- \longrightarrow RH^* \tag*{[I-38]}$$

$$RH^* \longrightarrow R\cdot + H\cdot \tag*{[I-39]}$$

$$\longrightarrow R(-H) + H_2 \tag*{[I-40]}$$

$$H\cdot + RH \longrightarrow H_2 + R\cdot \tag*{[I-41]}$$

$$N_2O + e^- \longrightarrow N_2O^- \relbar\joinrel\relbar N_2 + O^- \tag*{[I-42]}$$

$$O^- + RH \longrightarrow R\cdot + OH^- \tag*{[I-43]}$$

$$RH^+ + OH^- \longrightarrow R\cdot + H_2O \tag*{[I-44]}$$

Apparently electron capture by N_2O generates more radicals than geminate recombination of the electron and parent ion. Sherman (161) has measured nitrogen gas yields from irradiated cyclohexane-N_2O solutions containing various aromatic additives. The competition between N_2O and the aromatic scavenger was correlated with the electron affinities of the aromatic compounds.

Some gaseous perfluoro compounds such as sulfur hexafluoride and perfluoromethylcyclohexane are known to have large electron capture cross sections at low electron energies (162, 163, 164). Solutions of cyclic perfluorocarbons in n-hexane showed reduced radiolytic hydrogen yields comparable to those obtained from N_2O-cyclohexane solutions (165). The effects were ascribed to electron scavenging.

e) Labeled Indicator Molecules. Hardwick's extensive scavenger studies (148) showed that a residual yield of unscavengable hydrogen occurs in liquid alkane radiolysis. For twenty liquid alkanes (C_5 to C_{10}) at ca. 25°C, the "molecular" hydrogen was found to be $40 \pm 7\%$ of the total hydrogen yield. Four sources of the "molecular" hydrogen were suggested, "hot" hydrogen atoms were considered the most important. "Molecular" olefin yields were measured as well. The reaction of a "hot" hydrogen atom with a substrate molecule on first collision produces "caged" radicals which contribute "molecular" yields of the congruent olefin and dimer. A predominance of disproportionation in the reactions of the caged radical pair is required to explain the larger yield of "molecular" olefin over that of the dimer. There is some support for such behavior with several kinds of alkyl radicals produced pairwise in condensed media by photolysis of azoalkanes (166).

Some indication of the origin of the unscavengable hydrogen yield may be inferred from the radiolysis of deuterium labeled alkanes. Dorfman irradiated mixtures of C_2H_6 and C_2D_6 in the presence of ethylene and propylene as hydrogen atom scavengers (167). The results showed that up to 66% of the total hydrogen yield occurred through molecular detachment which might arise in a primary reaction such as

$$C_2H_6 \rightsquigarrow C_2H_4^{+} + H_2 + e^{-} \qquad [I\text{-}45]$$

Nevitt and Remsberg (168) applied the labeling technique to liquid phase cyclohexane radiolysis using mixtures of cyclo-C_6H_{12} and cyclo-C_6D_{12}. The results were complex. A maximum of 25% of the "molecular" hydrogen was estimated to arise by direct detachment, the remainder possibly originating in reactions of ions. Benzene reduced the total yield of hydrogen without changing the ratio of yields of the various isotopic forms in it. This supported the earlier suggestion that benzene inhibition involved both radical and non-radical processes (169).

The use of labeled indicator molecules in liquid alkane radiolysis was greatly extended by Dyne and coworkers (170, 171, 172). When using small amounts of cyclo-C_6D_{12} (up to 5 mole %) in a series of alkanes as "solvents" it was possible to distinguish between "activating" and "deactivating" alkanes from the increased or decreased yield of D_2 relative to the amount produced when cyclo-C_6D_{12} was added to cyclo-C_6H_{12} (172). The results correlated with the ionization potentials of the "solvents" (81). The limiting G value of D_2 per unit mole fraction of cyclo-C_6D_{12} in C_6H_{12} was 0.25 when the concentration of cyclo-C_6D_{12} was extrapolated to zero. This "molecular" yield of D_2 was reduced by the addition of benzene and iodine to the cyclo-C_6D_{12}-cyclo-C_6H_{12} system (171). It was concluded that the additives acted on a common precursor to the decomposition modes which generate hydrogen. Based to a large extent on such isotopic labeling experiments Dyne has summarized many observed radiolytic behavior patterns into a comprehensive mechanism (63). The mechanism consists of primary formation of ions, electrons, and excited molecules:

$$\mathrm{RH} \rightsquigarrow \mathrm{RH}^{+},\ e^{-},\ \mathrm{RH}^{*} \qquad [\mathrm{I}\text{-}46]$$

The ion-electron pairs can be converted <u>relatively slowly</u> to excited molecules indistinguishable from those produced directly by the ionizing radiation:

$$RH^{+} + e^{-} \longrightarrow RH^{*} \qquad [I\text{-}47]$$

Dyne says, " ... all subsequent decomposition proceeds through these excited molecules". RH* decomposes to give "molecular" products as well as freely diffusing intermediates. With respect to hydrogen formation the mechanism suggests

$$RH^{*} \longrightarrow H_2 + \text{products} \qquad [I\text{-}48]$$

$$\longrightarrow X_H + \text{products} \qquad [I\text{-}49]$$

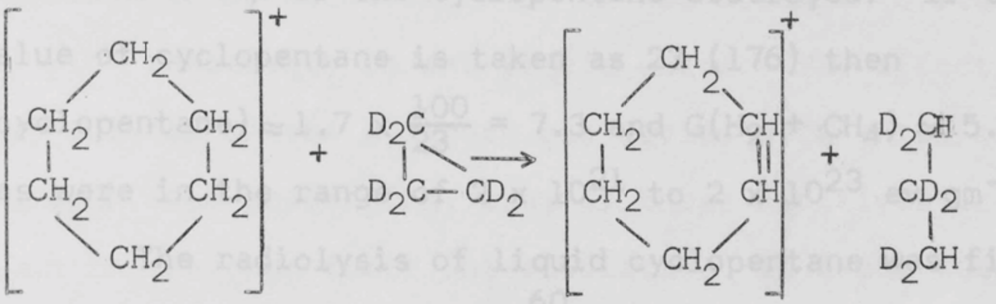
where X_H is an intermediate which reacts further with substrate to generate hydrogen:

$$X_H + RH \longrightarrow H_2 + \text{products} \qquad [I\text{-}50]$$

Scavengers may interact with RH^{+}, e^{-}, RH^{*}, and/or X_H.

Ausloos and coworkers studied several radiolyses using deuterium labeled alkane gases. Radical scavengers were often used, sometimes combined with the Essex electric field technique (173). In some cases separate vacuum ultraviolet photolysis experiments allowed an estimate of the contribution of excited neutral molecules to the radiolysis processes. An interesting H_2 transfer reaction between cyclohexane parent ion and cyclo-C_3D_6

was postulated to explain the formation of $CD_2HCD_2CD_2H$ as an important product in the radiolysis of cyclo-C_6H_{12}-cyclo-C_3D_6 mixtures.


[I-51]

With propylene-d_6 the postulated H_2 transfer reaction gave CD_3CDHCD_2H (78). The same reactions were observed with cyclohexane ion generated photolytically using the Kr resonance lines at 1236 Å and 1165 Å (174). At 1236 Å, as much as 90% of the hydrogen was formed by molecular detachment from an excited neutral cyclohexane molecule. The distribution of the isotopic forms of hydrogen in the photolysis of cyclohexane-1,1,2,2,3,3-d_6 at 1470 Å (a Xe resonance line) suggested that most of the hydrogen formed by molecular detachment from a single carbon atom of the neutral excited molecule.

2. Cyclopentane Radiolysis

In this section radiolysis studies which have involved cyclopentane will be briefly surveyed. The earliest study on cyclopentane was done in the gas phase at 25°C by Heisig (175) using α particles from radon decay. No mechanistic interpretation for the radiolytic action was given. Only noncondensable gases, hydrogen and methane, were measured. Heisig found $M(-C_5H_{10})/N$ was 1.7 and the amount of the noncondensable gas was about 74% of the cyclopentane destroyed. If the W value of cyclopentane is taken as 23 (176) then $G(\text{-cyclopentane}) \approx 1.7 \times \frac{100}{23} = 7.3$ and $G(H_2 + CH_4) \approx 5.5$. Doses were in the range of 2×10^{21} to 2×10^{23} ev gm^{-1}.

The radiolysis of liquid cyclopentane was first studied by Lepley (177) using ^{60}Co gamma radiation and gas chromatographic analytical techniques. The identities of several radiolysis products were assigned on the basis of retention times on several gas chromatographic columns. Because of the lack of a mass balance Lepley suggested that hydrogen deficient polymeric material was produced in an amount equivalent to a $G(H_2)$ of about 1.4. No attempt was made to determine this suspected polymeric material. Doses were in the range of 3×10^{20} to 2×10^{22} ev gm^{-1}. It was suggested that cyclopentane and cyclopentylcyclopentane formed by disproportionation and combination, respectively, of cyclopentyl radicals. Saturated C_1 to C_3 products, n-pentane, and n-pentylcyclopentane were thought to arise from excited molecules while unsaturated fragmentation products may have resulted from ion fragmentation. Pentene-1 may have formed from a biradical intermediate or an excited molecule.

By studying the radiolysis of cyclohexane-cyclopentane liquid mixtures Muccini and Schuler (89) inferred from the effect of dose rate on dimer yields that the cycloalkyl radicals abstract hydrogen atoms from the solvent and thus may change their identities.

Cyclopentane was one of several liquid hydrocarbons X-irradiated by Hardwick (178) in his attempt to study hydrogen atom reactivity in the liquid phase. The effects of several solutes on the hydrogen gas yields were interpreted as hydrogen atom scavenging; many of these additives are now known to scavenge ionic intermediates. In later work on cyclopentane (148), Hardwick determined yields of unsaturation by an olefin titration technique as well as the total radical yields by ESR spectroscopy.

R. A. Holroyd used ethylene as a hydrogen atom and alkyl radical scavenger in electron- and gamma-irradiated liquid cyclopentane (103). The effects of temperature on the major product yields in the range of -78° to 46° C were studied both in the absence and presence of ethylene. A mechanism for the formation of the major products invoked free radical intermediates. The Holroyd and Klein technique (179) for determining radical yields with ethylene-^{14}C has been applied to cyclopentane (180). Schuler and Kuntz (120) measured the methyl radical yield in γ-irradiated cyclopentane using radioiodine (^{131}I) as a radical scavenger. $G(CH_3^{\cdot})$ is about 0.019. From the measured $G(CH_3^{\cdot})$ in a host of saturated hydrocarbons these workers developed an empirical correlation between methyl yields and molecular structure. This correlation predicts, however, the absence of a methyl radical yield for unsubstituted cycloalkanes.

A study of the radiolysis of dilute solutions of c-C_6H_{12} and c-C_6D_{12} in cyclopentane by Dyne and Denhartog (181) showed a yield of cyclohexene greater than expected on the basis of the electron fraction of cyclohexane present. The increased olefin yield was attributed to a transfer of energy, initially absorbed in the cyclopentane, to the cyclohexane. The saturated dimeric products showed a bias towards the incorporation of cyclopentyl radicals in agreement with the findings of Muccini and Schuler (89). Stone(93) has extended this work of Dyne and Denhartog by studying the system over the complete composition range of c-C_5H_{10} - c-C_6H_{12}. c-C_6D_{12} was added in small amounts (2 to 5%) to investigate deviations from the "mixture law". Residual yields of the saturated dimers were observed in the presence of sufficient I_2 to remove freely diffusing radicals. These residual yields, attributed to radical - radical reactions in spurs, were formed in amounts predictable on the basis of the electron fraction of each cycloalkane in the mixtures.

Toma and Hamill (182) studied hydrogen gas formation in irradiated liquid cyclopentane containing solutes believed to be reactive with ionic intermediates. They concluded that (90) "...the major part of the hydrogen yield from the radiolysis of liquid cycloalkanes arises from charge neutralization of the respective molecular cation, producing C=C and two hot hydrogen atoms." Ultraviolet absorption spectroscopy of irradiated cyclopentane revealed a conjugated diolefinic product previously undetected.

Hughes and Hanrahan (183) reported radiolysis yields for several major and minor products of irradiated liquid cyclopentane. Hydrogen iodide and iodine were added as radical scavengers. Some temperature effects on hydrogen yields were also noted. The larger yields of fragmentation products and the congruent ring-opened olefin from cyclopentane compared to the yields of the analogous products from irradiated cyclohexane were attributed to the greater strain in the C_5 ring.

Yang and Marcus (92) measured the yields of dimers and olefins in irradiated cyclo-C_6H_{12} - cyclo-C_5H_{10} solutions. They conclude that the "nonideal" behavior of these mixtures can be attributed to the disproportionation processes:

$$\text{c-}C_6D_{11}\cdot + \text{c-}C_5H_9\cdot \xrightarrow{k_a} \text{c-}C_6D_{10} + \text{c-}C_5H_9D \qquad [\text{I-52}]$$

and

$$\text{c-}C_6D_{11}\cdot + \text{c-}C_5H_9\cdot \xrightarrow{k_b} \text{c-}C_6D_{11}H + \text{c-}C_5H_8 \qquad [\text{I-53}]$$

such that the rate constant k_a is greater than k_b. These workers point out that it is not necessary to invoke physical energy transfer processes like charge exchange from cyclopentane to cyclohexane to explain the biased formation of c-C_6D_{10} in this system. This conclusion is contrary to those of Dyne and Denhartog (181), Stone (93), and Toma and Hamill (90). Yang and Marcus have also studied binary cycloalkane-olefin solutions such as cyclopentene-cyclopentane, cyclohexene-cyclopentane, and cyclohexene-d_{10}-cyclopentane systems (184). Hydrogen atom scavenging appeared to be the dominant reaction affecting hydrogen gas formation at olefin contents below 1% whereas physical energy transfer to olefin was important at higher concentrations.

Ausloos and Lias (78) have reported a hydrogen transfer from the cyclo-$C_5H_{10}^+$ ion to several olefins and cyclopropane in the gas phase radiolysis of cyclopentane.

E. THE EXTENT OF THE PRESENT PROJECT

The present investigation is concerned mainly with the ^{60}Co gamma radiolysis of liquid cyclopentane at room temperature. A thorough product analysis was carried out in an attempt to acheive material balances. Product yields were measured as a function of dose.

A study is presented of the effects of several additives on the hydrogen yield from cyclopentane. Sulfur hexafluoride and octafluorocyclobutane were selected as electron scavenging reagents. ND_3 was added to scavenge a hydrocarbon positive ion acting as a Brønsted acid; the extent of acid scavenging was determined by measuring the HD content in the radiolytic hydrogen. The cyclopentane - benzene system was also examined. The effects of the additives on the hydrogen yield were interpreted in terms of the non-homogeneous kinetics of ion scavenging.

EXPERIMENTAL

A. VACUUM TECHNIQUES IN SAMPLE PREPARATION AND ANALYSIS

Samples of volatile materials for radiolysis studies are best prepared by techniques which enable the complete removal of dissolved air. The degassing and distillative transfer of hydrocarbons and other volatile materials used in this work was done with standard high vacuum equipment to be described briefly below. The design and construction of suitable equipment for radiolysis work are given by Dodd and Robinson (185), Melville and Gowenlock (186), Sanderson (187), and Rondeau (188). The analysis of irradiated materials for some low molecular weight products (H_2, CH_4, and C_2 hydrocarbons) was accomplished by low temperature fractionation which also required a vacuum system. The high vacuum system consisted of four functional units:

1) high vacuum and rough vacuum manifolds,
2) material storage sections,
3) sample preparation section, and
4) low temperature fractionation section for gas collection.

Figure II-1 shows the lay-out of the high vacuum and rough vacuum manifolds with a listing of their components and some sources.

FIGURE II - 1

High Vacuum and Rough Vacuum Manifold Components

OP1	Rotary oil pump, Welsh Duoseal model 1405 B
OP2	Rotary oil pump, Welsh Duoseal model 1400 B
S_1, S_5	Stopcocks, high vacuum, 2-mm oblique bore
S_2	Stopcock, high vacuum, 13-mm cranked
S_3, S_4	Stopcocks, high vacuum, 10-mm "L" shaped
T_1, T_2	Re-entrant cold traps, 4.0 cm x 30.0 cm with $ 45/50 joints.
DP	Mercury diffusion pump, speed of 1.5 litre per second; Cenco hot cone heater
PG	Pirani gauge and tube, Consolidated Vacuum Corp. type GP - 110

manifold tubing - Pyrex, 22 mm

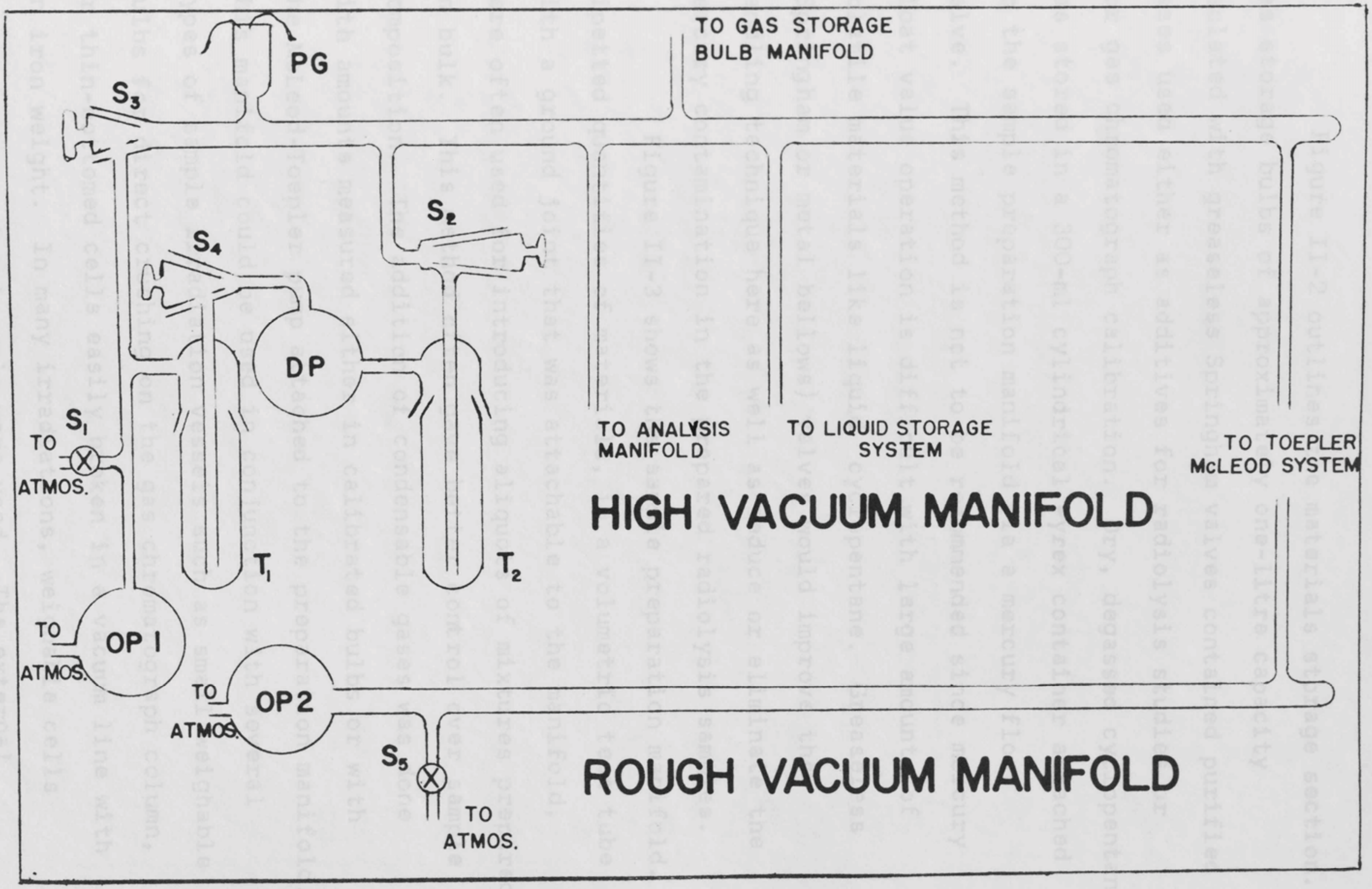

TO GAS STORAGE BULB MANIFOLD
PG
S3
S4
S2
DP
S1
TO ATMOS.
T1
T2
TO ANALYSIS MANIFOLD
TO LIQUID STORAGE SYSTEM
TO TOEPLER McLEOD SYSTEM
HIGH VACUUM MANIFOLD
TO ATMOS.
OP 1
TO ATMOS.
OP2
S5
TO ATMOS.
ROUGH VACUUM MANIFOLD

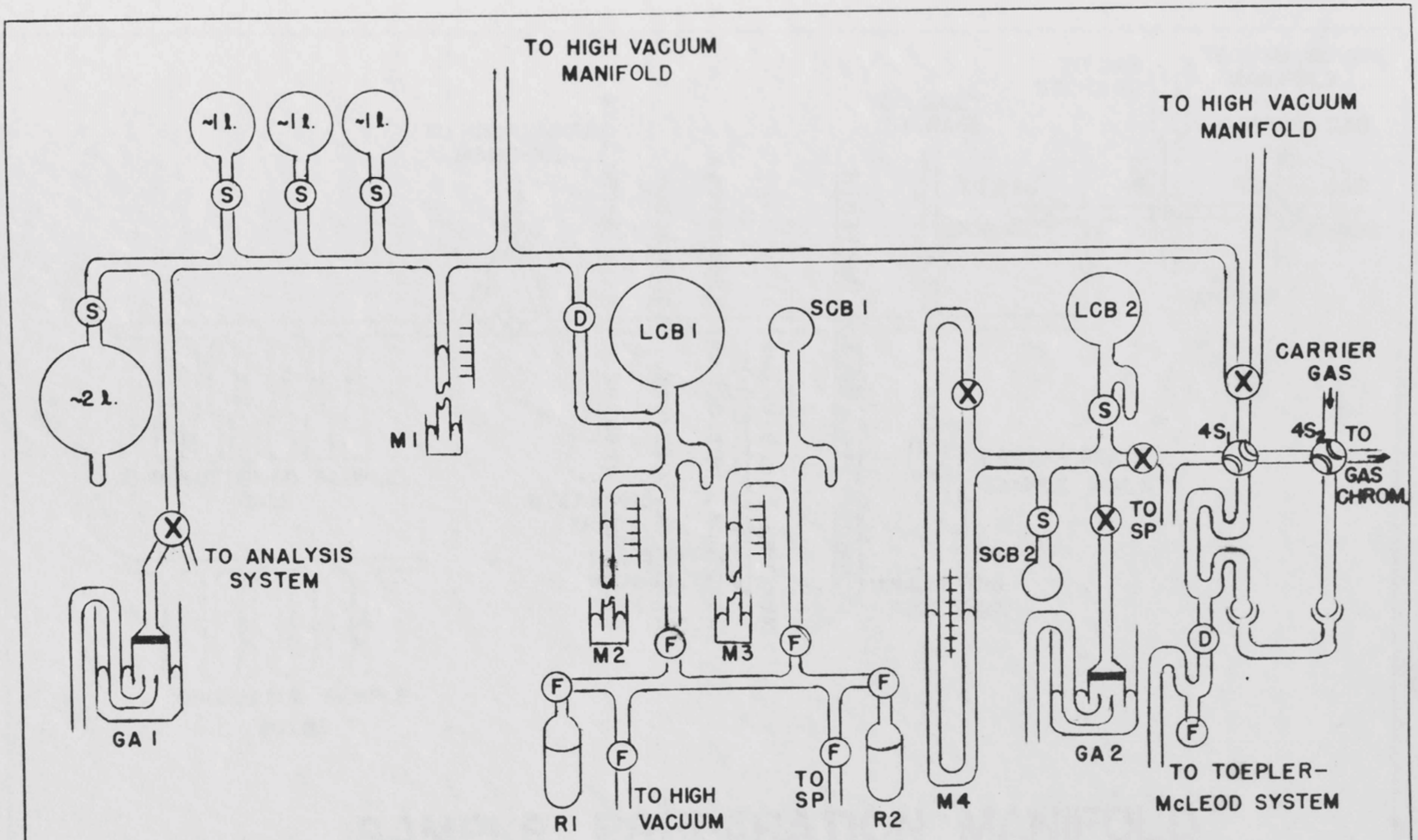
Figure II-2 outlines the materials storage section. Gas storage bulbs of approximately one-litre capacity isolated with greaseless Springham valves contained purified gases used either as additives for radiolysis studies or for gas chromatograph calibration. Dry, degassed cyclopentane was stored in a 300-ml cylindrical Pyrex container attached to the sample preparation manifold via a mercury float valve. This method is not to be recommended since mercury float value operation is difficult with large amounts of volatile materials like liquid cyclopentane. Greaseless (Springham or metal bellows) valves would improve the handling technique here as well as reduce or eliminate the mercury contamination in the prepared radiolysis samples.

Figure II-3 shows the sample preparation manifold. Pipetted quantities of materials, in a volumetric test tube with a ground joint that was attachable to the manifold, were often used for introducing aliquots of mixtures prepared in bulk. This method often gave better control over sample composition. The addition of condensable gases was done with amounts measured either in calibrated bulbs or with the McLeod-Toepler pump attached to the preparation manifold. This manifold could be used in conjunction with several types of sample irradiation vessels such as small weighable bulbs for direct crushing on the gas chromatograph column, or thin-bottomed cells easily broken in a vacuum line with an iron weight. In many irradiations, weighable cells having external break-seals were used. The external

FIGURE II - 2

Gas and Liquid Storage System

Ⓓ	Valve, Delmar, greaseless
Ⓕ	Mercury float valve
Ⓧ	Stopcock, greased
Ⓢ	Stopcock, Springham, greaseless
$4S_1$, $4S_2$	Stopcocks, greased, 4-way, 4-mm bore
GA1, GA2	Gas admittance valve consisting of a fritted glass funnel (porosity E) inverted into a mercury reservoir
M1, M2, M3	Manometer, mercury, open-ended
M4	Manometer, mercury
LCB1	Large calibrated bulb; 2139 ml to reference mark (50.00 cm on manometer)
SCB1	Small calibrated bulb; 178 ml to reference mark (50.00 cm on manometer)
SCB2	Small calibrated bulb; 102 ml
R1, R2	Liquid reservoir, ca 300 ml volume
SP	Sample preparation manifold

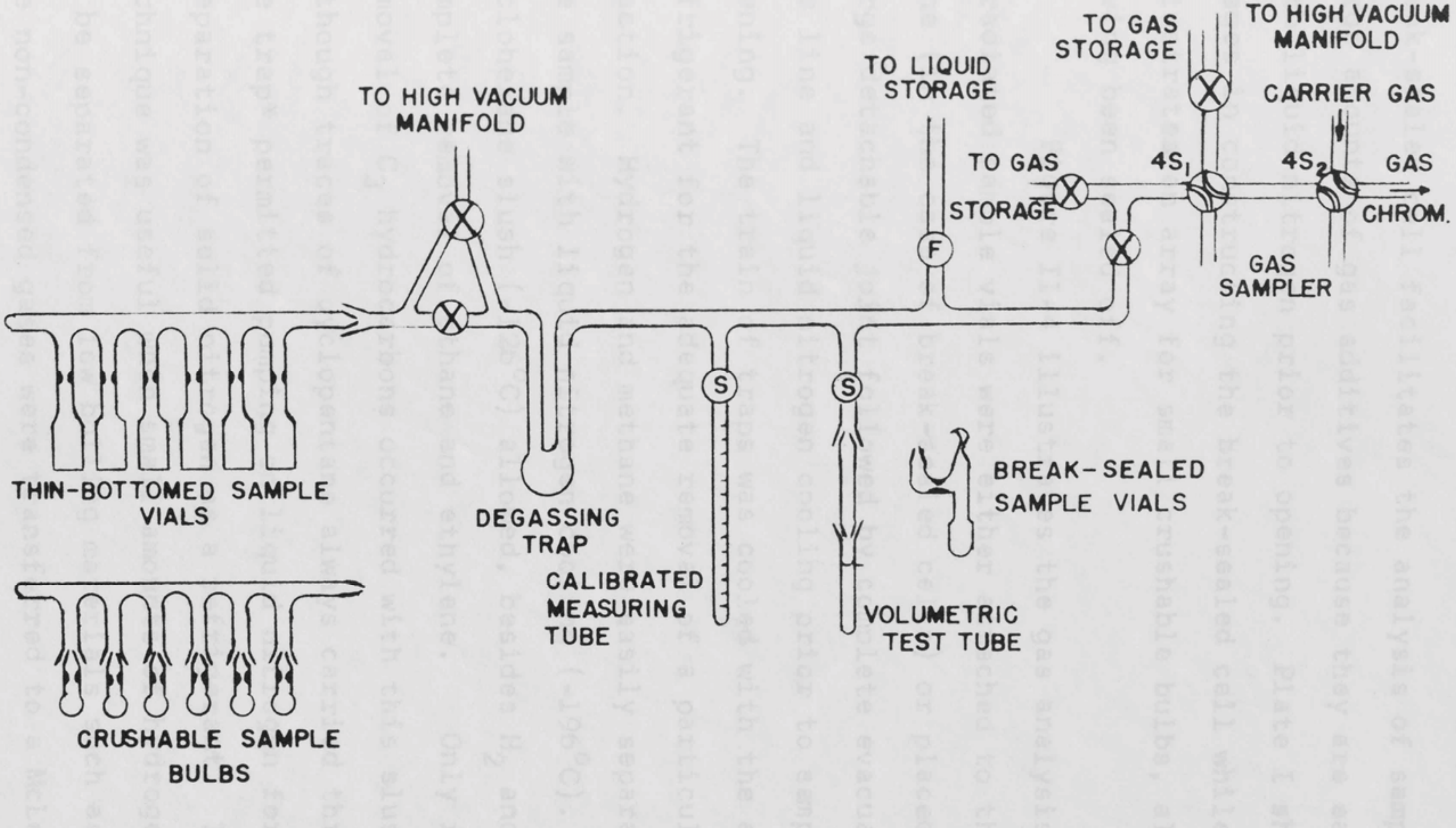


GAS AND LIQUID STORAGE SYSTEM

FIGURE II - 3

Sample Preparation Manifold

Ⓕ	Mercury float valve
Ⓢ	Stopcock, Springham, greaseless
Ⓧ	Stopcock, greased, high vacuum
$4S_1$, $4S_2$	Stopcock, greased, 4-way, 4-mm bore



SAMPLE PREPARATION MANIFOLD

break-sealed cell facilitates the analysis of samples containing large amounts of gas additives because they are easily frozen with liquid nitrogen prior to opening. Plate I shows the stages in constructing the break-sealed cell while Plate II illustrates an array for small crushable bulbs, all but one having been sealed off.

Figure II-4 illustrates the gas analysis manifold. Irradiated sample vials were either attached to the analysis line (in the case of break-sealed cells) or placed in a large detachable joint followed by complete evacuation of the line and liquid nitrogen cooling prior to sample opening. The train of traps was cooled with the appropriate refrigerant for the adequate removal of a particular gas fraction. Hydrogen and methane were easily separated from the sample with liquid nitrogen cooling (-196°C). Methylcyclohexane slush (-126°C) allowed, besides H_2 and CH_4, complete removal of ethane and ethylene. Only incomplete removal of C_3 hydrocarbons occurred with this slush although traces of cyclopentane always carried through. One trap* permitted pumping on liquid nitrogen for the preparation of solid nitrogen as a refrigerant. This technique was useful when small amounts of hydrogen were to be separated from low boiling materials such as ethylene. The non-condensed gases were transferred to a McLeod gauge system by the Toepler pump. A range of calibrated volumes in the McLeod gauge allowed a large variation in the number

* This trap was designed by J.W. Fletcher of the Radiation Chemistry Group.

PLATE I

Break-sealed Vials

Construction Stages

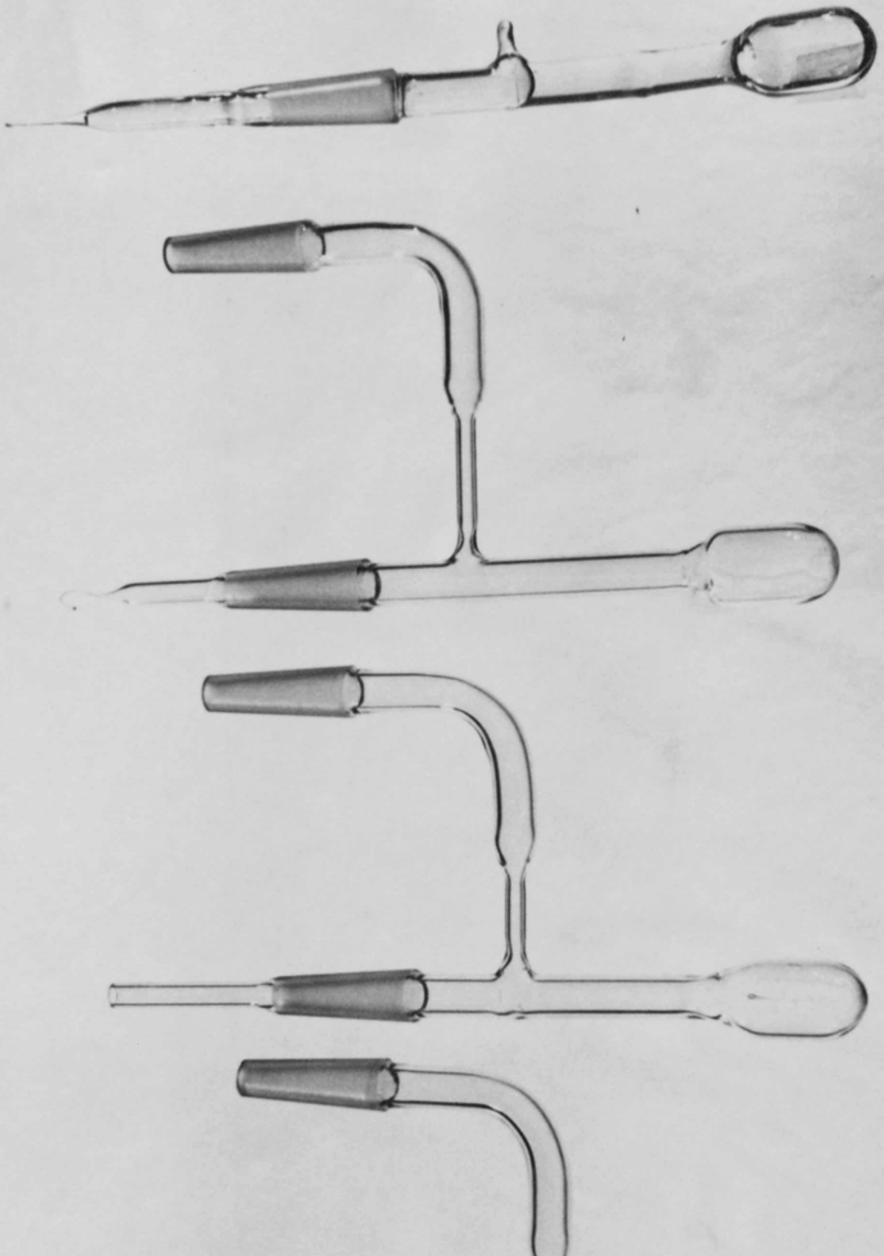


PLATE II

Crushable Bulb Preparation

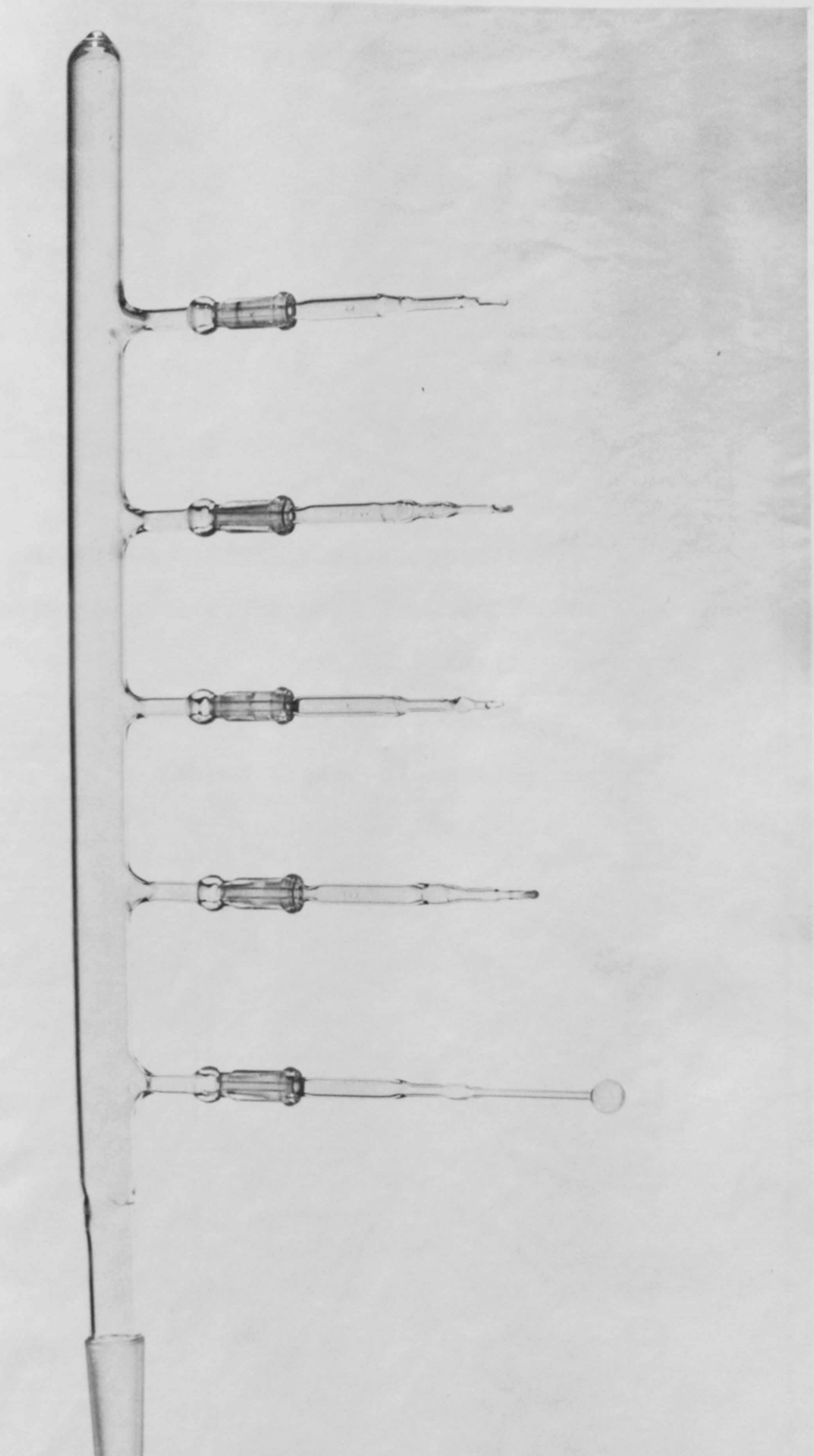
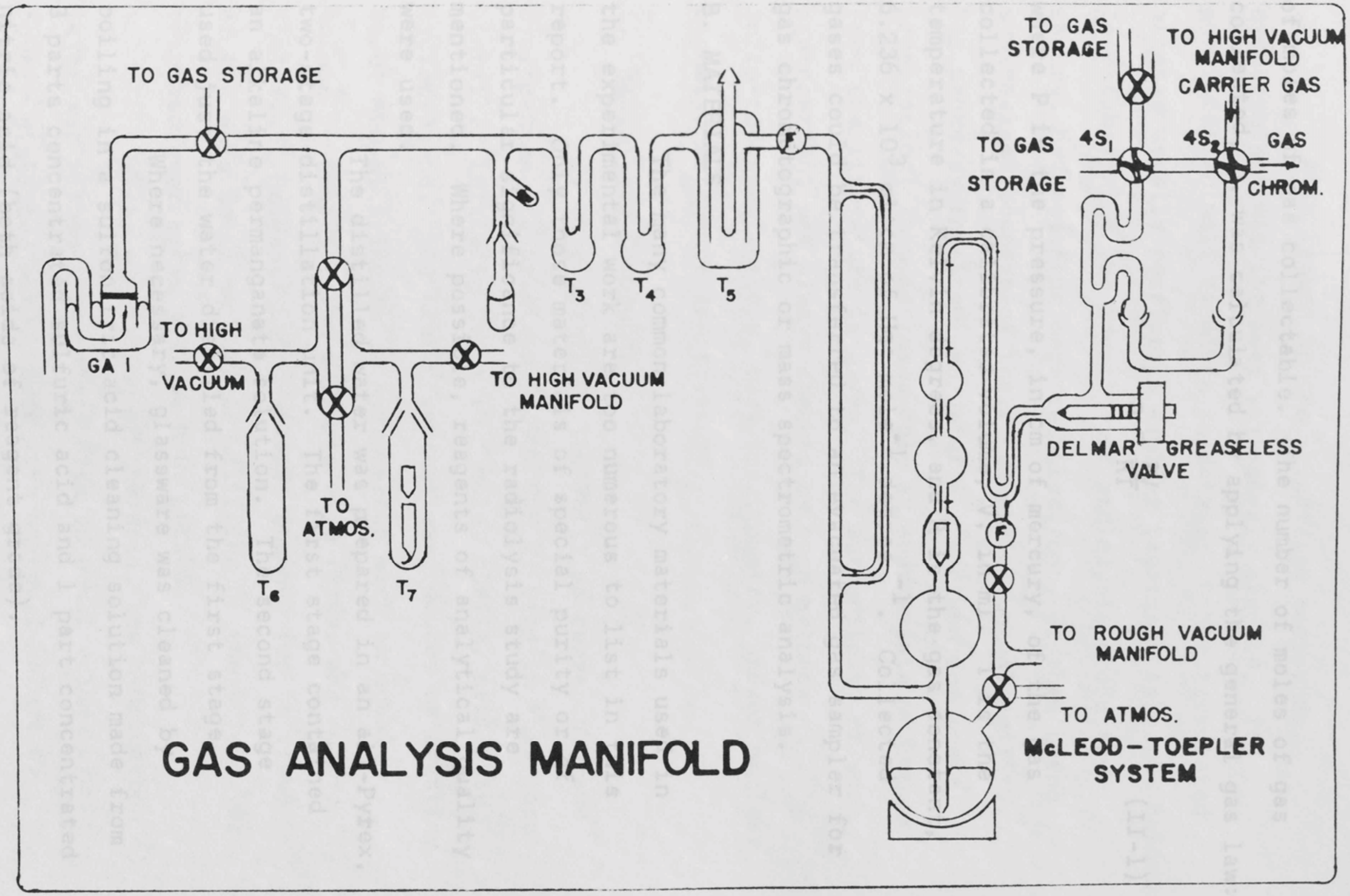


FIGURE II - 4

Gas Analysis Manifold

Ⓕ	Mercury float valve
Ⓧ	Stopcock, greased high vacuum
$4S_1$, $4S_2$	Stopcock, greased, 4-way, 4-mm bore
T_3, T_4	Traps
T_5	Trap, solid nitrogen
T_6, T_7	Evacuable sample holder
GA_1	Valve, gas admittance



GAS ANALYSIS MANIFOLD

of moles of gas collectable. The number of moles of gas collected, n, was calculated by applying the general gas law:

$$n = \frac{PV}{RT} \qquad \text{(II-1)}$$

where P is the pressure, in cm of mercury, of the gas collected in a calibrated volume, V, in ml. T is the temperature in Kelvin degrees, and R is the gas constant, 6.236×10^3 ml·cm of Hg· mole^{-1} degree^{-1}. Collected gases could be transferred to an evacuated gas sampler for gas chromatographic or mass spectrometric analysis.

B. MATERIALS

The many common laboratory materials used in the experimental work are too numerous to list in this report. Only those materials of special purity or of particular significance to the radiolysis study are mentioned. Where possible, reagents of analytical quality were used.

The distilled water was prepared in an all-Pyrex, two-stage distillation unit. The first stage contained an alkaline permanganate solution. The second stage used just the water distilled from the first stage.

Where necessary, glassware was cleaned by boiling in a sulfonitric acid cleaning solution made from 3 parts concentrated sulfuric acid and 1 part concentrated nitric acid (both acids of reagent grade).

With regard to the irradiated compounds, cyclopentane was the most extensively studied. Its purification will be given in detail. Other irradiated alkanes usually received a similar treatment as noted below. In establishing the identity of radiolysis products, several hydrocarbons were required, many of them being synthesized because of their commercial unavailability. For those synthesized, no details are given for their preparation; in some cases only an appropriate reference from the literature is given. The authenticity of such hydrocarbons was always checked by such methods as infra-red spectroscopy, mass spectrometry, and/or nuclear magnetic resonance spectroscopy.

1. Radiolysed Compounds

a) Cyclopentane The Phillips research grade cyclopentane (guaranteed 99.98% C_5H_{10}) used in this work contained initially 5.4×10^{-3} molar olefin, primarily cyclopentene. The olefin content was reduced by treating about 400-ml aliquots of hydrocarbon with an equal volume of concentrated sulfuric acid (Baker and Adamson Analytical Reagent) using several changes (up to five) of the acid until no further yellowing of the acid layer occurred over a twenty-four hour period.

After separating off the acid, the hydrocarbon layer was washed three times with an equal volume of doubly distilled water, once with an equal volume of

2% potassium carbonate solution and three final washes with doubly distilled water. The hydrocarbon was dried over anhydrous magnesium sulfate (Baker and Adamson Analytical Reagent) and finally distilled at atmospheric pressure (boiling point ca. 48°C). The first and last 15-ml portions were rejected. The acid-washed cyclopentane had no measurable olefin content (ie., less than 6.5×10^{-5} molar by the bromine titration technique discussed in section II-D-4).

For some experiments, for example, those involving addition of ammonia, the acid-washed cyclopentane was degassed and stored over a film of sodium metal for one week before transferring to a storage reservoir sealed by a mercury float valve.

As the acid-washed cyclopentane still contained traces of n-pentane and 2,2-dimethylbutane, it was necessary to prepare gas-chromatographically pure cyclopentane when a measure of the radiolytic n-pentane yield was required at low doses. At higher doses the plain acid-washed material was used for an n-pentane yield using a correction from the unirradiated material. A preparative o-tricresylphosphate column (20 feet) with the Aerograph Autoprep chromatograph was used with automatic injection and collection of the cyclopentane peak. The collected cyclopentane was given a necessary acid-washing and distillation treatment similar to that applied to the unchromatographed hydrocarbon.

Some radiolytic yields, for example G(H_2), obtained from both chromatographically purified as well as from the plain acid-washed cyclopentane were not in agreement with the contemporaneous published values (177, 178). Consequently a third method of purification was also tried. This involved a sulfonitric acid washing followed by a percolation through silica gel according to the method of Vinogradov (189). The cyclopentane thus purified gave results concordant with those obtained with both the plain acid-washed and the gas-chromatographed cyclopentane.

b) <u>n-Pentane</u> This material was Phillips research grade. It was given the sulfuric acid treatment. Distillation was done in a "cold-room" at 10°C.

c) <u>Spiropentane</u> This hydrocarbon was synthesized by the method of Applequist et al. (190). The spiropentane was purified gas-chromatographically using, in sucession, columns of silica gel (medium activity), silver nitrate-propylene glycol, and squalane, with helium carrier gas.

d) <u>Cyclohexane</u> Phillips research grade was given the sulfuric acid treatment, then water-washed, with a final distillation.

e) <u>Cyclohexane-d_{12}</u> This material was obtained from Stohler Isotope Chemicals. It was stated to have an isotopic purity exceeding 99.5 atom % D. A 10-ml sample was percolated through a 3-cm column of activated silica gel before using in radiolysis work. Cyclohexane-d_{12}

received from Merck, Sharpe and Dohme contained a halogen compound that could not be removed and which interferred in the radiolysis.

f) Cycloheptane Privately obtained chromatographically purified and sulphuric acid-washed cycloheptane was used in the radiolysis work. The olefin content was less than 6.5 x 10^{-5} molar.

g) Cyclooctane Matheson cyclooctane was zone-refined, gas-chromatographed, sulphuric acid-washed and water-washed, with a final distillation.

h) Cyclodecane A privately obtained sample was gas-chromatographically purified, sulphuric acid-washed, and water-washed, with a final distillation.

i) n-Decane Matheson n-decane was purified by forming a urea clatherate to remove branched chain hydrocarbons following a procedure outlined by Sixma (191).* This was followed by gas chromatography to remove other normal alkanes, a sulphuric acid washing, and a water washing with a final distillation.

j) Benzene Phillips research grade benzene was partially recrystallized and the supernatant liquid rejected. This was repeated three times. It was used without any further treatment.

k) Ammonia-d_3 This material was prepared by a modification of a procedure given by Crespi and Katz (192)

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* I am indebted to R. Schutte of the Radiation Chemistry Group for pointing out this procedure and for his translation of it.

after it was found that the ammonia-d_3 supplied by Merck, Sharpe and Dohme had an unsatisfactory deuterium content. The protium content of the synthetic ammonia-d_3 was determined by examining the proton magnetic resonance absorption using a Varian HA-100 spectrometer. Samples of the liquified ammonia were run at -40°C using an internal capillary of chloroform to give a reference frequency. Calibration mixtures were prepared by adding small amounts of NH_3 to the deutero-ammonia to give protium contents in the range of 2 to 5 atom % H. The protium content of the synthetic ND_3 was 0.8 atom % H (ie., about 98% ND_3 and 2% ND_2H). The capillary technique allowed recovery of the ammonia for subsequent radiolysis work. The ammonia-d_3 was stored in a two-litre calibrated bulb sealed with a mercury float valve.

l) <u>Sulfur Hexafluoride</u> Matheson sulfur hexafluoride was purified by trap-to-trap distillation as suggested by MacCormack and Schneider (193). The purified compound was stored in a one-litre bulb sealed with a Springham greaseless valve.

m) <u>Octafluorocyclobutane</u>* This material was supplied by Pennisular Chemical Co. It was purified and stored by the same techniques used with sulfur hexafluoride.

Table II - 1 gives the sources for many of the hydrocarbons used as reference compounds in product identification.

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* I am indebted to Dr. O.P. Strausz for a sample of this compound.

TABLE II - 1

2. Reference Compounds

HD	Merck, Sharpe, and Dohme
D_2	Matheson
Methane	Phillips research grade
Ethane	Phillips research grade
Ethylene	Phillips research grade
Acetylene	Matheson
Propane	Phillips research grade
Propylene	Phillips research grade
Cyclopropane	Ohio Chemical Co.
Methylacetylene	Matheson
n-Butane	Phillips research grade
Methylcyclopropane	American Petroleum Institute
Butene-1	Phillips research grade
Butene-2, cis and trans	Phillips research grade
Isobutylene	Phillips research grade
Butadiene-1,3	Matheson
n-Pentane	see section (a)
Pentene-1	Phillips research grade
Pentene-2, cis and trans	Phillips pure grade
2-Methylbutane	Phillips pure grade
2,2-Dimethylbutane (Neopentane)	Matheson
Cyclopentene	Phillips research grade
Bicyclo[2·1·0]pentane	Synthesized by the method of Criegee and Rimmelin (194)

Spiropentane	See section (a)
Pentadiene-1,4	Synthesized by the method of Schniepp and Geller (195)
Pentadiene-1,3	Chemical Procurements Laboratories, Inc.
Cyclopentane	See section (a)
Isoprene	Eastman white label
1,1-Dimethylcyclopropane	Synthesized by the method of Shortridge et al. (196)
Ethylcyclopropane	Synthesized by the method of Volkenburgh et al. (197)
Cyclopentadiene	Synthesized by depolymerization of endodicyclopentadiene
Methylenecylobutane*	Aldrich Chemical Co.
Vinylcyclopropane	Synthesized by the method of Overburger and Halek (198)
Cyclohexane	Phillips research grade
Cyclohexene	Matheson
Bicyclo [3·1·0] hexane	Synthesized by the method of Simmons and Smith (199) using an improved zinc-copper couple suggested by LeGoff (200)
Cyclohexadiene-1,3	Aldrich Chemical Co.
Cyclohexadiene-1,4	Aldrich Chemical Co.
Benzene	Phillips research grade
Methylcyclopentane	Phillips research grade
Ethylcyclopentane	Synthesized by hydrogenation of vinylcyclopentane
Hexadiene-1,5	K and K Laboratories, Inc.
Vinylcyclopentane	American Petroleum Institute

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* I am indebted to G.R. DeMare for a sample of this compound.

n-Propylcyclopentane	Synthesized by hydrogenating allylcyclopentane
Allylcyclopentane	Synthesized by a Wurtz reaction of allyl bromide and bromocyclopentane
n-Pentylcyclopentane	Synthesized by a Wurtz reaction of n-pentyl iodide and bromocyclopentane
n-Decane	See section (a)
Cyclopentylcyclopentane	Synthesized by the hydrogenation of 3-(3-cyclopentenyl)cyclopentene
3-Cyclopentylcyclopentene	Synthesized by partial hydrogenation of 3-(3-cyclopentenyl)cyclopentene
Meso-, d-, and l-3(3-cyclopentenyl)cyclopentene	Privately obtained sample
cis-Decahydronaphthalene	Separated by gas chromatography from Fisher decalin
trans-Decahydronaphthalene	Separated by gas chromatography from Fisher decalin
Cyclodecane	See section (a)
cis- and trans-Cyclodecene	Synthesized from cyclodecane by photobromination following the method of Blomquist et al. (201)
endo-Dicyclopentadiene	Privately obtained sample
cis-Decahydroazulene	Synthesized by the hydrogenation of azulene
Azulene	Synthesized by the method of Anderson and Nelson (202) from 1,6-cyclodecandione. The latter compound was prepared by ozonolysis of $\Delta^{9,10}$octalin as well as by the method of S. Dev (203). The aromatization step used an improved catalyst described by Chaudron and Pallaud (204).

Cyclopentylbenzene	Synthesized by the method of Turova-Pollyak and Davydova (205)
1-Cyclopentylcyclohexadiene-1,4	Synthesized by the method of Dryden et al. (206) using the Birch reduction of cyclopentylbenzene
Cyclopentylcyclohexane	Synthesized by the hydrogenation of 1-cyclopentylcyclohexadiene-1.4
4-Cyclopentylcyclohexene	Synthesized from p-cyclopentylphenol (207) by high pressure hydrogenation and dehydration (208)
5-Cyclopentylcyclohexadiene-1,3	Synthesized by the dehydrobromination of the dibromide obtained by brominating 4-cyclopentylcyclohexene. The method of Mousseron and Winternitz (209) uas used in the dehydrobromination with 2,4,6-collidine
1,3-Dicyclopentylcyclopentane	Synthesized by the method of Goheen (210) from cyclopentanone by an aldol condensation reaction

C. RADIATION SOURCES AND DOSIMETRY

Two radiation sources were used in this work One source of about 300 curies was contained in a walk-in cave with the ^{60}Co source retractable into a lead shield by a remote manual operation. The sample mounting in the cave is illustrated in Plate III. The other source was an Atomic Energy of Canada, Ltd., Gammacell 220 with a strength of about 10,000 curies. Plate IV shows part of this equipment with the drawer raised and several samples contained in an aluminum sample holder ready for irradiation. The normal irradiating temperatures in the cave were $22 \pm 2^{\circ}C$ while those in the Gammacell were in the range of $25 \pm 3^{\circ}C$. A Dewar vessel for low temperature irradiations, illustrated in Plate V, was used with the Gammacell.

Dosimetry of the radiation intensities of the two sources was done with Fricke dosimeter solution (211). $G(Fe^{+3})$ was taken as 15.6. A value of 2201 $molar^{-1}cm^{-1}$ was used for the molar absorptivity of Fe^{+3} at 304 nm (peak) in the irradiated dosimeter solution at $25.0^{\circ}C$ with a 0.7% increase for each centigrade degree rise in temperature. The absorbance of the dosimeter solution was measured on a Cary Recording Spectrophotometer (model 14) by scanning the wave length region 320 nm to 290 nm. The calibration of the spectrophotometer was checked with at least one of two ultraviolet spectral standard solutions.

PLATE III

Samples Mounted in Cave

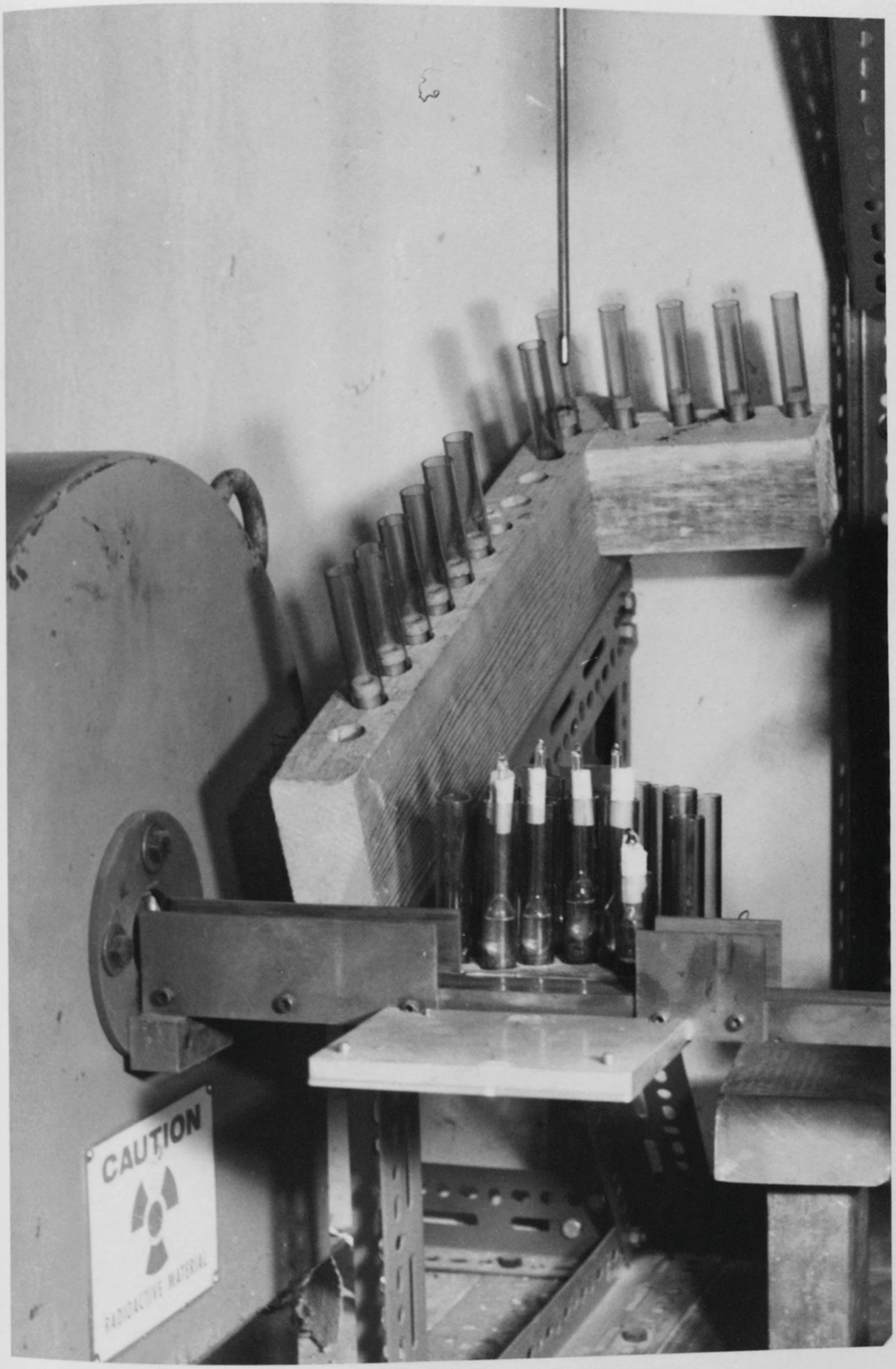

CAUTION
RADIOACTIVE MATERIAL

PLATE IV

Aluminum Holder with Samples for the Gammacell 220

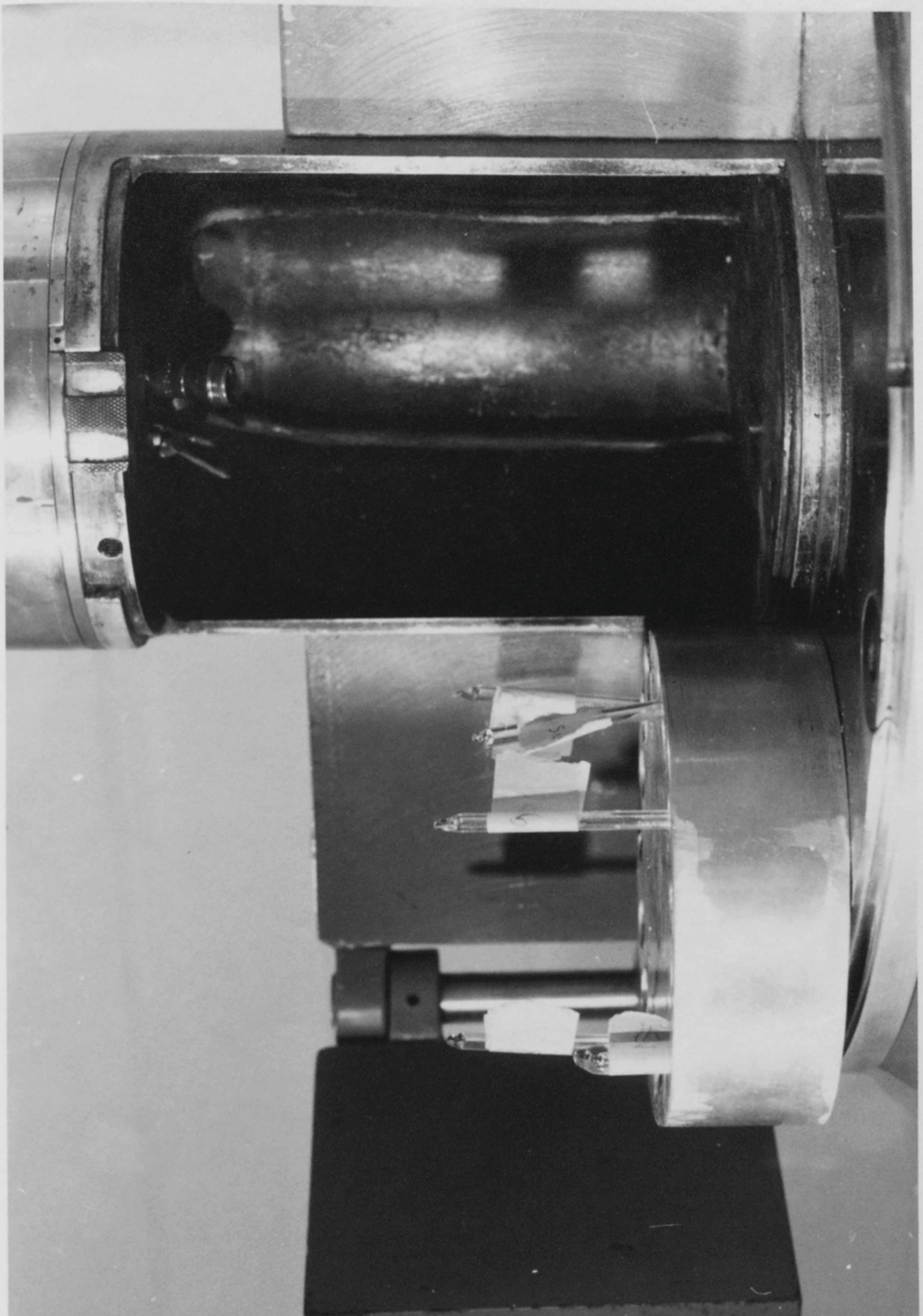


PLATE V

Low Temperature Dewar for the Gammacell 220

These consisted of either an alkaline chromate solution (212) or an acid dichromate solution (213). Several samples of a fixed volume of dosimeter solution were irradiated for different times up to 40 min. with the cave source or no longer than 4 min. in the Gammacell. Figure II - 5 shows a typical irradiation time--absorbance plot obtained at a wavelength of 304 nm for Fricke solution irradiated in the Gammacell. The finite intercept in this Figure occurs because the timer is actuated only when the sample drawer is in its final lowered position. The dose rate received by a sample was given by the following equation:

$$I = \frac{\text{Absorbance produced per hour} \times N_o}{156 \times \rho_\epsilon \times 2201\ [1 + 0.007\ (T - 25.0)]} \qquad \text{(II-2)}$$

where I is the dose rate in ev (electron-mole)$^{-1}$ hr^{-1},

N_o is Avagadro's number,

ρ_ϵ is the electron density of Fricke solution at the temperature of irradiation and at 25°C equals 0.566 electron-moles ml^{-1}, and

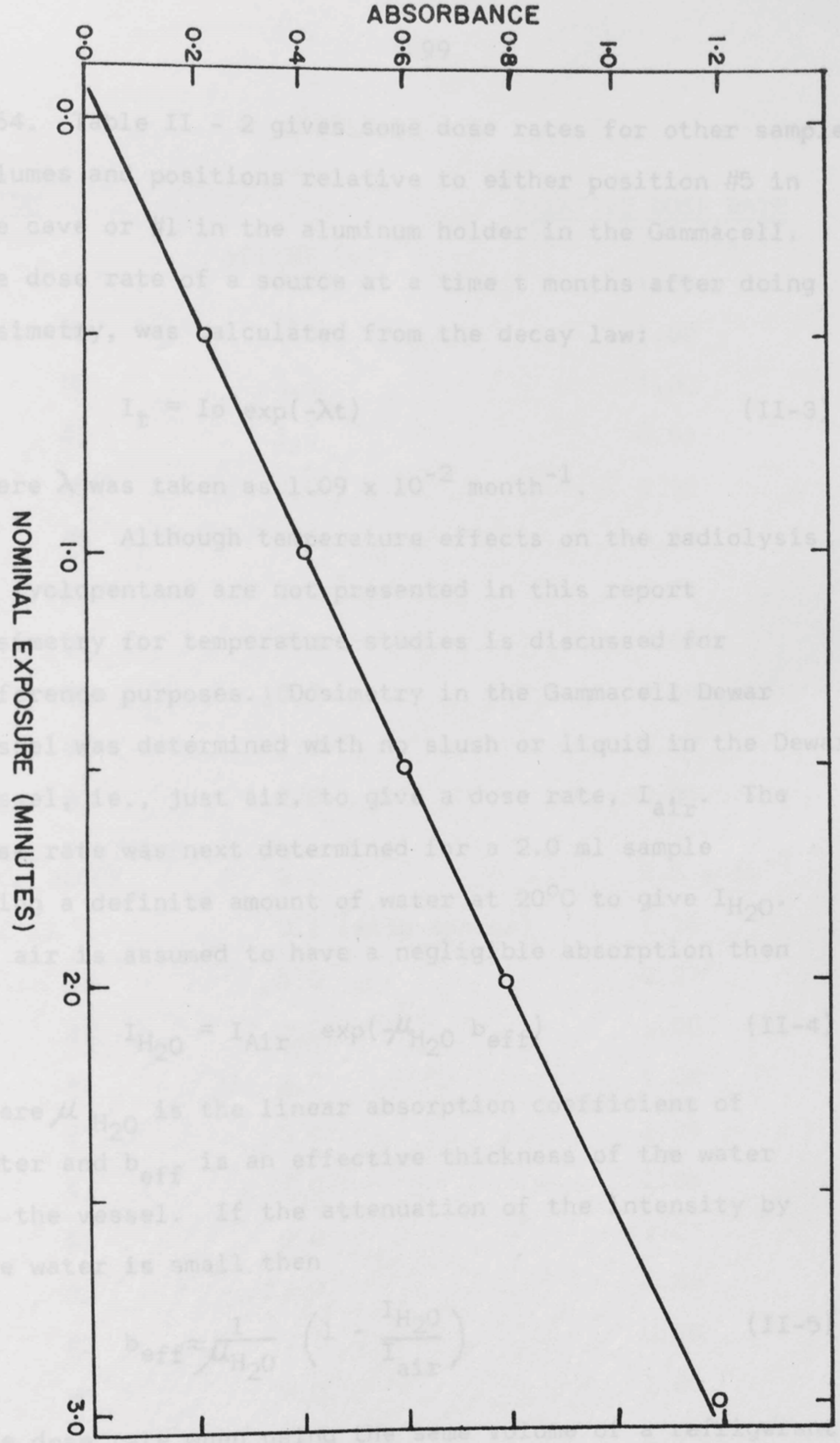
T is the temperature of the aliquot analysed in the spectrophotometer in degrees centigrade.

The cave source had a dose rate of 1.32×10^{19} ev (electron-mole)$^{-1}$ hr^{-1} for a 2.0 ml sample in position #5 on January 1, 1963. For 2.0 ml in position #1 of the aluminum holder in the Gammacell the dose rate was found to be 9.63×10^{19} ev (electron-mole)$^{-1}$ hr^{-1} on January 1,

FIGURE II - 5

Typical Irradiation Time - Absorbance Plot for Gammacell Dosimetry

Absorbance of Fricke Dosimeter Solution for several irradiation times.


ABSORBANCE
0·0
0·2
0·4
0·6
0·8
1·0
1·2
NOMINAL EXPOSURE (MINUTES)
0·0
1·0
2·0
3·0

1964. Table II - 2 gives some dose rates for other sample volumes and positions relative to either position #5 in the cave or #1 in the aluminum holder in the Gammacell. The dose rate of a source at a time t months after doing dosimetry, was calculated from the decay law:

$$I_t = I_o \exp(-\lambda t) \qquad \text{(II-3)}$$

where λ was taken as 1.09×10^{-2} month^{-1}.

Although temperature effects on the radiolysis of cyclopentane are not presented in this report dosimetry for temperature studies is discussed for reference purposes. Dosimetry in the Gammacell Dewar vessel was determined with no slush or liquid in the Dewar vessel, ie., just air, to give a dose rate, I_{air}. The dose rate was next determined for a 2.0 ml sample using a definite amount of water at 20°C to give I_{H_2O}. If air is assumed to have a negligible absorption then

$$I_{H_2O} = I_{Air} \exp(-\mu_{H_2O}\, b_{eff}) \qquad \text{(II-4)}$$

where μ_{H_2O} is the linear absorption coefficient of water and b_{eff} is an effective thickness of the water in the vessel. If the attenuation of the intensity by the water is small then

$$b_{eff} \approx \frac{1}{\mu_{H_2O}} \left(1 - \frac{I_{H_2O}}{I_{air}}\right) \qquad \text{(II-5)}$$

The dose rate when using the same volume of a refrigerant X was determined by the following relations:

TABLE II - 2

POSITION	VOLUME (ml)	RELATIVE DOSE RATE
CAVE	0.10	1.09
Position #5	1.0	1.02
" #5	2.0	1.00
" #5	3.0	0.96
" #5	4.0	0.90
" #5	5.0	0.84
" #5	7.0	0.73
" #5	9.0	0.64
" #5	10.0	0.59
" #1	2.0	1.02
" #2	2.0	0.86
FARTHEST POSITION IN WOOD BLOCK	2.0	8.5×10^{-3}
GAMMACELL	0.1 (with spacer)	1.16
Position #1	1.0	0.97^5
" #1	2.0	1.00
" #1	3.0	1.02
" #1	5.0	1.04
" #1	7.0	1.06
" #1	9.0	1.07
" #1	10.0	1.08
" #3	2.0	0.98
" #5	2.0	1.00
" #8	2.0	1.00

TABLE II - 2 cont.

POSITION		RELATIVE DOSE RATE
Position #11	2.0	1.01
" #13	2.0	1.00

$$I_x = I_{air} \exp - \mu_x b_{eff} \qquad \text{(II-6)}$$

$$\approx I_{air}\left(1 - \mu_x \, b_{eff}\right) \qquad \text{(II-7)}$$

Substituting b_{eff} from (II-5), (II-7) becomes

$$I_x \approx I_{air}\left(1 - \frac{\mu_x}{\mu_{H_2O}}\left[1 - \frac{I_{H_2O}}{I_{air}}\right]\right) \qquad \text{(II-8)}$$

$$\approx I_{air} - \left(I_{air} - I_{H_2O}\right) \frac{\text{electron density of X}}{\text{electron density of } H_2O} \qquad \text{(II-9)}$$

The electron densities of several refrigerants are given in Table II - 3 relative to water at 0°C.

On January 1, 1964 the dose rate in the Gammacell Dewar vessel was 8.36×10^{19} ev $(\text{electron mole})^{-1}$ hr^{-1} for air and 7.56×10^{19} ev $(\text{electron mole})^{-1}$ hr^{-1} for water.

TABLE II - 3

Approximate Electron Densities of Various Refrigerants

REFRIGERANT	APPROX. TEMP. °C	APPROX. ELECTRON DENSITY (ϵ moles ml^{-1})	RELATIVE ELECTRON DENSITY (H_2O = 1.00)
H_2O - ice	0	0.56	1.00
CCl_4 slush	-23	0.84	1.5
monochlorobenzene slush	-44	0.62	1.1
chloroform slush	-64	0.82	1.5
ethylacetate slush	-84	0.56	1.0
ethanol	+41	0.44	0.79
	-22	0.46	0.83
	-75	0.50	0.89
	-91	0.51	0.91
methylcyclohexane slush	-126	0.52	0.93
2-methylbutane slush	-160	0.50	0.89
liquid nitrogen	-196	0.40	0.73

D. METHODS OF PRODUCT IDENTIFICATION AND QUANTITATIVE PRODUCT MEASUREMENT

1. Gas Chromatography

Gas chromatographic separation of radiolysis products served for both their identification through characteristic retention times and for their quantitative estimation. Figure II - 6 shows the lay-out of the gas chromatograph components. Quantitative determination of hydrocarbon materials was usually accomplished by the conversion technique of Zlatkis et al. (214, 215). This method employs hydrogen carrier gas and a nickel "hydrocracking" catalyst at 450°C. Hydrocarbons in this carrier are converted quantitatively to methane on passing through the catalyst column. The detector needs only to be calibrated for methane sensitivity. One detector was reserved exclusively for the converted hydrocarbon analyses. The "hydrocracking" catalyst was replaced approximately once a year. Except for accidental filament burn-outs, the sensitivity of the detector remained constant. The amount of a hydrocarbon, C_n, having n carbon atoms per molecule which generates a chromatogram peak area, A, is given by the relation:

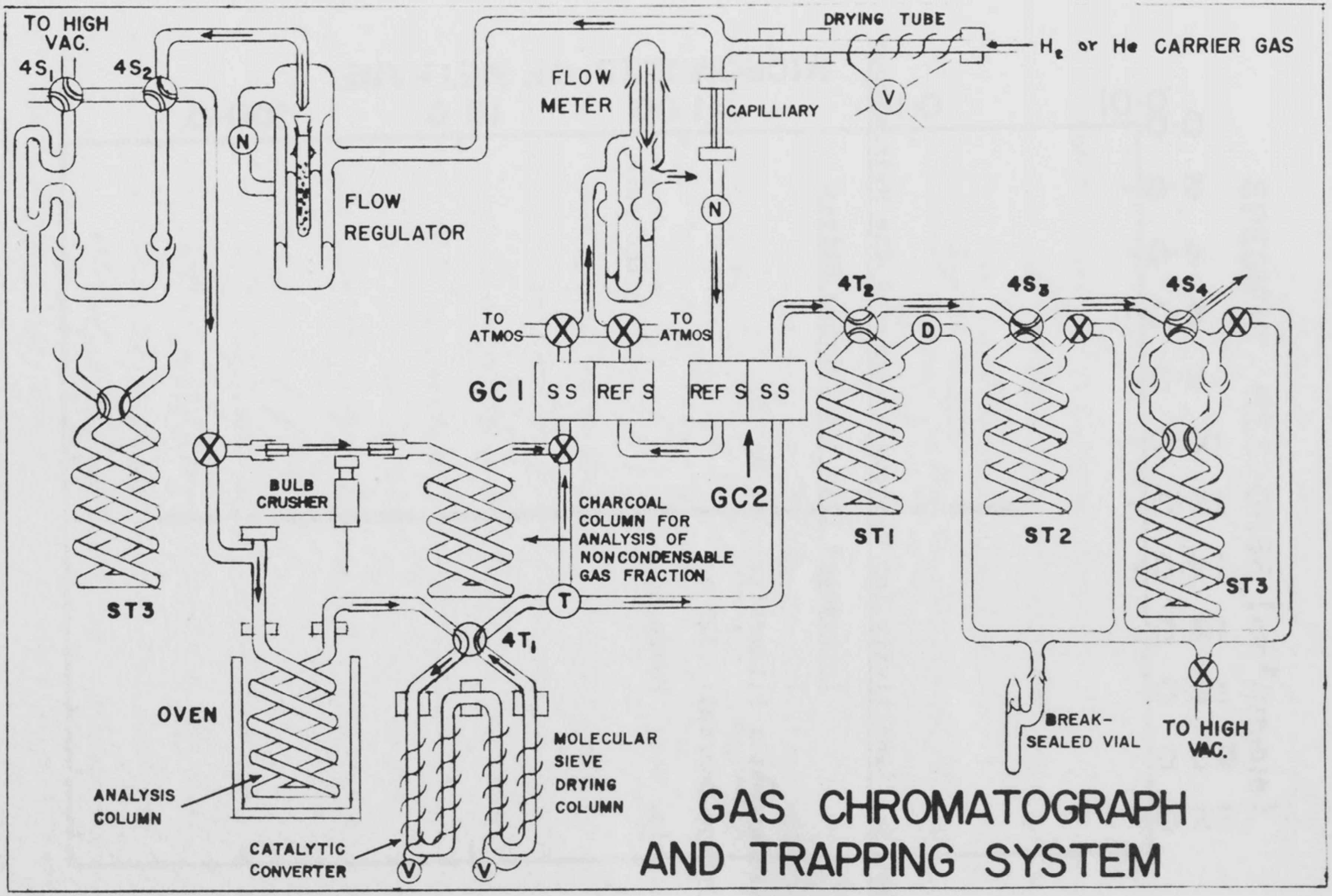
$$\mu \text{ moles of hydrocarbon, } C_n, = \frac{A}{nS} \qquad \text{(II-10)}$$

where S is the sensitivity of the Katharometer detector for methane in $cm^2\ (\mu moles)^{-1}$. Figure II - 7 shows the typical sensitivity over a wide range of the quantity of methane

FIGURE II - 6

Gas Chromatograph and Trapping System

Ⓓ	Delmar greaseless stopcock
Ⓝ	Needlevalve, Edwards "Speedivac" Type LBIA
Ⓣ	Stopcock, Corning #41024F 3 way Teflon
Ⓧ	Stopcock, greased
4S, $4S_2$, $4S_3$, $4S_4$	Stopcock, greased, 4-way 4 mm bore
4T, $4T_2$	Stopcock, Teflon, 4-way, 4 mm bore
ST1, ST2, ST3	Spiral traps, 6 ft.
Ⓥ	Autotransformer, Powerstat 120V, 7 amp
GC1, GC2	Gow Mac Katharometer detector TRIIB with Gow Mac Power Supply Control unit model 9999C and Sargent recorder model SR. SS is the cell for the sample stream and Ref S is the cell for the reference stream.
	Drying tube used Burrell high activity silica gel
	Carrier gas at 12 to 15 psi



GAS CHROMATOGRAPH AND TRAPPING SYSTEM

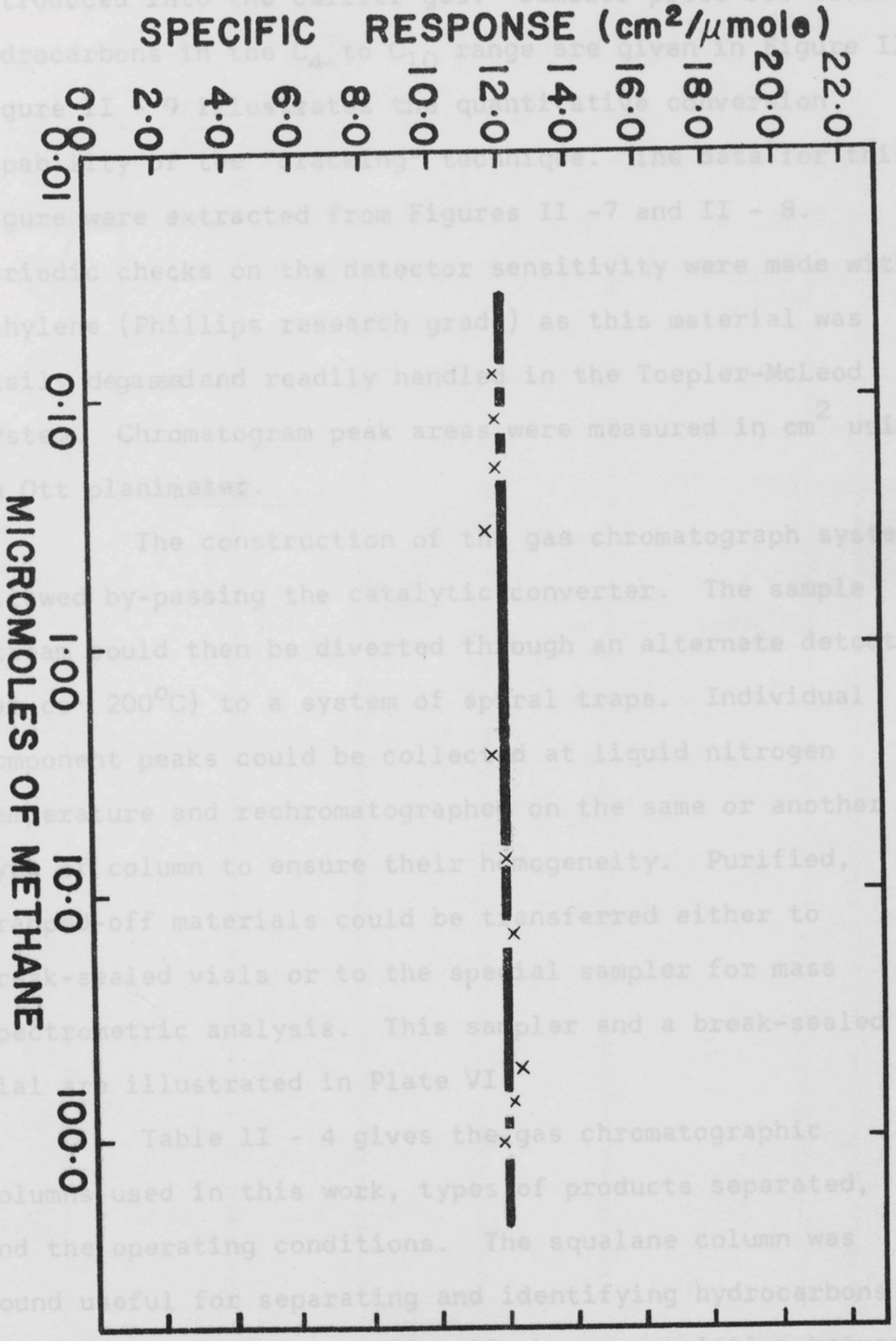
FIGURE II - 7

Methane Sensitivity for Various Amounts of the Hydrocarbon Introduced into the Carrier Stream

Katharometer Filaments: Gow Mac W1

Bridge Current: 325 ma

Carrier Gas: Hydrogen


SPECIFIC RESPONSE (cm²/μmole)
0·0
2·0
4·0
6·0
8·0
10·0
12·0
14·0
16·0
18·0
20·0
22·0
0·01
0·10
1·00
10·0
100·0
MICROMOLES OF METHANE

introduced into the carrier gas. Similar plots for several hydrocarbons in the C_4 to C_{10} range are given in Figure II - 8. Figure II - 9 illustrates the quantitative conversion capability of the "cracking" technique. The data for this figure were extracted from Figures II -7 and II - 8. Periodic checks on the detector sensitivity were made with ethylene (Phillips research grade) as this material was easily degassed and readily handled in the Toepler-McLeod system. Chromatogram peak areas were measured in cm^2 using an Ott planimeter.

The construction of the gas chromatograph system allowed by-passing the catalytic converter. The sample stream could then be diverted through an alternate detector (at ca. 200°C) to a system of spiral traps. Individual component peaks could be collected at liquid nitrogen temperature and rechromatographed on the same or another type of column to ensure their homogeneity. Purified, trapped-off materials could be transferred either to break-sealed vials or to the special sampler for mass spectrometric analysis. This sampler and a break-sealed vial are illustrated in Plate VI.

Table II - 4 gives the gas chromatographic columns used in this work, types of products separated, and the operating conditions. The squalane column was found useful for separating and identifying hydrocarbons in the C_5 range. Figure II - 10 shows correlation between

FIGURE II - 8

<u>Sensitivity Calibration for Several Hydrocarbons Containing Various Numbers of Carbon Atoms. Hydrocarbons Converted by Catalytic Converter</u>

Katharometer Filaments: Gow Mac W1

Bridge Current: 325 ma

Carrier Gas: Hydrogen

□	n - butane
⬠	cyclopentane
⬟	cyclopentene
⬡	cyclohexane
⬢	benzene
○	cycloheptane
●	cyclooctane
△	n - decane
✡	cyclopentylcyclopentane

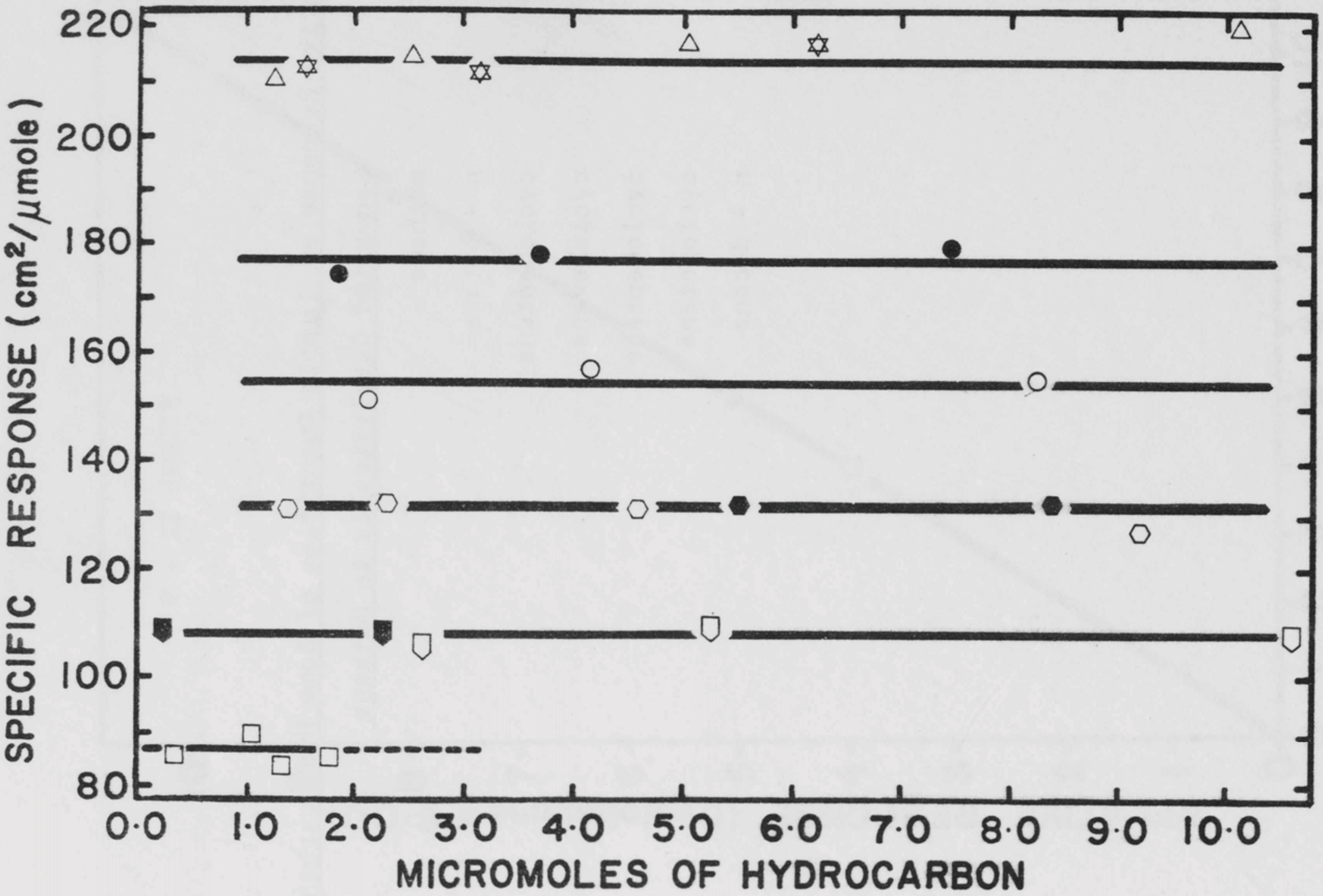

SPECIFIC RESPONSE (cm²/μmole)
220
200
180
160
140
120
100
80
0·0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10·0
MICROMOLES OF HYDROCARBON

FIGURE II - 9

Relative Response of 1μmole Quantities of Some Hydrocarbons Converted Catalytically to Methane

×	methane
□	n - butane
⬟	cyclopentene
⬡	cyclohexane
○	cycloheptane
●	cyclooctane
△	n - decane

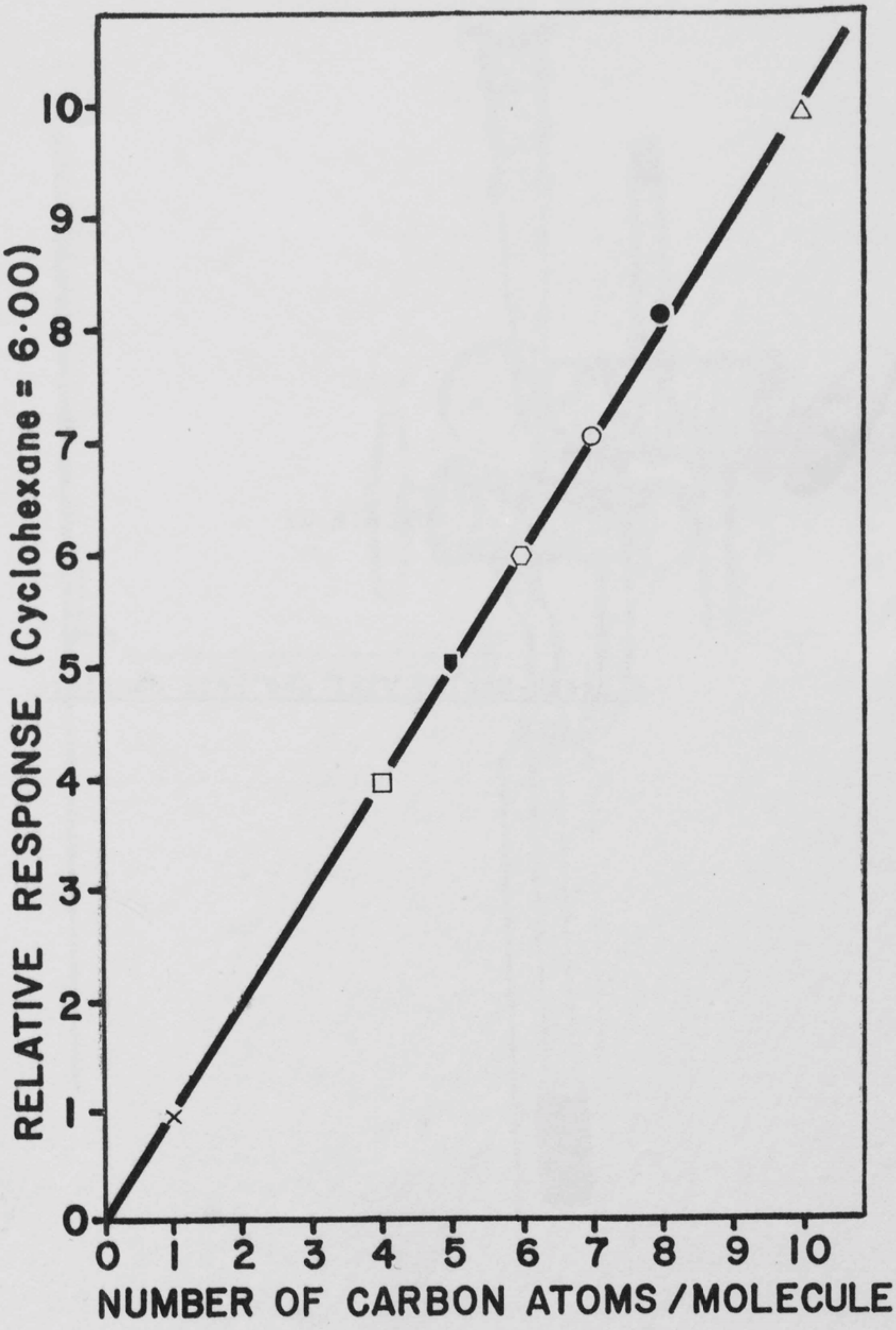

RELATIVE RESPONSE (Cyclohexane = 6·00)
NUMBER OF CARBON ATOMS / MOLECULE
0
1
2
3
4
5
6
7
8
9
10

PLATE VI

A Break-Sealed Vial and Peak Sampler

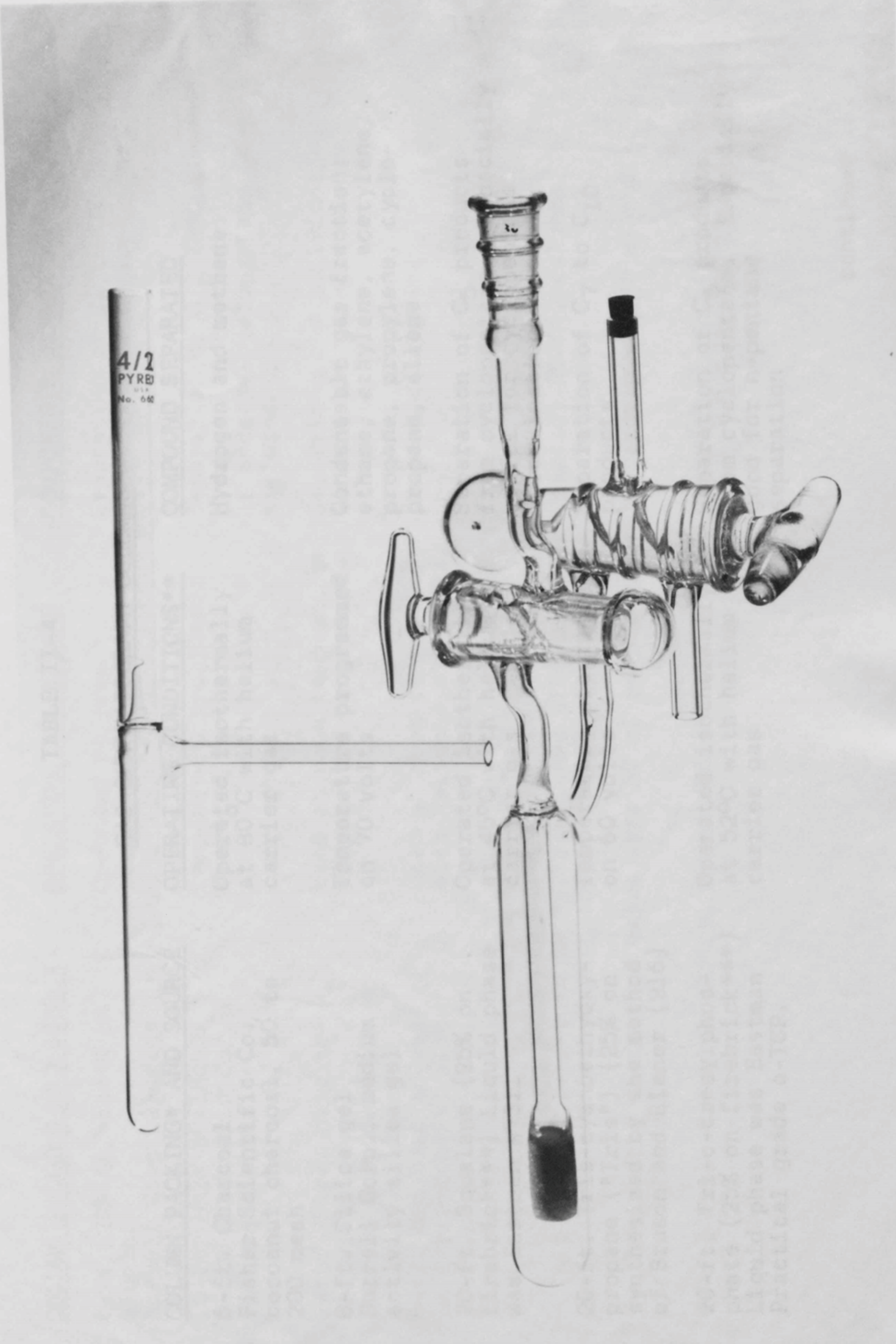

4/2
PYREX
No. 66

TABLE II-4

GAS CHROMATOGRAPH COLUMNS

COLUMN PACKING* AND SOURCE	OPERATING CONDITIONS**	COMPOUND SEPARATED
6-ft. Charcoal Fisher Scientific Co. cocoanut charcoal, 50 to 200 mesh	Operated isothermally at 80°C with helium carrier gas	Hydrogen and methane
8-ft. Silica gel Burrell Corp., medium activity silica gel	Temperature programmed on 70 volts	Condensable gas fraction; ethane, ethylene, acetylene, propane, propylene, cyclopropane, allene
20-ft. Squalane (25% on firebrick***) Liquid phase was Eastman #7311	Operated isothermally at 45°C with helium carrier gas	Separation of C_5 products from cyclopentane. Especially useful for cyclopentene determination
20-ft. Tris-cyanoethyoxypropane ("Tris") (25% on synthesized by the method of Bruson and Riener (216)	Temperature programmed on 60 volts	Separation of C_7 to C_{10} products
20-ft. Tri-o-cresylphosphate (25% on firebrick***) Liquid phase was Eastman Practical grade o-TCP.	Operated isothermally at 52°C with helium carrier gas	Separation of C_5 products from cyclopentane. Especially good for n-pentane separation

continued . . .

COLUMN PACKING AND SOURCE	OPERATING CONDITIONS	COMPONENTS SEPARATED
6-ft. 20% Apiezon N on alumina Burrell Corp. alumina	Operated at room temperature	Separation of C_2 to C_4 products from cyclopentane
15-ft. Ucon 50-LB550X F & M Scientific Corp. packing #LP158	Temperature programmed on 60 volts	Separation of C_{10} to C_{12} products in the radiolysis of benzene-cyclopentane mixtures
6-ft. Silver nitrate-propylene glycol packing #LP106	Used at room temperature with helium carrier gas	Separation and purification of bridged hydrocarbons
6-ft. Mercuric acetate on firebrick***. Prepared by method of Kerr and Trotman-Dickenson (217).	Used at room temperature with helium carrier gas	Removal of olefins

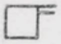
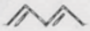
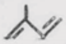
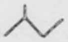
* All columns less than 20 ft. consisted of 6.mm Pyrex spirals; 20-ft. columns were fabricated from ¼-inch copper tubing with Swagelok fittings.

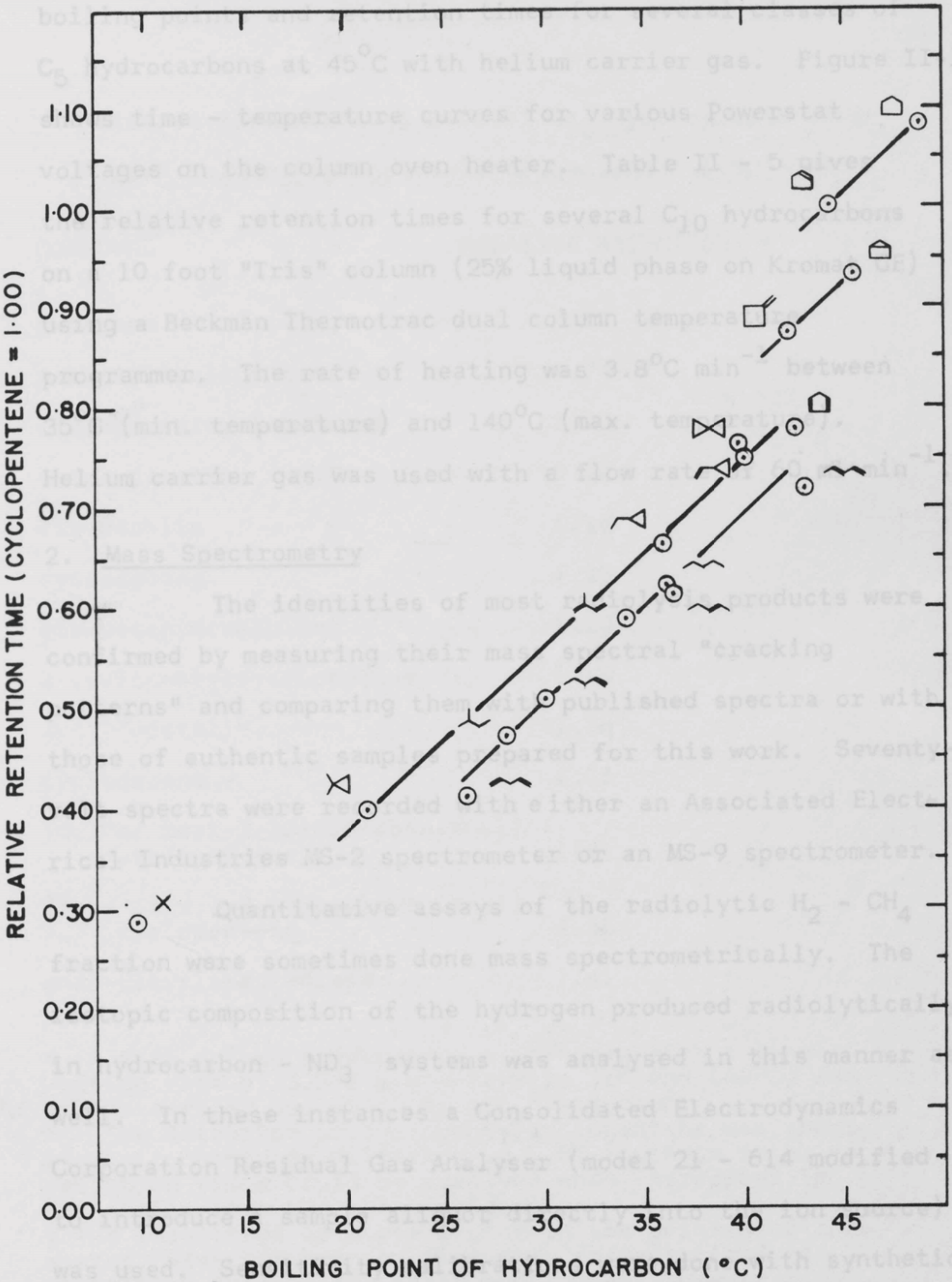
** Flow rates of carrier gases were 60 ml per minute for hydrogen and 40 ml per minute with helium

*** Burrell Corp. firebrick, Kromat FB (30 to 60 mesh)

FIGURE II - 10

Retention times for some C_5 hydrocarbons on Squalane relative to cyclopentene. Temperature: 45°C; Carrier gas: Helium at 40 ml min^{-1}.

	cyclopentane
	cyclopentene
	bicyclo[2·1·0] pentane
	cyclopentadiene
	methylenecyclobutane
	spiropentane
	ethylcyclopropane
	vinylcyclopropane
	1,1-dimethylcyclopropane
	pentadiene-1,4
	pentadiene-1,3
	pentene-2
	pentene-1
	isoprene
	n-pentane
	methylbutane
	neopentane


RELATIVE RETENTION TIME (CYCLOPENTENE = 1·00)
1·10
1·00
0·90
0·80
0·70
0·60
0·50
0·40
0·30
0·20
0·10
0·00
10
15
20
25
30
35
40
45
BOILING POINT OF HYDROCARBON (°C)

boiling points and retention times for several classes of C_5 hydrocarbons at 45°C with helium carrier gas. Figure II-11 shows time - temperature curves for various Powerstat voltages on the column oven heater. Table II - 5 gives the relative retention times for several C_{10} hydrocarbons on a 10 foot "Tris" column (25% liquid phase on Kromat CE) using a Beckman Thermotrac dual column temperature programmer. The rate of heating was 3.8°C min^{-1} between 35°C (min. temperature) and 140°C (max. temperature). Helium carrier gas was used with a flow rate of 60 ml min^{-1}.

2. Mass Spectrometry

The identities of most radiolysis products were confirmed by measuring their mass spectral "cracking patterns" and comparing them with published spectra or with those of authentic samples prepared for this work. Seventy-volt spectra were recorded with either an Associated Electrical Industries MS-2 spectrometer or an MS-9 spectrometer.

Quantitative assays of the radiolytic H_2 - CH_4 fraction were sometimes done mass spectrometrically. The isotopic composition of the hydrogen produced radiolytically in hydrocarbon - ND_3 systems was analysed in this manner as well. In these instances a Consolidated Electrodynamics Corporation Residual Gas Analyser (model 21 - 614 modified to introduce a sample aliquot directly into the ion source) was used. Sensitivity calibrations were done with synthetic gas mixtures having compositions similar to the radiolytic gases.

TABLE II - 5

Relative Retentions of Several C_{10} Hydrocarbons on a "Tris" Column (cyclopentylcyclopentane = 1.00)*,**

COMPOUND	RELATIVE RETENTION
n-decane	0.57
n-pentylcyclopentane	0.74
cyclopentylcyclopentane	1.00
trans-decalin	0.94
cis-decalin	1.18
cyclodecane	1.23
cis-decahydroazulene	1.10
3-cyclopentylcyclopentene	1.19
$\Delta^{9,10}$-octalin	1.36
cyclodecene	1.35
†d,l or meso-3-(3-cyclopentenyl) cyclopentene	1.31
†meso or d,l-3-(3-cyclopentenyl) cyclopentene	1.36
endo-dicyclopentadiene	1.41

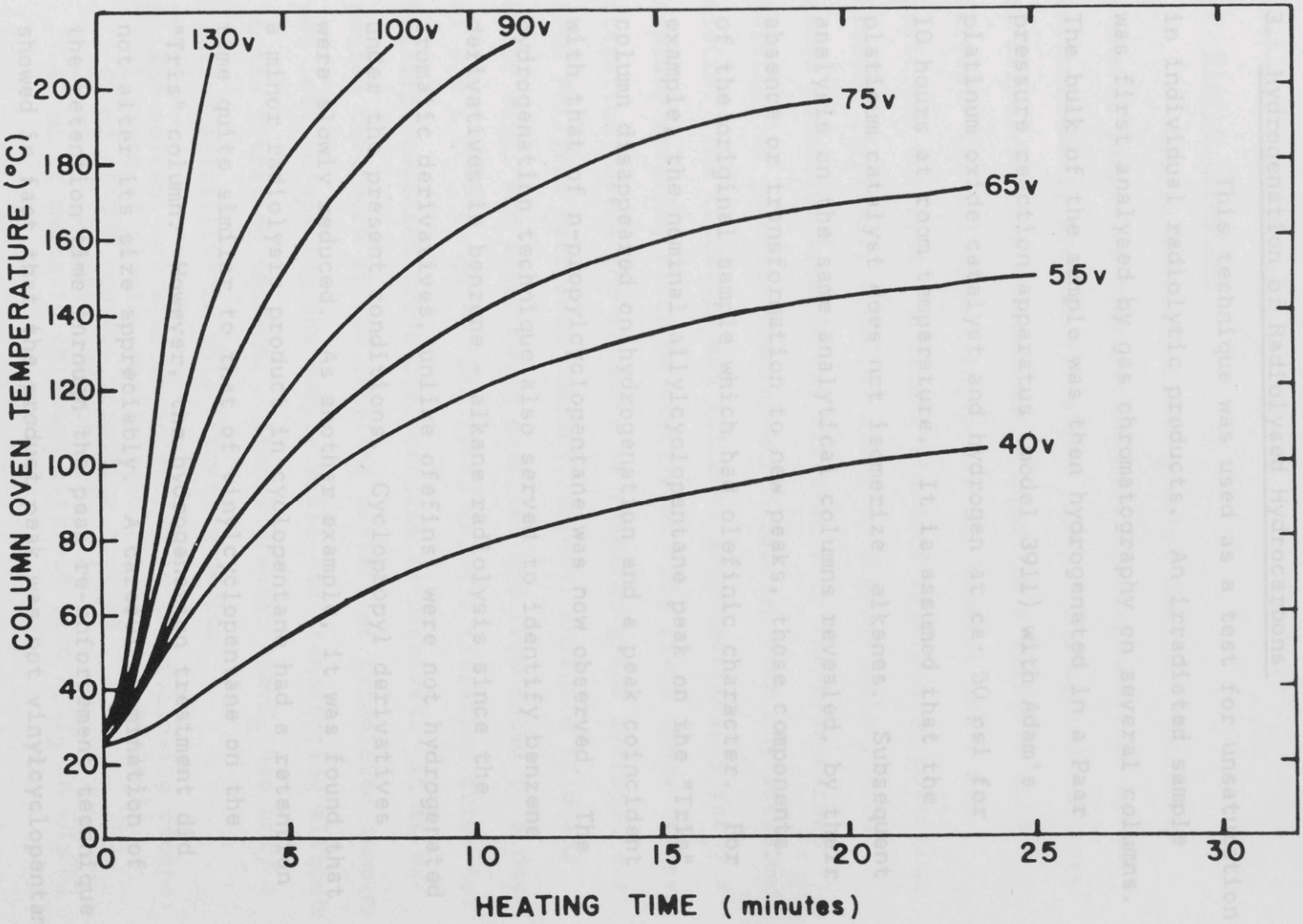
* A dual column temperature programmer with a linear heating rate of 3.8°C min^{-1} between 35° and 140°C, and helium carrier gas at 60 ml min^{-1} was used.

** The retention of cyclopentylcyclopentane was about 14 min. Compounds differing by 0.07 in their relative retention times could be resolved when introduced in quantities less than about 10 μmoles.

† the identities of these isomers in the opinion of this worker, have not been sufficiently characterized to warrant an unequivocal assignment. See, however, reference (219)

FIGURE II - 11

Time - Temperature Curves for the Column Oven for Various Voltages on the Heater Powerstat



130v
100v
90v
75v
65v
55v
40v
COLUMN OVEN TEMPERATURE (°C)
200
180
160
140
120
100
80
60
40
20
0
0
5
10
15
20
25
30
HEATING TIME (minutes)

3. Hydrogenation of Radiolysed Hydrocarbons

This technique was used as a test for unsaturation in individual radiolytic products. An irradiated sample was first analysed by gas chromatography on several columns. The bulk of the sample was then hydrogenated in a Paar pressure reaction apparatus (model 3911) with Adam's platinum oxide catalyst and hydrogen at ca. 50 psi for 10 hours at room temperature. It is assumed that the platinum catalyst does not isomerize alkanes. Subsequent analysis on the same analytical columns revealed, by their absence or transformation to new peaks, those components of the original sample which had olefinic character. For example, the nominal allylcyclopentane peak on the "Tris" column disappeared on hydrogenation and a peak coincident with that of n-propylcyclopentane was now observed. The hydrogenation technique also served to identify benzene derivatives in benzene - alkane radiolysis since the aromatic derivatives, unlike ofefins, were not hydrogenated under the present conditions. Cyclopropyl derivatives were slowly reduced. As another example, it was found that a minor radiolysis product in cyclopentane had a retention time quite similar to that of vinylcyclopentane on the "Tris" column. However, the hydrogenation treatment did not alter its size appreciably. A careful examination of the retention time through the peak re-enforcement technique showed in fact that the product peak was not vinylcyclopentane.

Contrary to a statement of Lepley (177), G(vinylcyclopentane) was found to be less than 0.1.

4. <u>Olefin Titration</u>

Olefin concentrations greater than 10^{-4} molar in a one-ml sample of hydrocarbon were readily measured by the Kolthoff-Bovey bromine titration (218). The method consists of dissolving the hydrocarbon aliquot in a suitable acid solvent* (20 ml) containing potassium bromide and a mercuric ion catalyst. A dilute standard solution of potassium bromate (typically 0.000167 molar or 0.00167 molar) with added potassium bromide was titrated into the hydrocarbon solution to generate bromine which reacted with any dissolved olefin. The titration was followed amperometrically using a rapidly rotating platinum electrode. Fig II-12 shows typical titration curves for aliquots of research grade cyclopentane from Phillips Petroleum Company, after a sulfuric acid and water wash, and after being purified and irradiated to a dose of 2.9 x 10^{18} ev gm^{-1}. Fig II-13 shows a titration curve for Phillips research grade cyclopentane as received. It is expected that much of the ethylene content of irradiated samples was lost on opening the sample vials and transferring aliquots to the titration solvent. Alkanes greater than C_6 had only a limited solubility in this titration medium.

---

* The solvent was made up according to the following recipe:
1 litre of glacial acetic acid (analytical reagent)
40 ml of 40% aqueous potassium bromide
24 ml of 12 molar hydrochloric acid
40 ml of mercuric chloride catalyst (10% $HgCl_2$ in CH_3OH)

FIGURE II - 12

Amperometric Titration of Olefin in Cyclopentane

○ solvent + 2 ml of purified, unirradiated research grade cyclopentane

△ solvent + 2 ml of purified research grade cyclopentane irradiated to a dose of 2.94×10^{18} ev gm^{-1}. Olefin concentration is 1.2×10^{-4} molar.

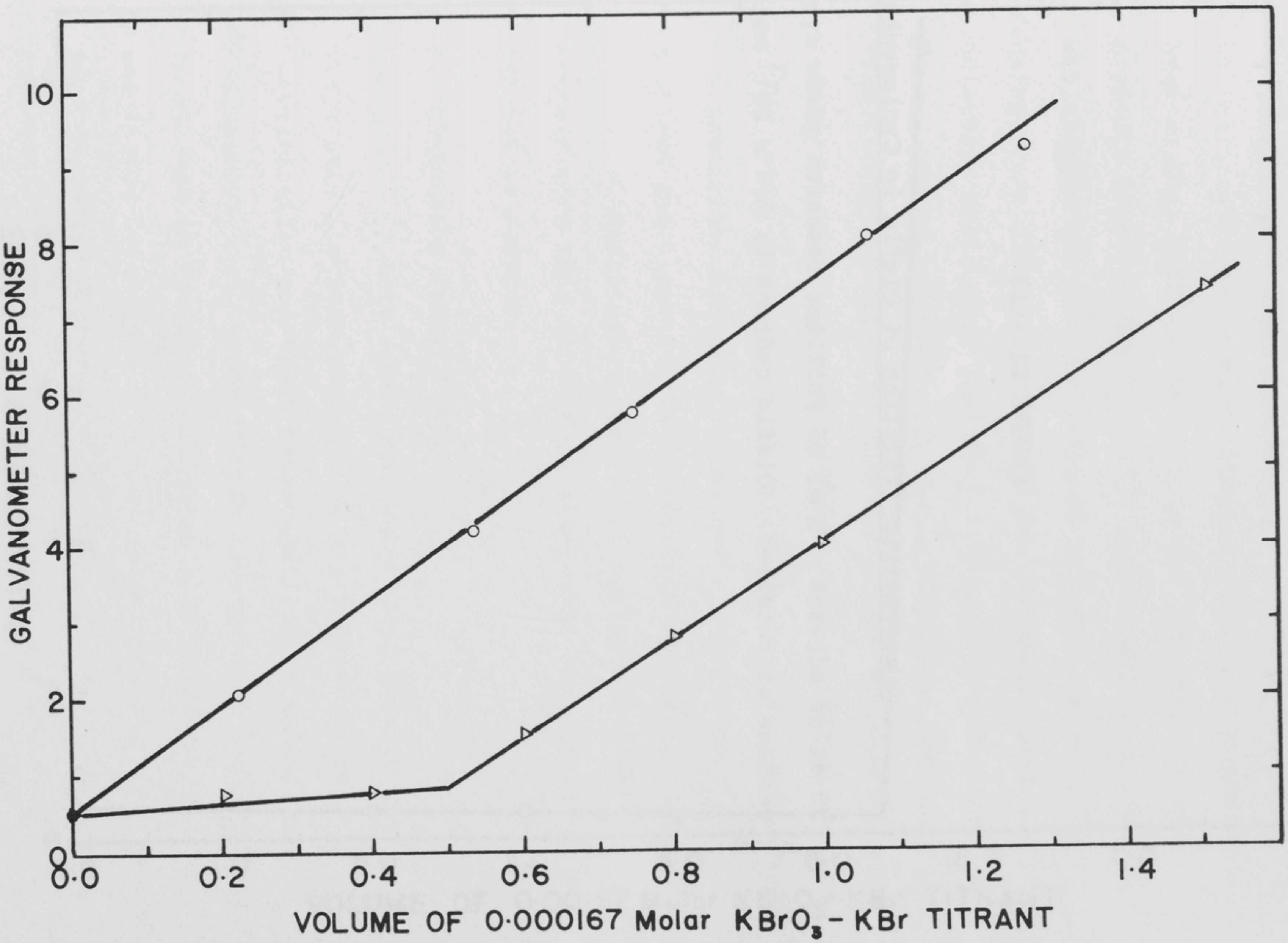
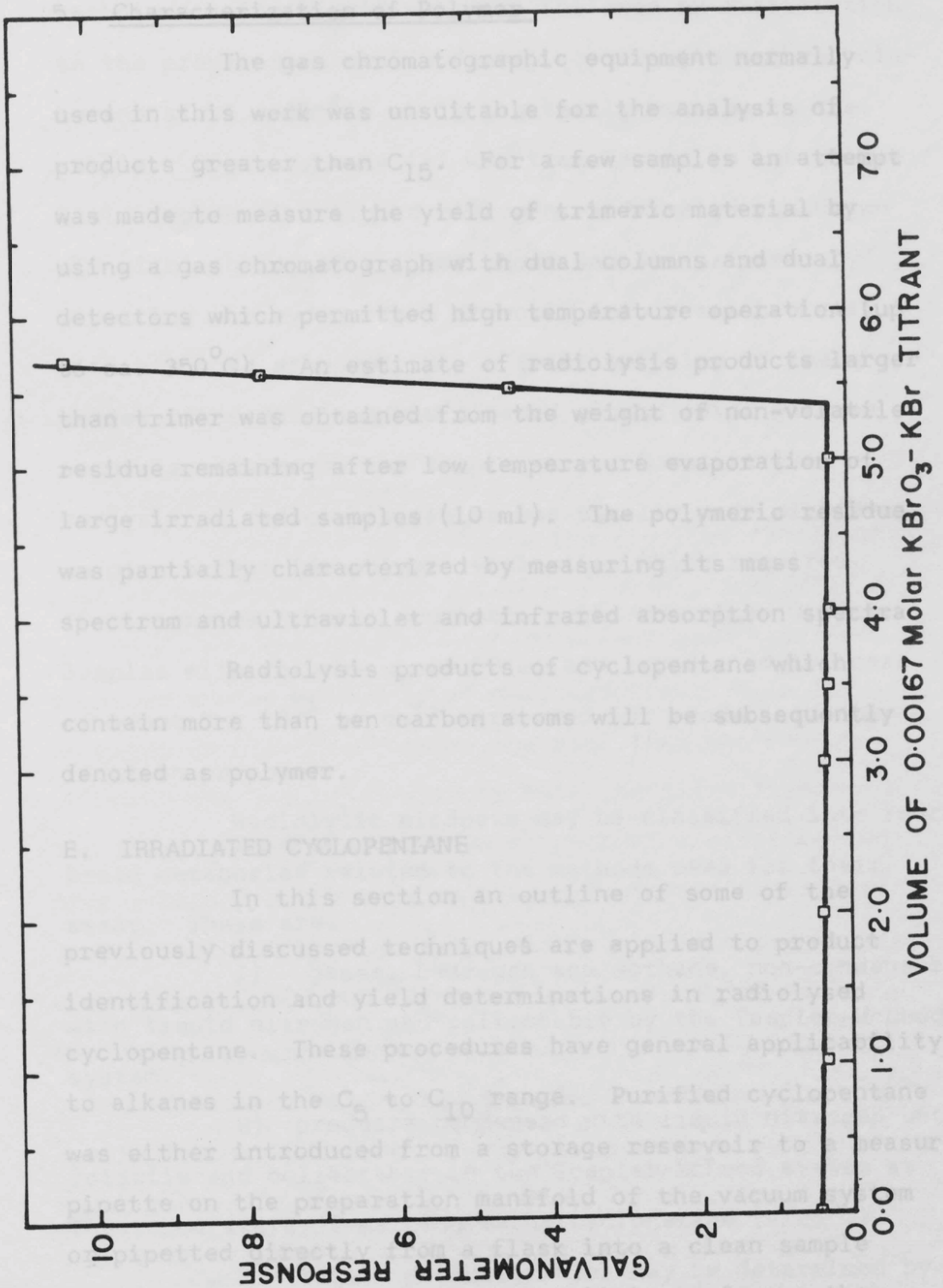

GALVANOMETER RESPONSE
10
8
6
4
2
0
0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
VOLUME OF 0·000167 Molar $KBrO_3$ - KBr TITRANT

FIGURE II - 13

Amperometric Titration of Olefin in Cyclopentane

20 ml of solvent - 5 ml of Phillips research grade cyclopentane as received. Olefin content is 5.4×10^{-3} molar.



5. Characterization of Polymer

The gas chromatographic equipment normally used in this work was unsuitable for the analysis of products greater than C_{15}. For a few samples an attempt was made to measure the yield of trimeric material by using a gas chromatograph with dual columns and dual detectors which permitted high temperature operation (up to ca. 350°C). An estimate of radiolysis products larger than trimer was obtained from the weight of non-volatile residue remaining after low temperature evaporation of large irradiated samples (10 ml). The polymeric residue was partially characterized by measuring its mass spectrum and ultraviolet and infrared absorption spectra.

Radiolysis products of cyclopentane which contain more than ten carbon atoms will be subsequently denoted as polymer.

E. IRRADIATED CYCLOPENTANE

In this section an outline of some of the previously discussed techniques are applied to product identification and yield determinations in radiolysed cyclopentane. These procedures have general applicability to alkanes in the C_5 to C_{10} range. Purified cyclopentane was either introduced from a storage reservoir to a measuring pipette on the preparation manifold of the vacuum system or pipetted directly from a flask into a clean sample vial. Degassing was done by a preliminary freeze-thaw

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Radiolytic products may be classified into four broad catagories related to the methods used for their assay. These are:

1) gases, hydrogen and methane, non-condensable with liquid nitrogen and collectable by the Toepler-McLeod system.

2) products condensed with liquid nitrogen but volatile and collectable in the Toepler-McLeod system at the temperature of melting methylcyclohexane (-126^{o}C).

3) liquid products which may be determined by suitable analysis of aliquots of the irradiated hydrocarbon.

and, 4) polymer.

The G value for the yield of a product, X, was calculated from its yield in μ moles for aliquot volume V_A in ml by

$$G(X) = \frac{\text{moles of X in the aliquot} \cdot N_o \cdot 100 \cdot \text{total volume in ml}}{\text{dose in ev received by total sample} \cdot V_A} \qquad \text{(II-11)}$$

where N_o is Avogadro's number.

1. Non-condensable Gases

After giving a sample the required radiation dose it was attached to the vacuum system's analysis manifold, and the line completely evacuated. Reference readings on the McLeod gauge were recorded. With liquid nitrogen on all three traps, the vial seal was broken allowing the sample to distill into the first trap. The Toepler pump was operated throughout a distillation with a McLeod gauge reading taken after each distillation step. Two distillation steps with concurrent gas collection were necessary to quantitatively remove methane from the irradiated cyclopentane. Methane and hydrogen were the only significant components in this non-condensable gas fraction. Gas chromatographic as well as mass spectrometric analysis of this fraction from heavily irradiated samples (ca. 2 x 10^{20} ev gm^{-1}) showed that less than 0.03% of the ethylene yield was carried over in the distillations at liquid nitrogen temperature.

The composition of this fraction was determined by transferring the gas quantitatively to the gas chromatograph and analysing it on the charcoal column with helium carrier gas.* The hydrogen yield was determined as the difference between the total yield of non-condensable gases collected and the yield of methane obtained by the gas chromatographic analysis. For some samples of irradiated cyclopentane the gas fraction was assayed by mass spectrometry.

2. Condensable Gases

Ethane and ethylene, although held back at liquid nitrogen temperature, could be quantitatively removed from the sample by the trap-to-trap distillation procedure by using methylcyclohexane slush (-126° C) as the refrigerant. Three distillation steps were done. After collection in the McLeod gauge this fraction was analysed on the silica gel column with hydrogen carrier gas and catalytic conversion of the hydrocarbons to methane.

Products in the C_3 to C_4 range were only partially removed at this temperature while at -95° C, the melting point of cyclopentane, large amounts of cyclopentane transferred over to the McLeod gauge. The direct crushing of irradiated bulbs containing known amounts of

---

* The sensitivity of methane was larger with helium carrier gas than with hydrogen carrier gas by a factor of 2.34.

cyclopentane of the order of 0.1 ml gave fair data for the yields of compounds in the C_3 to C_4 range. Plate VII illustrates the bulb crusher without its heating tape. It was used at about 80°C.

The following techniques were used for product identification. One hundred ml of degassed research grade cyclopentane, treated to remove olefin impurities, in a 200-ml bulb with break seal were irradiated in the Gammacell to a dose of about 1.5×10^{21} ev gm^{-1}. The irradiated sample was opened on the analysis manifold after freezing down with liquid nitrogen. The non-condensable gases were pumped away. The liquid nitrogen was removed and the sample allowed to melt while the condensable gas fraction was distilled into a trap cooled with liquid nitrogen. Distillation was stopped when all the solid had melted. The stripped liquid was removed for later analysis of higher boiling products [see sections c) and d)].

The condensable gas fraction collected was resolved into several components using gas chromatography with the silica gel column and helium carrier gas. The individual peaks were trapped off and re-run to improve their purity. Each was then transferred to a sampler or break-sealed vial for mass spectrometric confirmation of a tentative identification based on gas chromatographic retention time. Figure II - 14 shows a chromatogram

PLATE VII

Bulb Crusher

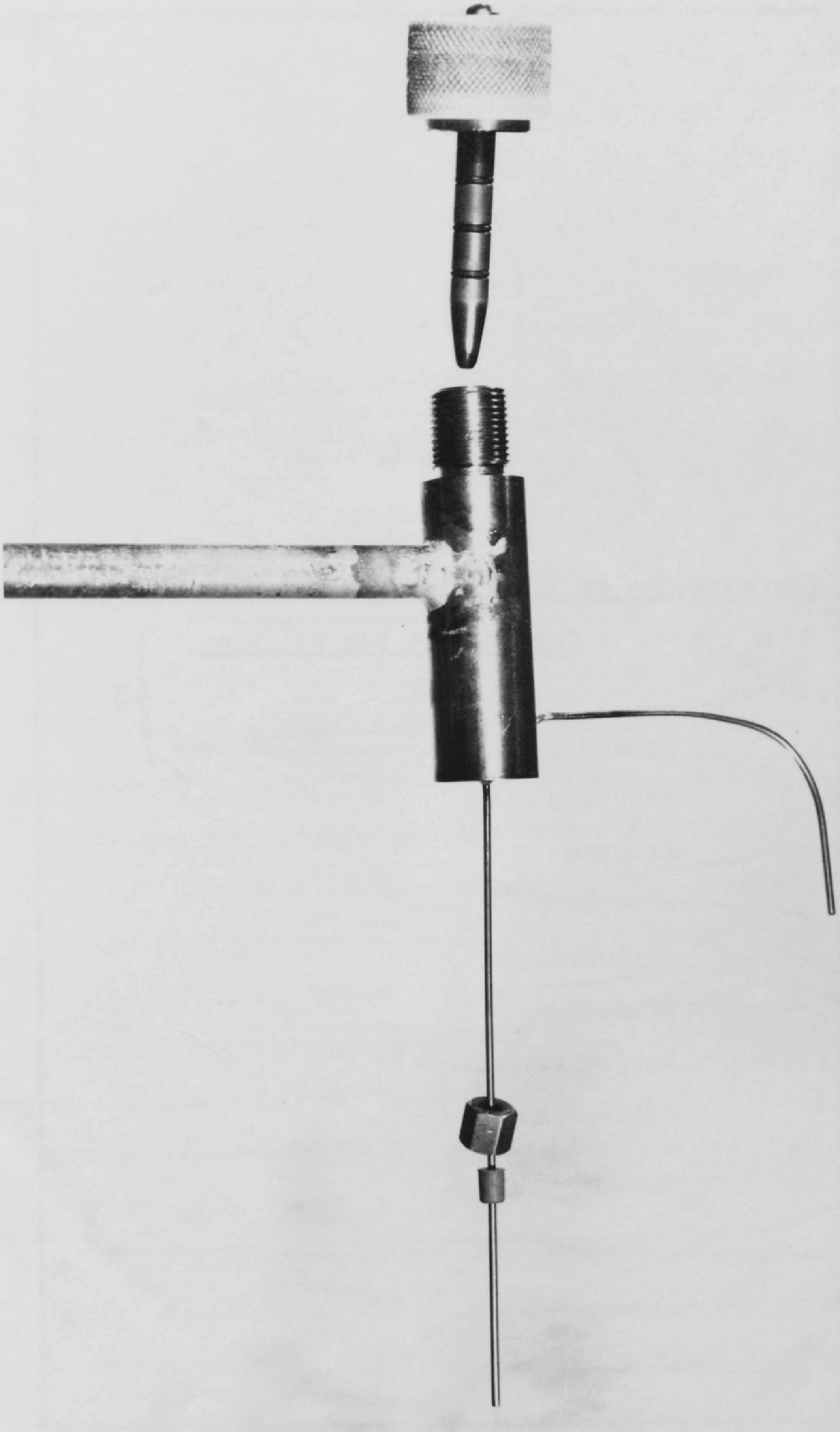
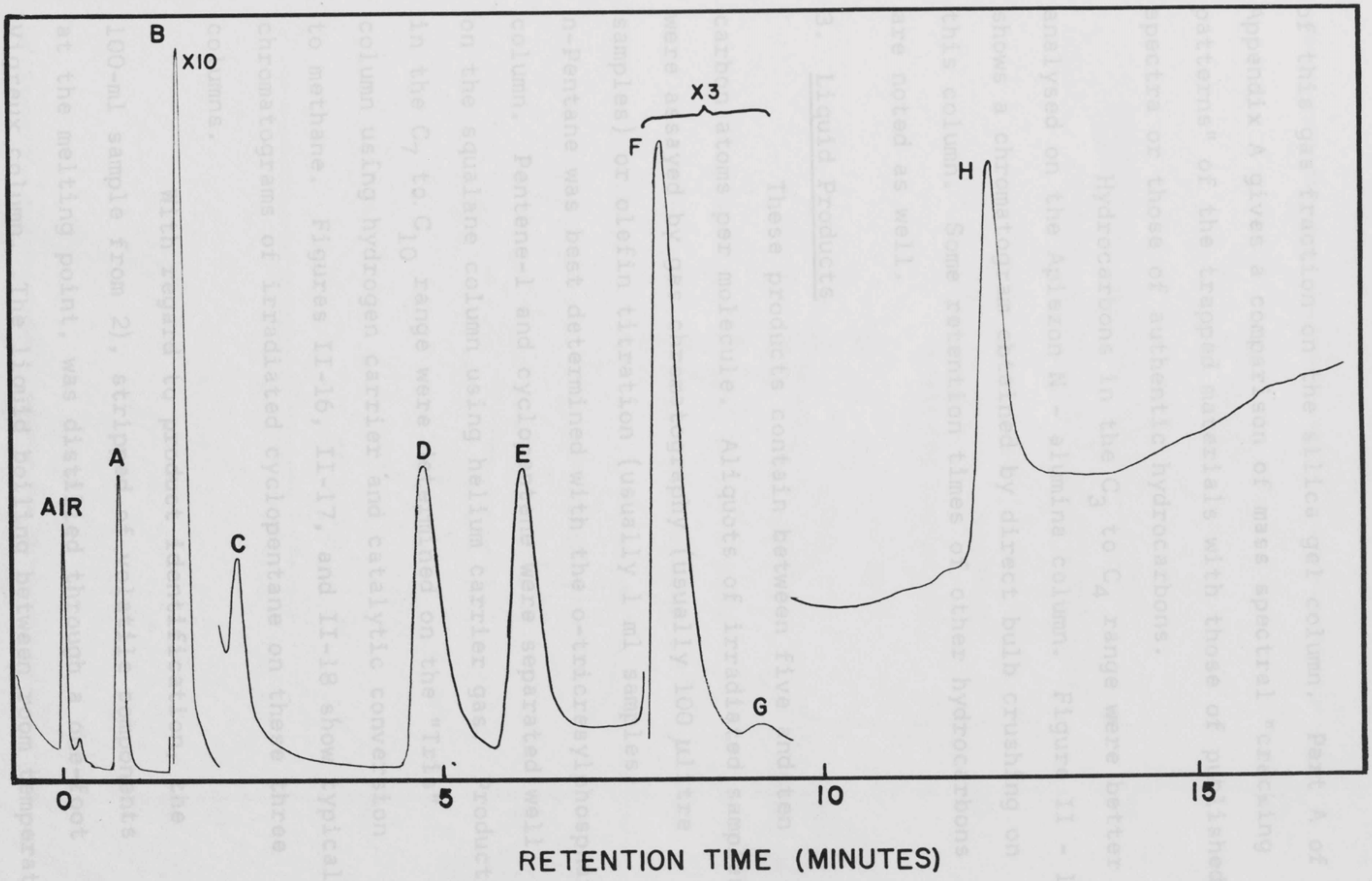


FIGURE II - 14

Chromatogram of Irradiated Cyclopentane on Silica Gel:
Condensable Gas Fraction

A	Ethane
B	Ethylene
C	Propane
D	Acetylene
E	Cyclopropane
F	Propane
G	Propadiene(allene)
H	Cyclopentane


AIR
A
B
X10
C
D
E
F
X3
G
H
0
5
10
15
RETENTION TIME (MINUTES)

of this gas fraction on the silica gel column. Part A of Appendix A gives a comparison of mass spectral "cracking patterns" of the trapped materials with those of published spectra or those of authentic hydrocarbons.

Hydrocarbons in the C_3 to C_4 range were better analysed on the Apiezon N - alumina column. Figure II - 15 shows a chromatogram obtained by direct bulb crushing on this column. Some retention times of other hydrocarbons are noted as well.

3. Liquid Products

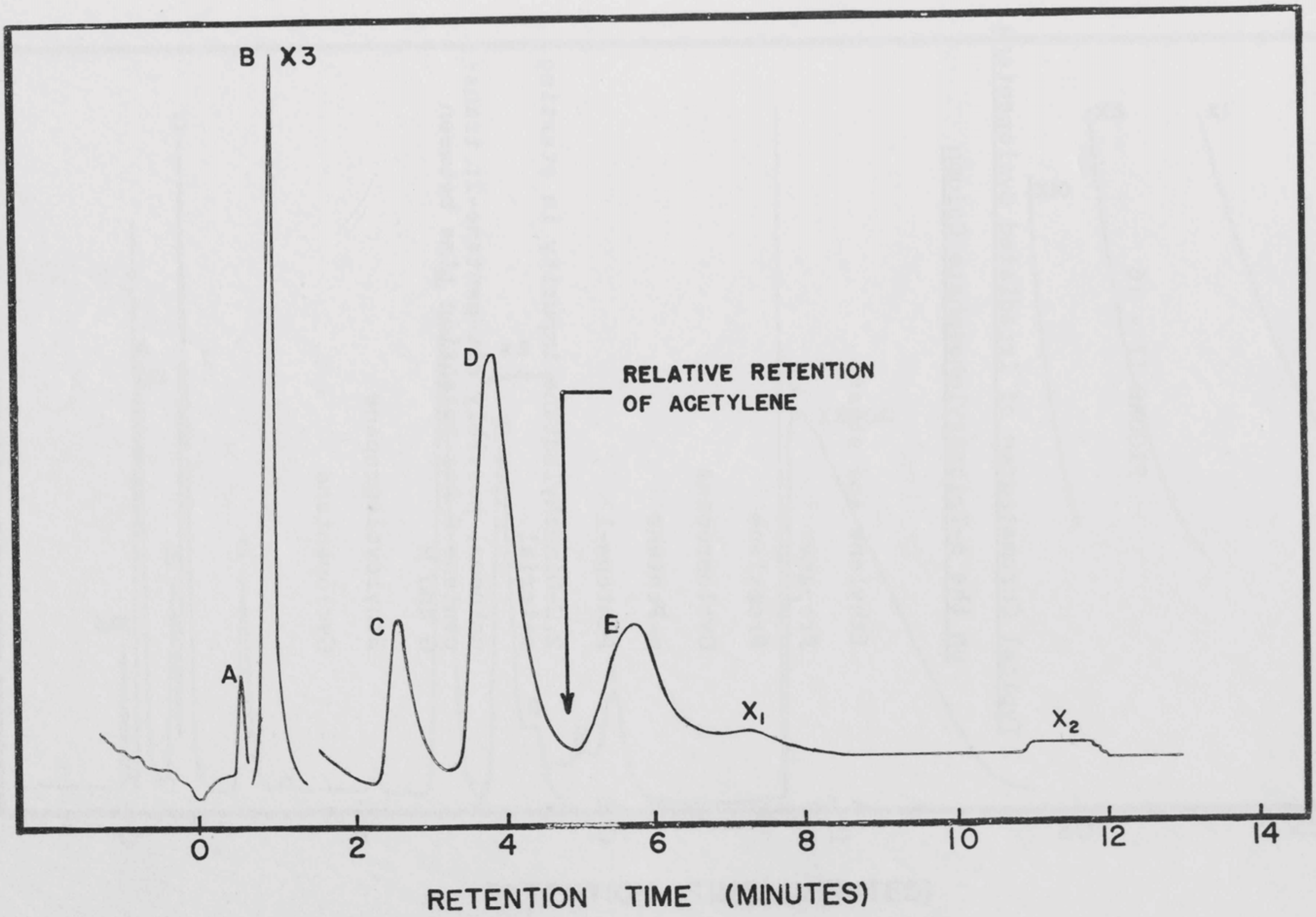
These products contain between five and ten carbon atoms per molecule. Aliquots of irradiated samples were assayed by gas chromatography (usually 100 μlitre samples) or olefin titration (usually 1 ml samples) n-Pentane was best determined with the o-tricresylphosphate column. Pentene-1 and cyclopentene were separated well on the squalane column using helium carrier gas. Products in the C_7 to C_{10} range were determined on the "Tris" column using hydrogen carrier and catalytic conversion to methane. Figures II-16, II-17, and II-18 show typical chromatograms of irradiated cyclopentane on these three columns.

With regard to product identification, the 100-ml sample from 2), stripped of volatile components at the melting point, was distilled through a one-foot Vigreux column. The liquid boiling between room temperature

FIGURE II - 15

Typical Chromatogram of irradiated cyclopentane on the Alumina-Apiezon N Column

A	Methane
B	Ethane and ethylene
C	Propane
D	Propylene
E	Cyclopropane
X_1	Unidentified product, probably allene
X_2	Unidentified product, not n-butane



B
X3
A
C
D
E
X$_1$
X$_2$
RELATIVE RETENTION
OF ACETYLENE
0
2
4
6
8
10
12
14
RETENTION TIME (MINUTES)

FIGURE II - 16

Typical Chromatogram of Irradiated Cyclopentane on the o-Tricresylphosphate Column

A	Ethylene and ethane
B	Propane
C	Propylene
D	Cyclopropane
E	n-Pentane
F	Pentene-1
G	2,2-Dimethylbutane impurity in starting material
H	unknown, possibly cis-pentene-2; trans-pentene-2 has retention time between G and H
I	Ethylcyclopropane
J	Cyclopentane

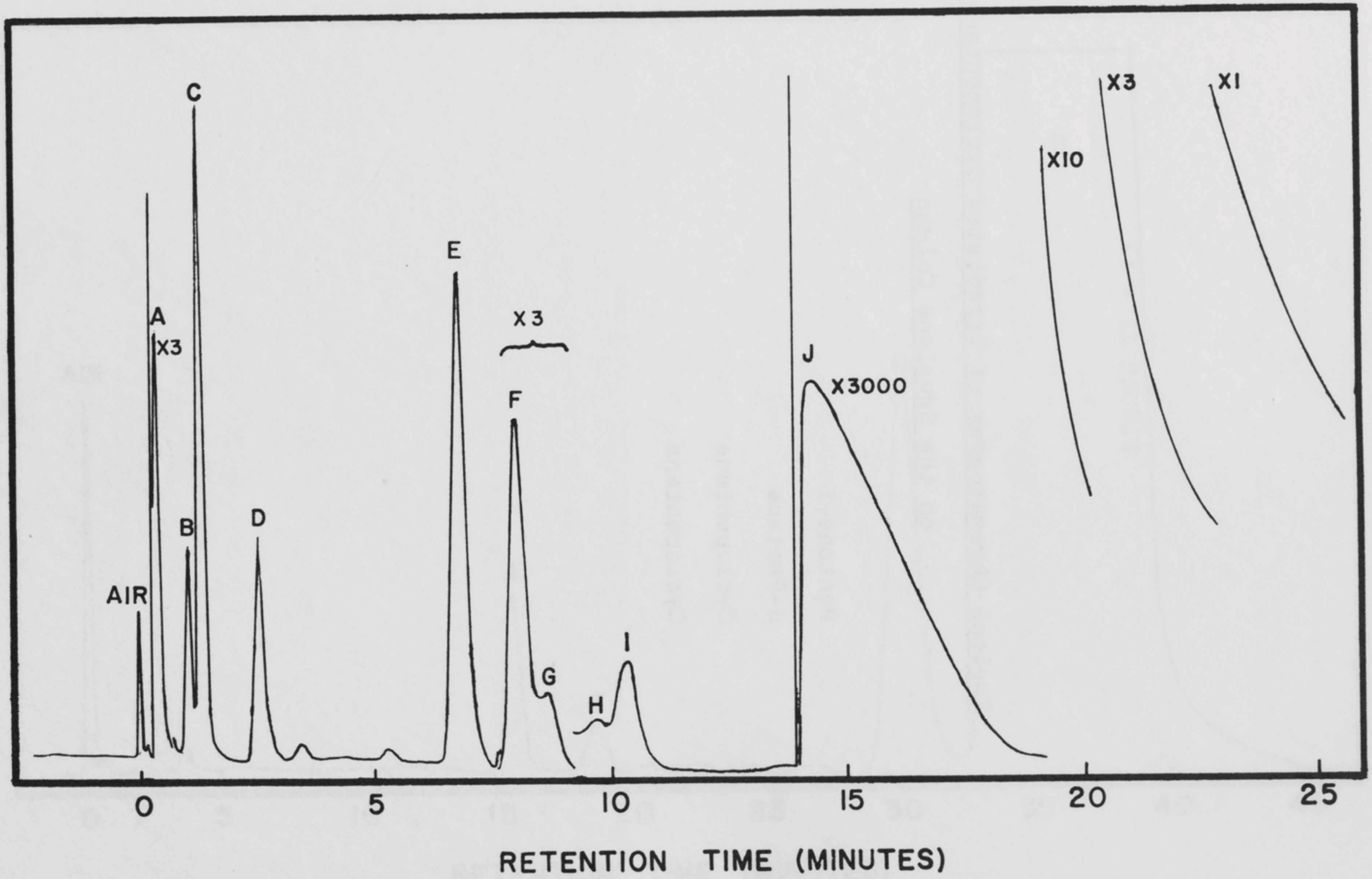

AIR
A
X3
B
C
D
E
X3
F
G
H
I
J
X3000
X10
X3
X1
0
5
10
15
20
25
RETENTION TIME (MINUTES)

FIGURE II - 17

Typical Chromatogram of Irradiated Cyclopentane on the Squalane Column

A	Pentene-1
B	n-Pentane
C	Cyclopentene
D	Cyclopentane

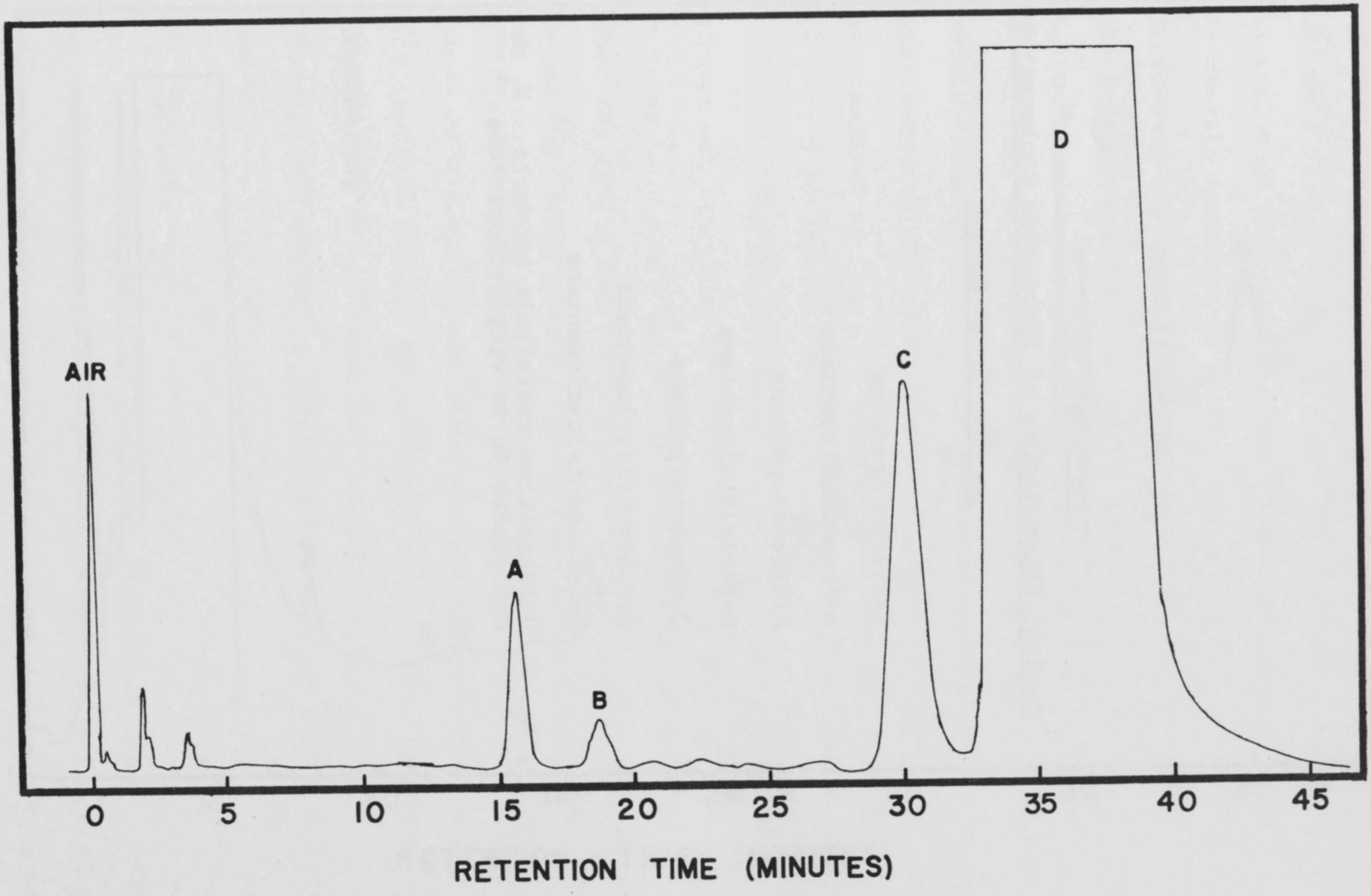
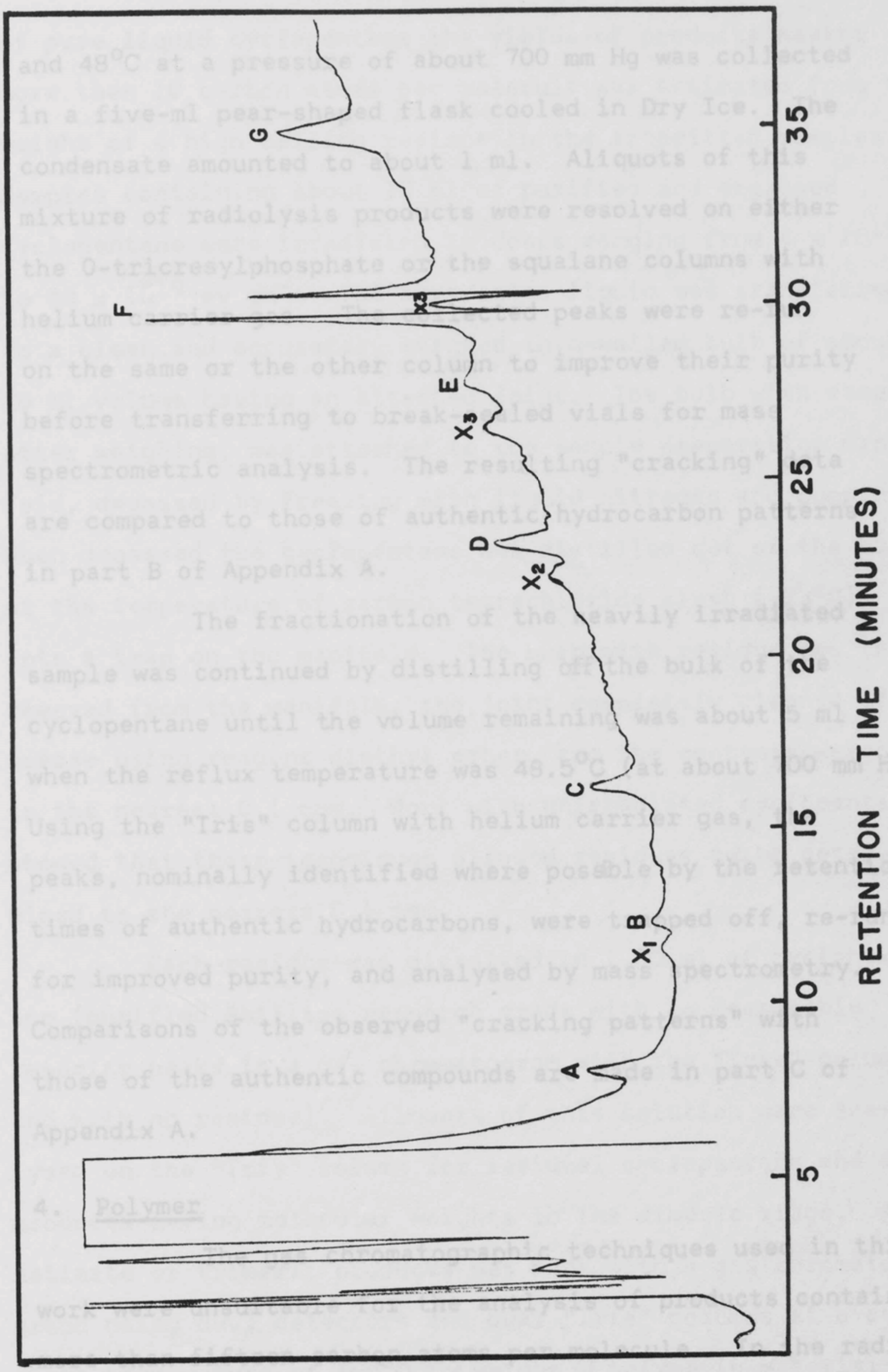

AIR
A
B
C
D
0
5
10
15
20
25
30
35
40
45
RETENTION TIME (MINUTES)

FIGURE II - 18

Typical Chromatogram of Irradiated Cyclopentane on the "Tris" Column

A	Ethylcyclopentane
B	n-Propylcyclopentane
C	Allylcyclopentane
D	n-Pentylcyclopentane
E	Cyclopentylpentene
F	Cyclopentylcyclopentane
G	3-Cyclopentylcyclopentene
X_1, X_2, X_3	Unidentified radiolysis products. X_1 does not appear to be vinylcyclopentane.



and 48°C at a pressure of about 700 mm Hg was collected in a five-ml pear-shaped flask cooled in Dry Ice. The condensate amounted to about 1 ml. Aliquots of this mixture of radiolysis products were resolved on either the O-tricresylphosphate or the squalane columns with helium carrier gas. The collected peaks were re-run on the same or the other column to improve their purity before transferring to break-sealed vials for mass spectrometric analysis. The resulting "cracking" data are compared to those of authentic hydrocarbon patterns in part B of Appendix A.

The fractionation of the heavily irradiated sample was continued by distilling off the bulk of the cyclopentane until the volume remaining was about 5 ml when the reflux temperature was 48.5°C (at about 700 mm Hg). Using the "Tris" column with helium carrier gas, [illegible] peaks, nominally identified where possible by the retention times of authentic hydrocarbons, were tapped off, re-run for improved purity, and analysed by mass spectrometry. Comparisons of the observed "cracking patterns" with those of the authentic compounds are made in part C of Appendix A.

4. Polymer

The gas chromatographic techniques used in this work were unsuitable for the analysis of products containing more than fifteen carbon atoms per molecule. In the radiolysis and 48°C at a pressure of about 700 mm Hg was collected in a five-ml pear-shaped flask cooled in Dry Ice. The condensate amounted to about 1 ml. Aliquots of this mixture of radiolysis products were resolved on either the O-tricresylphosphate or the squalane columns with helium carrier gas. The collected peaks were re-run on the same or the other column to improve their purity before transferring to break-sealed vials for mass spectrometric analysis. The resulting "cracking" data are compared to those of authentic hydrocarbon patterns in part B of Appendix A.

The fractionation of the heavily irradiated sample was continued by distilling off the bulk of the cyclopentane until the volume remaining was about 5 ml when the reflux temperature was 48.5°C (at about 700 mm Hg). Using the "Tris" column with helium carrier gas, the peaks, nominally identified where possible by the retention times of authentic hydrocarbons, were trapped off, re-run for improved purity, and analysed by mass spectrometry. Comparisons of the observed "cracking patterns" with those of the authentic compounds are made in part C of Appendix A.

4. Polymer

The gas chromatographic techniques used in this work were unsuitable for the analysis of products containing more than fifteen carbon atoms per molecule. In the radiolysis of pure liquid cyclopentane the yields of products having more than 10 carbon atoms per molecule was estimated from the weight of a high boiling residue in the irradiated samples. Samples containing about 10 ml of purified and degassed cyclopentane were irradiated to doses ranging from 4 x 10^{19} to 58 x 10^{19} ev gm^{-1}. The irradiated liquid was transferred to a clean and accurately weighed thin-walled bulb of about 20 ml volume having an attached joint. The bulb with sample after weighing, was attached to the sample preparation manifold, degassed by freezing with liquid nitrogen and pumping. When degassed the cyclopentane was distilled out of the bulb at the temperature of carbon tetrachloride slush (-23°C) into a trap on the manifold. The bulb with residue was then removed from the manifold, the joint completely cleaned of grease using reagent diethyl ether, and the contents weighed to the nearest 0.1 mgm. Work with unirradiated cyclopentane showed that these techniques allowed residues to be determined to the nearest 0.1 mgm.

Each residue was dissolved in 1.00 ml of cyclohexane (purified Phillips research grade with no measurable impurity peaks in a gas chromatogram with the "Tris" column and with no residue). Aliquots of this solution were analysed on the "Tris" column for residual cyclopentane and for products having molecular weights to the dimeric stage. An estimate of trimeric products was made with a gas chromatograph using dual detectors and dual "Tris" columns at a constant temperature of 160°C. The weight of polymeric material in a residue was determined by subtracting from the total weight of residue, the weight of residual cyclopentane and other products up to the dimers. The G value of this polymeric material was expressed in terms of the number of cyclopentane molecules incorporated in it for each 100 ev absorbed in the treated aliquot (usually more than 95% of the original sample.)

For some samples the ultraviolet absorption spectrum (200 nm to 350 nm) of the cyclohexane solution was recorded on the Cary model 14 spectrophotometer using 1 mm quartz cells.

Mass spectra of residual materials were obtained by evaporating aliquots (100 to 200 μl) of the cyclohexane solutions onto the direct probe of the MS-9 spectrometer.

The infrared absorption spectrum of a residue from one sample (dose of 3.7×10^{20} ev gm^{-1}) was obtained by transferring some of it by a glass rod to the surface of a potassium bromide disc. The disc was placed in a vial and attached to the high vacuum manifold and pumped-on for about ten minutes at room temperature. A Perkin-Elmer model 337 grating infrared spectrophotometer was used to obtain the spectrum. The amount of residue was too small to obtain a satisfactory spectrum.

F. CYCLOPENTANE SOLUTIONS FOR SCAVENGER STUDIES

The following four systems containing cyclopentane were studied over a range of composition at room temperature:

a) cyclo-C_5H_{10}-SF_6

b) cyclo-C_5H_{10}-cyclo-C_4F_8

c) cyclo-C_5H_{10}-ND_3

d) cyclo-C_5H_{10}-benzene

The techniques for preparing, irradiating, and analysing these solutions were similar to those used with pure liquid cyclopentane. Benzene-cyclopentane solutions were formulated by weight from the purified Phillips research grade components. Samples of these solutions were prepared by pipetting aliquots into an evacuable joint, degassing, transferring to a weighed irradiation vial, etc. Gas chromatography on the "Tris" and Ucon columns was used for liquid product analyses.

The gaseous additives, SF_6, c-C_4F_8, and ND_3 were transferred to a measured amount of cyclopentane from calibrated storage volumes at a measured temperature and pressure. The amount of additive was calculated using Eqt (II-1). The McLeod-Toepler pump was used for adding amounts of gas less than 350 μmoles.

Products derived from the additives were measured only in the cyclopentane-benzene and cyclopentane-ND_3 systems. Several liquid products derived from benzene were found in irradiated benzene solutions. Figure (II-19) is a typical chromatogram of an irradiated benzene solution obtained on the Ucon column. Figure (II-20) shows the effects of hydrogenating this solution. Hydrogenation had little effect on the amounts of aromatic

FIGURE II - 19

Typical Chromatogram of Irradiated Cyclopentane-Benzene Solution (0.20 electron fraction C_6H_6) on The Ucon Column

Dose: 1.98×10^{20} ev gm^{-1}

A	Cyclopentane
B	Benzene
C	Cyclopentylcyclopentane and 3-cyclopentylcyclopentene
D	Unknown component; possibly consists, in part, of cyclopentylcyclohexane
E	Cyclopentylcyclohexadienes
F	Cyclopentylbenzene
G	Biphenyl

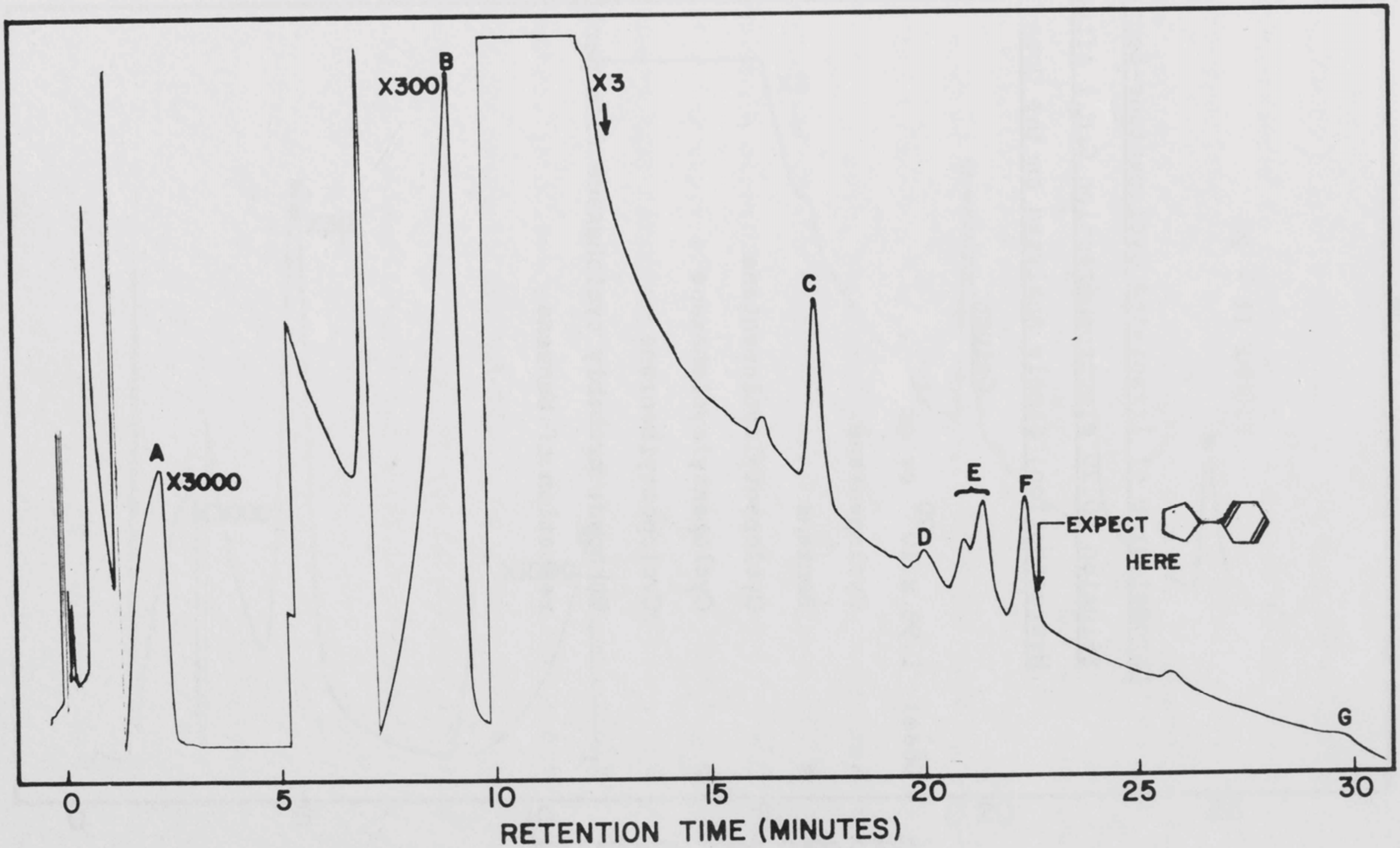
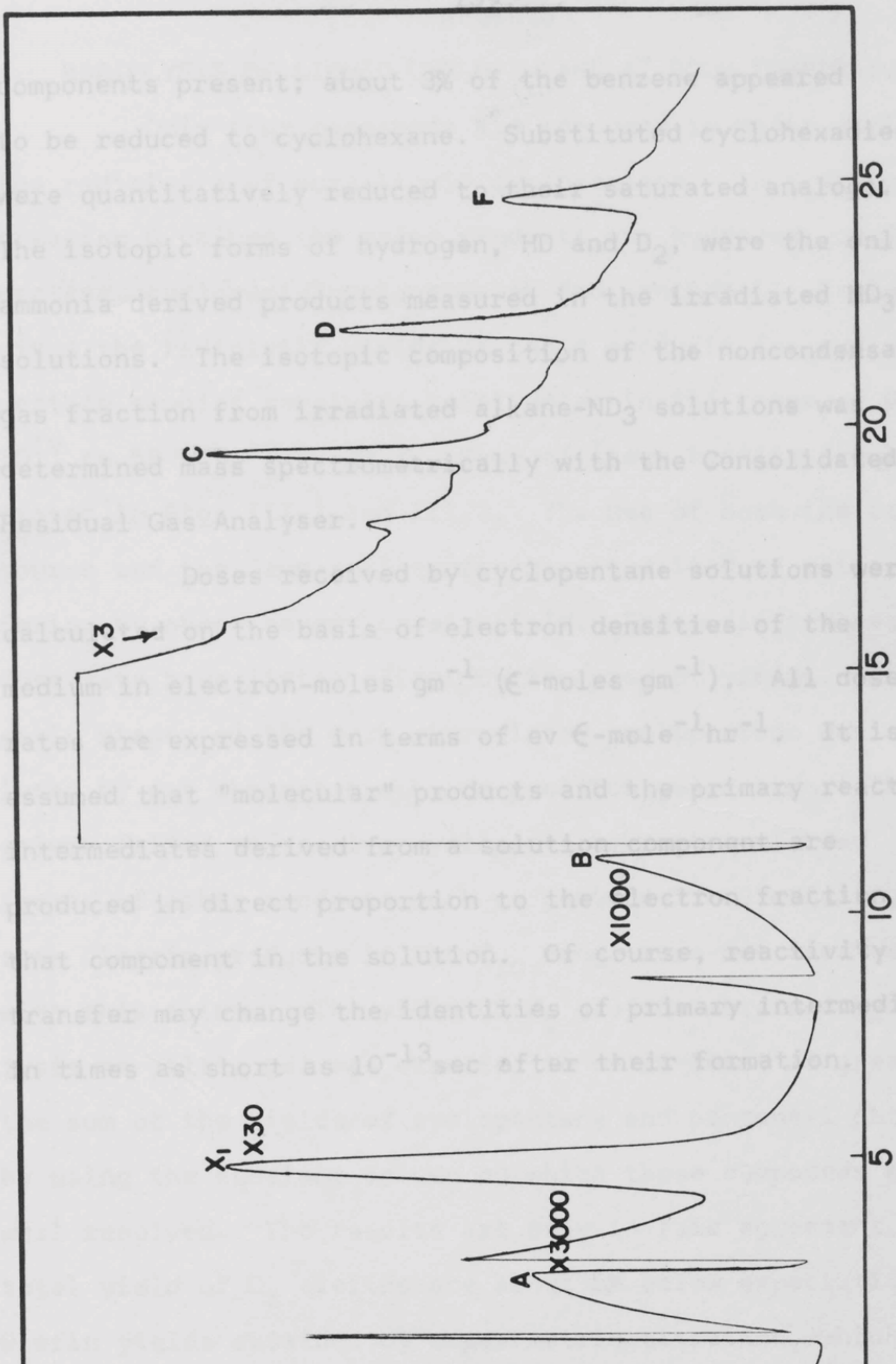

A
X3000
X300
B
X3
C
D
E
F
EXPECT
HERE
G
0
5
10
15
20
25
30
RETENTION TIME (MINUTES)

FIGURE II - 20

Chromatogram of Irradiated Cyclopentane-Benzene Solution (0.20 electron fraction C_6H_6) after Hydrogenation; Sample Analysed on the Ucon Column

Dose: 1.98 x 10^{20} ev gm^{-1}

A	Cyclopentane
B	Benzene
C	Cyclopentylcyclopentane
D	Cyclopentylcyclohexane
F	Cyclopentylbenzene
X_1	Unknown; probably cyclohexane from partial reduction of benzene


X1
X30
X3000
A
X1000
B
X3
C
D
F
0
5
10
15
20
25
RETENTION TIME (MINUTES)

components present; about 3% of the benzene appeared to be reduced to cyclohexane. Substituted cyclohexadienes were quantitatively reduced to their saturated analogs. The isotopic forms of hydrogen, HD and D_2, were the only ammonia derived products measured in the irradiated ND_3 solutions. The isotopic composition of the noncondensable gas fraction from irradiated alkane-ND_3 solutions was determined mass spectrometrically with the Consolidated Residual Gas Analyser.

Doses received by cyclopentane solutions were calculated on the basis of electron densities of the medium in electron-moles gm^{-1} (ϵ-moles gm^{-1}). All dose rates are expressed in terms of ev ϵ-$mole^{-1}hr^{-1}$. It is assumed that "molecular" products and the primary reactive intermediates derived from a solution component are produced in direct proportion to the electron fraction of that component in the solution. Of course, reactivity transfer may change the identities of primary intermediates in times as short as 10^{-13}sec after their formation.

RESULTS

A. RADIOLYSIS OF LIQUID CYCLOPENTANE AT ROOM TEMPERATURE

Only four compounds are produced in major yields in the radiolysis of pure liquid cyclopentane. In order of decreasing G values the major products are hydrogen, cyclopentene, cyclopentylcyclopentane, and pentene-1. Table III-1 gives the radiolytic yields of these products for cyclopentane samples receiving total doses in the range of 0.34 x 10^{19} to 58 x 10^{19} ev gm^{-1}. Some of these results are illustrated in Figs III-1 and III-2. The use of both the cave source and the Gammacell source resulted in dose rates differing by about seven- or eightfold. These differences in dose rate have little effect on the product yields. In the early stages of the work, irradiated cyclopentane was analysed by gas chromatography on a silica gel column. This column failed to resolve cyclopentene, pentene-1, and traces of other products such as pentene-2. Similarily some dimeric products in the C_{10} range were not resolved with this column. The yield of C_5 olefins obtained by analysis on silica gel was expected to be at least as great as the sum of the yields of cyclopentene and pentene-1 obtained by using the squalane column on which these compounds were well resolved. The results are only in fair agreement. The total yield of C_5 olefins are about 5% below expectation. Olefin yields obtained by amperometric titration, which are also given in Fig III-2, are in fair agreement with the

TABLE III-1

Pure Liquid Cyclopentane: Dose Dependence of Major Product Yields

		G VALUES							
Dose (10^{19} ev gm^{-1})	Dose rate (10^{19} ev ϵ^{-1} $mole^{-1}$ hr^{-1})	H_2 [a]	$c-C_5H_8$ [b]	Pentene-1 (converted) [c]	Pentene-1 (not converted) [c]	Cyclopentyl-cyclopentane [d]	C_5 Olefins [e]	Saturated C_{10} products [e]	Olefins by titration
0.336	7.63	5.26	--	--	--	1.17	--	--	--
0.476	1.25	5.32	--	--	--	--	--	--	--
1.36	1.18	--	--	--	--	--	3.25	1.41	3.52
1.45	7.63	--	--	--	--	1.30	--	--	--
1.76	7.70	5.29	--	--	--	--	--	--	--
1.77	1.19	--	--	--	--	--	3.54	1.36	3.67
2.12	8.96	--	2.88	--	0.75	--	--	--	--
2.46	1.08	--	2.80	--	0.75	--	--	--	--
2.58	1.25	--	--	--	--	--	3.10	1.26	3.48
2.91	7.63	5.19	2.75	--	0.71	--	--	--	--
3.88	6.78	--	2.90	--	0.73	1.28	--	--	--
3.88	6.78	--	2.97	--	0.74	1.21	--	--	--
6.54	7.63	5.18	2.84	0.69	0.71	--	3.42	1.47	--
6.97	1.25	--	--	--	--	1.36	--	--	--
6.97	1.25	5.12	--	--	--	--	3.60	1.36	3.34
7.73	6.78	--	3.07	--	0.72	1.16	--	--	--
9.93	7.63	5.04	--	--	--	--	--	--	--
10.1	7.14	5.06	2.91	0.66	0.70	--	3.58	1.42	--
13.6	1.17	--	--	0.66	--	--	--	--	3.18
15.1	7.15	5.14	2.80	--	0.67	1.16	3.43	1.37	--

TABLE III-1 (continued)

Pure Liquid Cyclopentane: Dose Dependence of Major Product Yields

		G VALUES							
Dose (10^{19}ev gm^{-1})	Dose Rate (10^{19} ev ε-mole^{-1}hr^{-1})	H_2 [a]	Cyclo-C_5H_8 [b]	pentene-1 (converted) [c]	pentene-1 (not converted) [c]	cyclopentyl-cyclopentane [d]	C_5 olefins [e]	saturated C_{10} products [e]	olefins by titration
19.9	7.20	--	2.91	0.67	0.70	1.26	3.37	1.21	--
19.9	7.63	4.95	--	--	--	--	--	--	--
20.5	1.37	5.01	--	--	--	--	--	--	--
22.7	1.08	--	2.70	--	0.63	--	--	--	--
27.1	6.78	--	2.90	--	0.70	1.07	--	--	--
30.5	7.20	4.94	2.66	0.68	0.65	1.13	3.54	1.30	--
37.4	6.78	--	2.68	--	0.58	1.18	3.29	1.33	--
39.7	1.28	4.85	--	--	--	--	--	--	--
54.0	1.28	4.81	--	--	--	--	--	--	--
58.1	6.78	--	2.52	--	0.61	1.11	--	--	--

---

a $G(H_2)$ is based on the yield of non condensable gas corrected for $G(CH_4)$

b Cyclopentene determined on squalane column without conversion to methane using helium carrier gas

c Pentene-1 determined on the squalane column

d Cyclopentylcyclopentane determined on the "Tris" column with conversion to methane

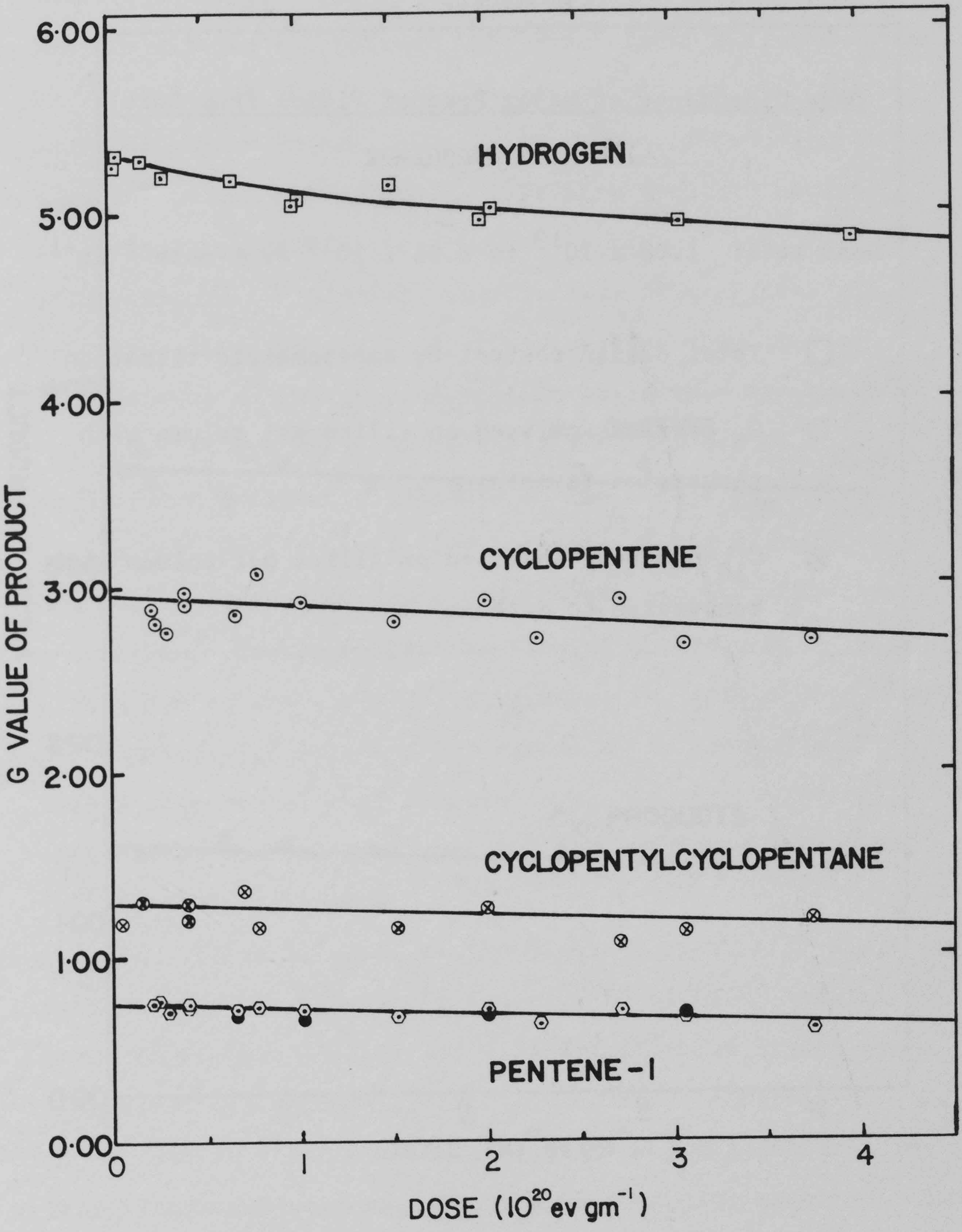
e Samples analysed on the silica gel column with conversion to methane

FIGURE III-1

Dose Dependence of Major Product Yields in Pure Liquid Cyclopentane

Dose rate: 1.08 x 10^{19} to 8.96 x 10^{19} ev ϵ-mole^{-1} hr^{-1}

□	Hydrogen
○	Cyclopentene analysed on squalane column without conversion to methane
⊗	Cyclopentylcyclopentane analysed on "Tris" column with conversion to methane
⬡	Pentene-1 analysed on squalane column without conversion to methane
●	Pentene-1 analysed on squalane column with conversion to methane



HYDROGEN
CYCLOPENTENE
CYCLOPENTYLCYCLOPENTANE
PENTENE-1
G VALUE OF PRODUCT
6·00
5·00
4·00
3·00
2·00
1·00
0·00
0
1
2
3
4
DOSE (10^{20} ev gm^{-1})

FIGURE III-2

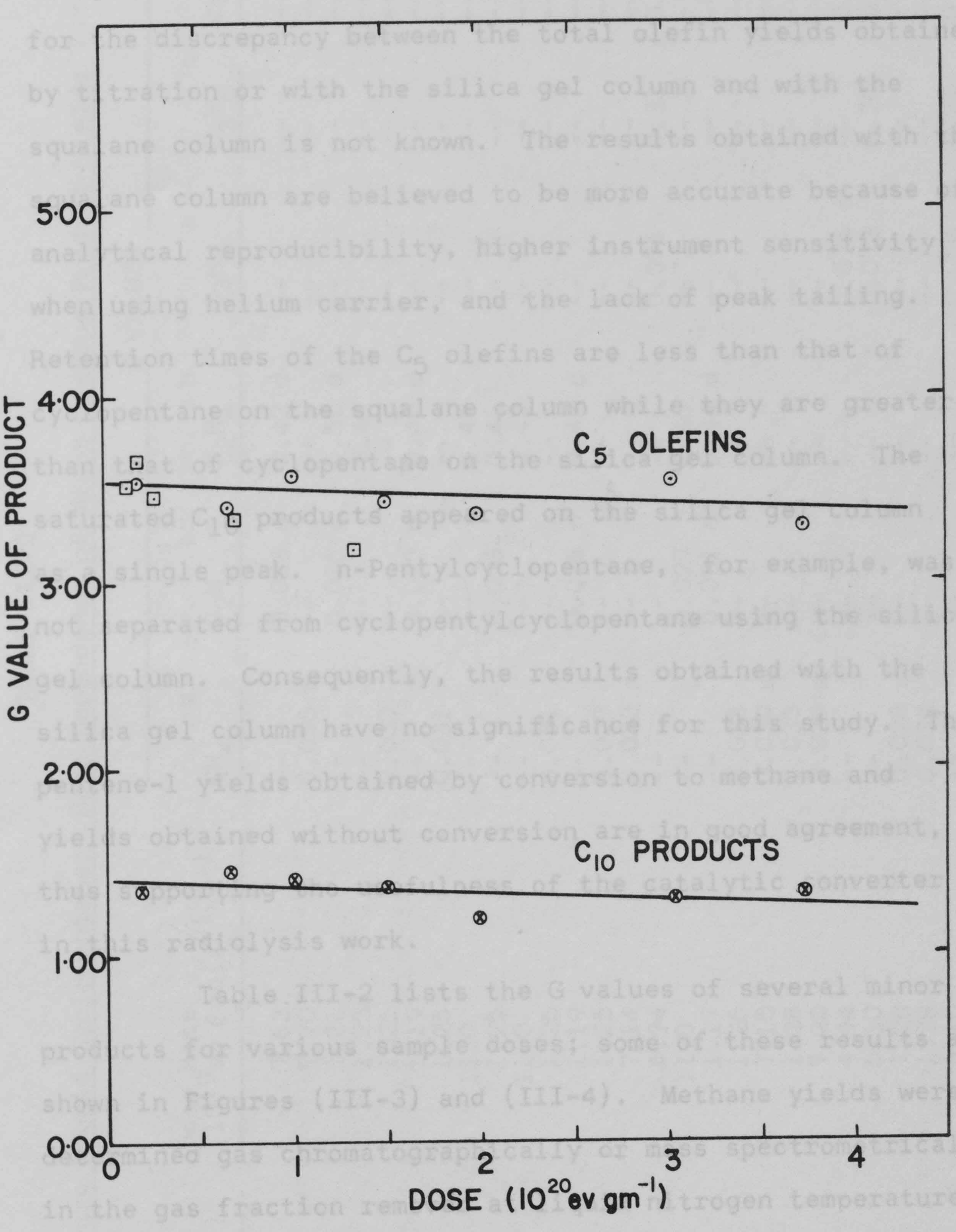
Dose Dependence of Major Product Yields from Pure Liquid Cyclopentane

Dose rate: 1.08×10^{19} to 8.96×10^{19} ev ϵ-mole^{-1} hr^{-1}

□ Total olefin content by amperometric titration

○ C_5 olefins analysed on silica gel column with conversion to methane

⊗ C_{10} products analysed on silica gel column with conversion to methane


G VALUE OF PRODUCT
5·00
4·00
3·00
2·00
1·00
0·00
0
1
2
3
4
DOSE (10^{20} ev gm^{-1})
C_5 OLEFINS
C_{10} PRODUCTS

analytical results from the silica gel column. The reason for the discrepancy between the total olefin yields obtained by titration or with the silica gel column and with the squalane column is not known. The results obtained with the squalane column are believed to be more accurate because of analytical reproducibility, higher instrument sensitivity when using helium carrier, and the lack of peak tailing. Retention times of the C_5 olefins are less than that of cyclopentane on the squalane column while they are greater than that of cyclopentane on the silica gel column. The saturated C_{10} products appeared on the silica gel column as a single peak. n-Pentylcyclopentane, for example, was not separated from cyclopentylcyclopentane using the silica gel column. Consequently, the results obtained with the silica gel column have no significance for this study. The pentene-1 yields obtained by conversion to methane and yields obtained without conversion are in good agreement, thus supporting the usefulness of the catalytic converter in this radiolysis work.

Table III-2 lists the G values of several minor gas products for various sample doses; some of these results are shown in Figures (III-3) and (III-4). Methane yields were determined gas chromatographically or mass spectrometrically in the gas fraction removed at liquid nitrogen temperature from irradiated samples. The two methods gave results in good agreement. Some ethylene and ethane yields were obtained

TABLE III-2

Pure Liquid Cyclopentane: Dose Dependence of Minor Gaseous Product Yields

Dose (10^{19} ev gm^{-1})	Dose Rate (10^{19} ev ϵ mole^{-1} hr^{-1})	G VALUES					
		CH_4 [a]	C_2H_6 [b]	C_2H_4 [b]	C_3H_8 [c]	C_3H_6 [c]	cyclo-C_3H_6 [c]
0.34	7.63	--	0.028 d	0.42 d	--	--	--
0.51	7.70	0.035 m	--	--	--	--	--
1.38	1.21	--	0.036 d	0.51 d	--	--	--
2.28	1.25	--	--	0.44	--	--	--
2.58	1.25	0.030	--	--	--	--	--
2.86	1.19	--	0.025 d	0.40 d	--	--	--
3.09	1.25	0.031	--	--	--	--	--
3.14	11.0	--	--	0.42	--	--	--
4.29	1.25	--	0.026	0.46	--	--	--
4.80	11.0	--	--	0.49	--	--	--
5.20	1.25	0.031	--	--	--	--	--
5.82	1.19	--	0.038 d	0.47 d	--	--	--
6.97	1.25	0.028	--	--	--	--	--
10.0	7.14	0.030 m	--	--	--	--	--
11.2	4.94	--	--	--	0.076	0.31	0.13
12.5	11.0	--	0.027	0.46	--	--	--
13.6	1.17	--	0.031 d	0.44 d	--	--	--
15.1	1.26	0.033	--	--	--	--	--
15.1	7.15	0.030 m	--	--	--	--	--
16.9	1.28	0.033	--	--	--	--	--
19.9	7.20	0.029 m	--	--	--	--	--
28.2	4.94	--	--	--	0.075 s	--	0.12 s
29.1	5.10	--	--	--	0.073	0.26	0.12
30.5	7.20	0.028 m	--	--	--	--	--
39.7	1.28	0.034	--	--	--	--	--
40.7	5.10	--	--	--	0.066	0.26	0.11
54.0	1.28	0.033	--	--	--	--	--
55.3	5.10	--	--	--	0.095	0.27	0.13
70.0	5.10	--	--	--	0.093	0.30	0.10

a	Methane determined in the noncondensable gas fraction either gas chromatographically on the charcoal column or mass spectrometrically (m)
b	Analysed by direct bulb crushing or from the gas fraction removed at -126°C (methylcyclohexane slush). Silica gel column was used with conversion to methane
c	Direct bulb crushing on the Alumina-Apiezon column with conversion to methane
d	Low temperature distillation
m	Mass spectrometric assay
s	Silica gel column used in this analysis

FIGURE III-3

Dose Dependence of the Ethane and Ethylene Yields From Pure Liquid Cyclopentane

□ Ethylene analysed on the silica gel column with conversion to methane

○ Ethane analysed on the silica gel column with conversion to methane

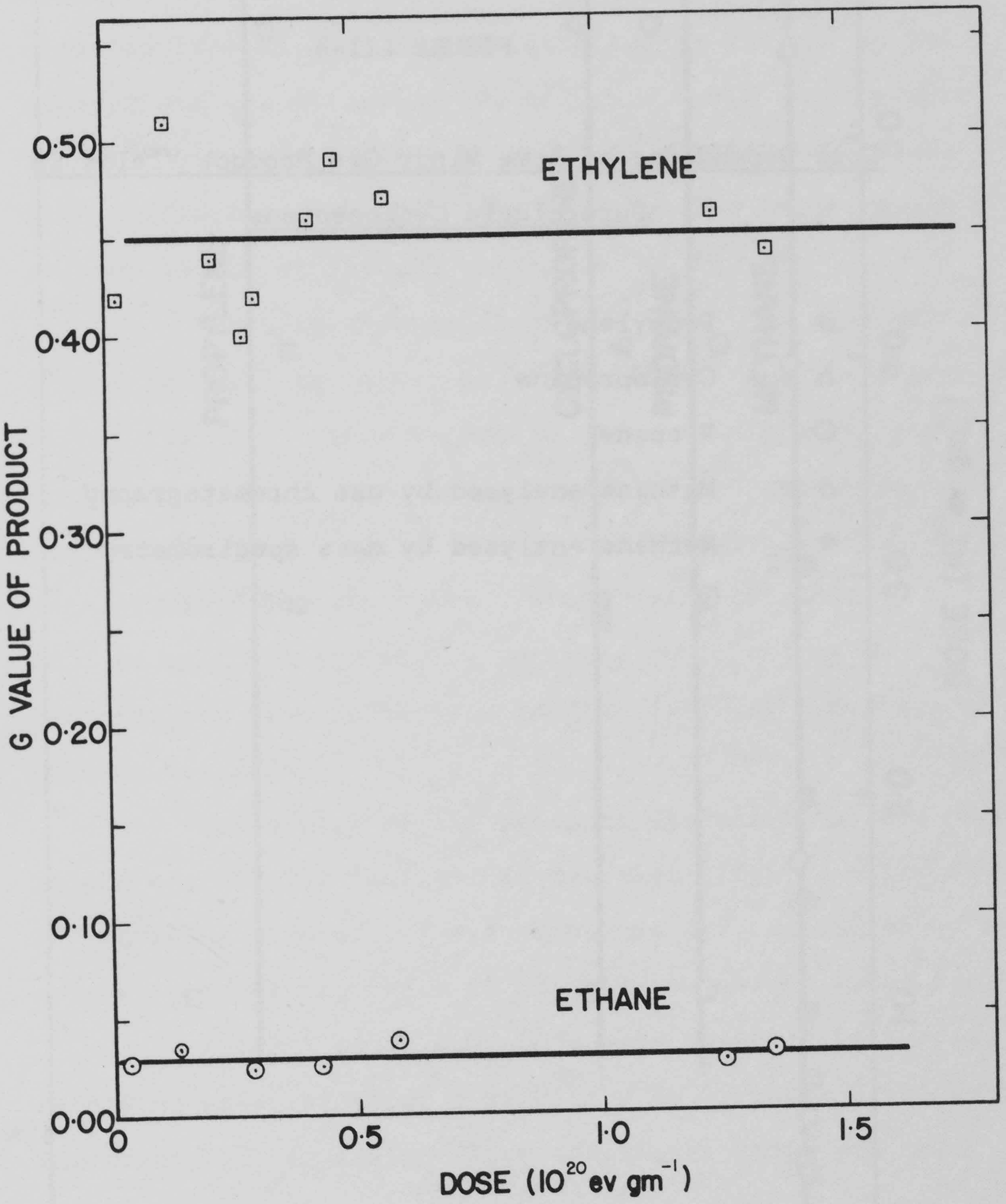
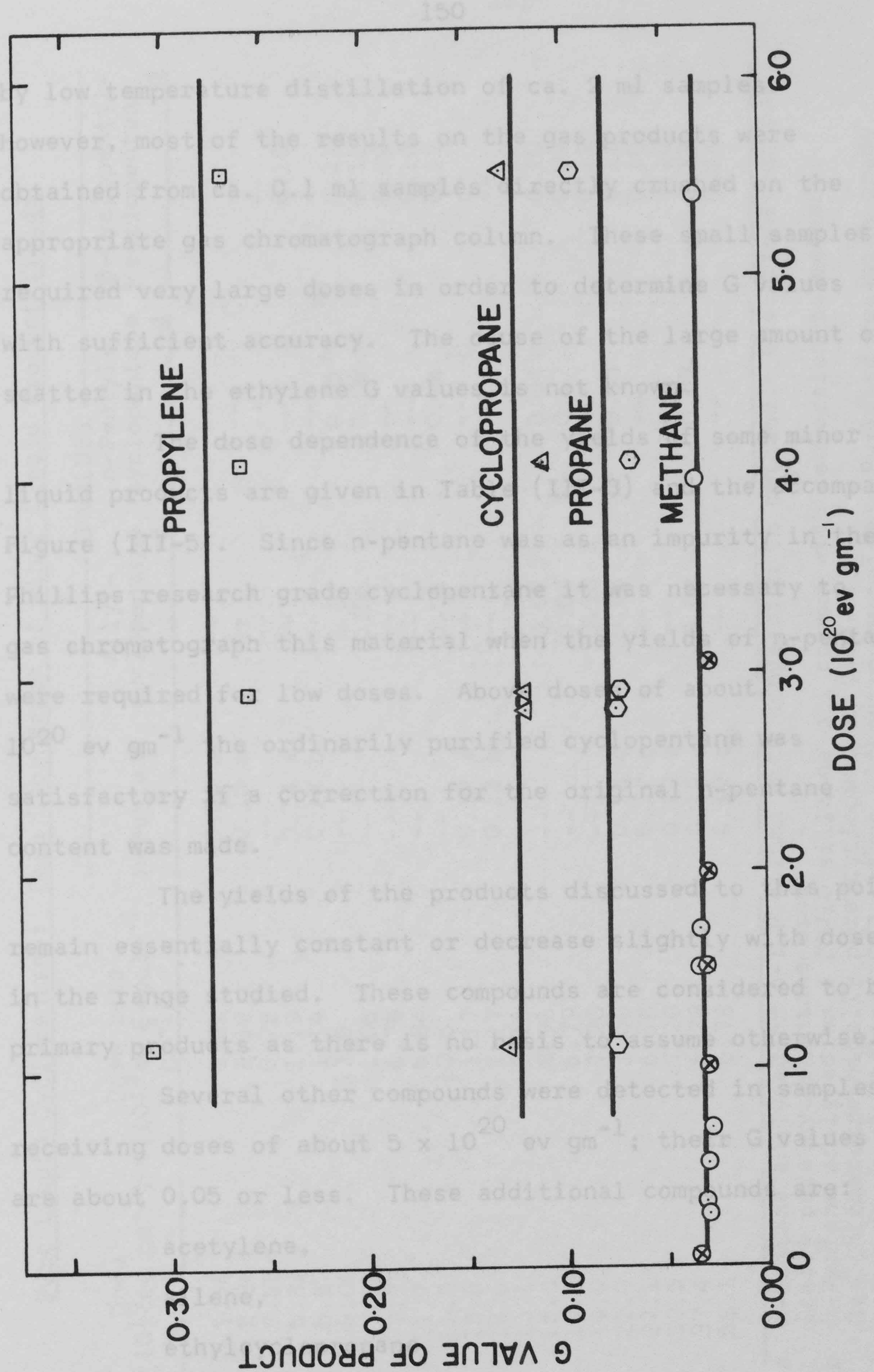

ETHYLENE
ETHANE
G VALUE OF PRODUCT
0·50
0·40
0·30
0·20
0·10
0·00
0
0·5
1·0
1·5
DOSE (10^{20} ev gm^{-1})

FIGURE III-4

Dose Dependence of Some Minor Gas Product Yields in Pure Liquid Cyclopentane

□	Propylene
△	Cyclopropane
⬡	Propane
○	Methane analysed by gas chromatography
⊗	Methane analysed by mass spectrometry


PROPYLENE
CYCLOPROPANE
PROPANE
METHANE
G VALUE OF PRODUCT
0·00
0·10
0·20
0·30
DOSE (10^{20} ev gm^{-1})
0
1·0
2·0
3·0
4·0
5·0
6·0

by low temperature distillation of ca. 2 ml samples. However, most of the results on the gas products were obtained from ca. 0.1 ml samples directly crushed on the appropriate gas chromatograph column. These small samples required very large doses in order to determine G values with sufficient accuracy. The cause of the large amount of scatter in the ethylene G values is not known.

The dose dependence of the yields of some minor liquid products are given in Table (III-3) and the accompanying Figure (III-5). Since n-pentane was as an impurity in the Phillips research grade cyclopentane it was necessary to gas chromatograph this material when the yields of n-pentane were required for low doses. Above doses of about 10^{20} ev gm^{-1} the ordinarily purified cyclopentane was satisfactory if a correction for the original n-pentane content was made.

The yields of the products discussed to this point remain essentially constant or decrease slightly with dose in the range studied. These compounds are considered to be primary products as there is no basis to assume otherwise.

Several other compounds were detected in samples receiving doses of about 5 x 10^{20} ev gm^{-1}; their G values are about 0.05 or less. These additional compounds are:

acetylene,

allene,

ethylcyclopropane,

TABLE III-3

Pure Liquid Cyclopentane: Dose Dependence of Minor Liquid Product Yields

Dose (10^{19}ev gm^{-1})	Dose rate (10^{19}ev €-mole^{-1} hr^{-1})	G VALUES n-Pentane	 Allyl-cyclopentane [d]	 n-Pentyl-cyclopentane [d]	 3-Cyclopentyl-cyclopentene [d]
1.38	1.21	0.16 a	--	--	--
2.86	1.19	0.15 a	--	--	--
3.88	6.78	--	--	--	--
5.82	1.19	0.14 a	--	--	0.10
5.82	1.19	0.14 b	--	--	--
6.00	10.5	--	0.07	0.05	0.11
7.58	1.06	--	0.06	0.06	0.11
7.73	6.78	--	--	--	0.09
11.7	6.84	--	--	--	0.10
11.9	10.5	--	0.06	0.04	0.12
13.6	1.17	0.12 a	--	--	--
13.6	1.17	0.13 b	--	--	--
15.1	7.15	--	0.09	--	0.10
15.3	8.96	--	0.07	0.04	0.10
19.3	6.79	--	0.07	0.07	0.09
19.9	7.20	--	0.10	--	0.12
22.7	1.08	0.13 c	0.06	0.05	0.11
27.1	6.78	0.12 c	--	--	0.10
30.5	7.20	0.10 c	--	--	0.10
37.4	6.78	0.12 c	0.08	0.07	0.13
58.1	6.78	0.12 c	--	--	0.14

a n-Pentane analysed on o-TCP column with conversion to methane. Gas chromatographically pure cyclopentane used.

b n-Pentane analysed on a DC710 silicone oil column with conversion to methane. Gas chromatographically pure cyclopentane used.

c n-Pentane analysed on o-TCP column without conversion. Purified research grade cyclopentane used which required blank correction for n-pentane.

d Liquid product analysed on "Tris" column with conversion to methane.

FIGURE III-5

Dose Dependence of Some Minor Liquid Product Yields in Pure Liquid Cyclopentane

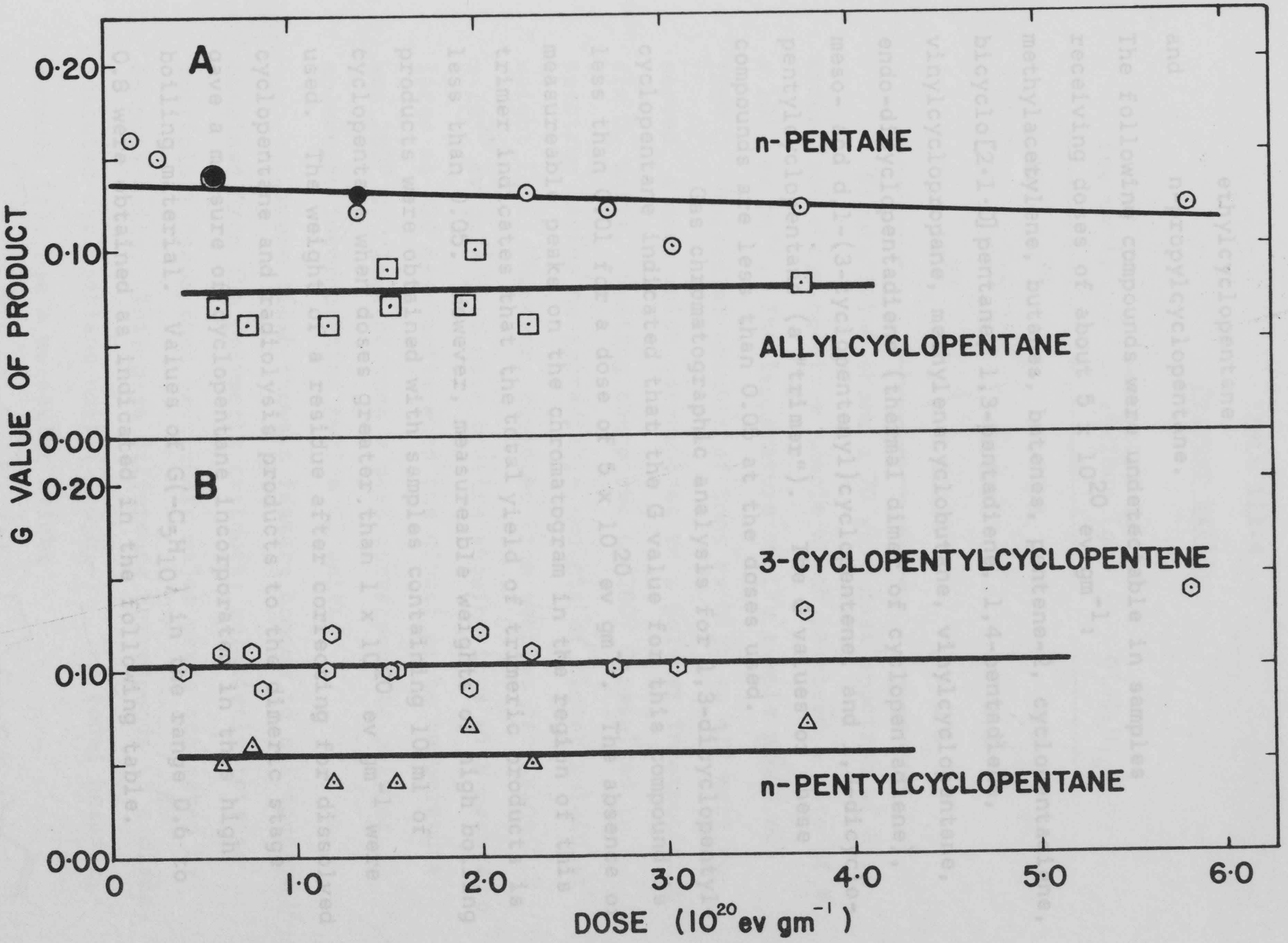
A ○ n-Pentane analysed on o-TCP column

● n-Pentane analysed on DC710 column with conversion to methane

□ Allylcyclopentane analysed on "Tris" column with conversion to methane

B ⬡ 3-Cyclopentylcyclopentene analysed on "Tris" column with conversion to CH_4

△ n-Pentylcyclopentane analysed on "Tris" column with conversion to CH_4


A
n-PENTANE
ALLYLCYCLOPENTANE
B
3-CYCLOPENTYLCYCLOPENTENE
n-PENTYLCYCLOPENTANE
G VALUE OF PRODUCT
0·20
0·10
0·00
0·20
0·10
0·00
0
1·0
2·0
3·0
4·0
5·0
6·0
DOSE (10^20 ev gm^-1)

ethylcyclopentane,

and n-propylcyclopentane.

The following compounds were undetectable in samples receiving doses of about 5 x 10^{20} ev gm^{-1}: methylacetylene, butanes, butenes, pentene-2, cyclopentadiene, bicyclo[2·1·0]pentane, 1,3-pentadiene, 1,4-pentadiene, vinylcyclopropane, methylenecyclobutane, vinylcyclopentane, endo-dicyclopentadiene (thermal dimer of cyclopentadiene), meso- and d,l-(3-cyclopentenyl)cyclopentene, and 1,3-dicyclopentylcyclopentane (a "trimer"). The G values of these compounds are less than 0.05 at the doses used.

Gas chromatographic analysis for 1,3-dicyclopentylcyclopentane indicated that the G value for this compound is less than 0.01 for a dose of 5 x 10^{20} ev gm^{-1}. The absence of measureable peaks on the chromatogram in the region of this trimer indicates that the total yield of trimeric products is less than 0.05. However, measureable weights of high boiling products were obtained with samples containing 10 ml of cyclopentane when doses greater than 1 x 10^{20} ev gm^{-1} were used. The weight of a residue after correcting for dissolved cyclopentane and radiolysis products to the dimeric stage gave a measure of cyclopentane incorporated in this high boiling material. Values of $G(-C_5H_{10})$ in the range 0.6 to 0.8 were obtained as indicated in the following table.

TABLE III-4

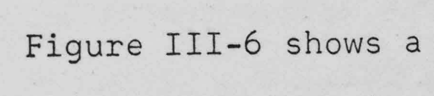
Polymer Yields

Dose (ev gm^{-1})	Corrected weight of residue (gm)	G(-C_5H_{10})
1.17 x 10^{20}	0.0008	0.8
1.93 x 10^{20}	0.0011	0.7
3.91 x 10^{20}	0.0021	0.6

Figure III-6 shows a 70 volt mass spectrum of a residue from a cyclopentane sample which received a dose of 4 x 10^{19} ev gm^{-1}. The temperature of the sample probe was 165° C. Molecular weights of ions as high as 412 were observed, a mass which corresponds to a polymer incorporating six C_5 units. Heating the probe to 280° C resulted in a spectrum having no appreciable amounts of higher molecular weight ions. However, residues from samples receiving 5.8 x 10^{20} ev gm^{-1} gave mass spectra showing ions with masses as large as 820 mass units when the direct probe temperature was 280° C. Ions of such a mass correspond to polymer molecules incorporating twelve C_5 units.

Figure III-6 shows a feature common to all spectra obtained from the polymeric residues; relatively intense multiplets occur that have their major peaks separated by 68 mass units. This mass difference corresponds to a disubstituted cyclopentane unit (–c-C_5H_8–). The model hexamer, formula (a), has a molecular weight

(a)



(b)

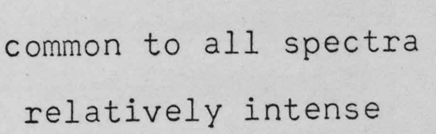


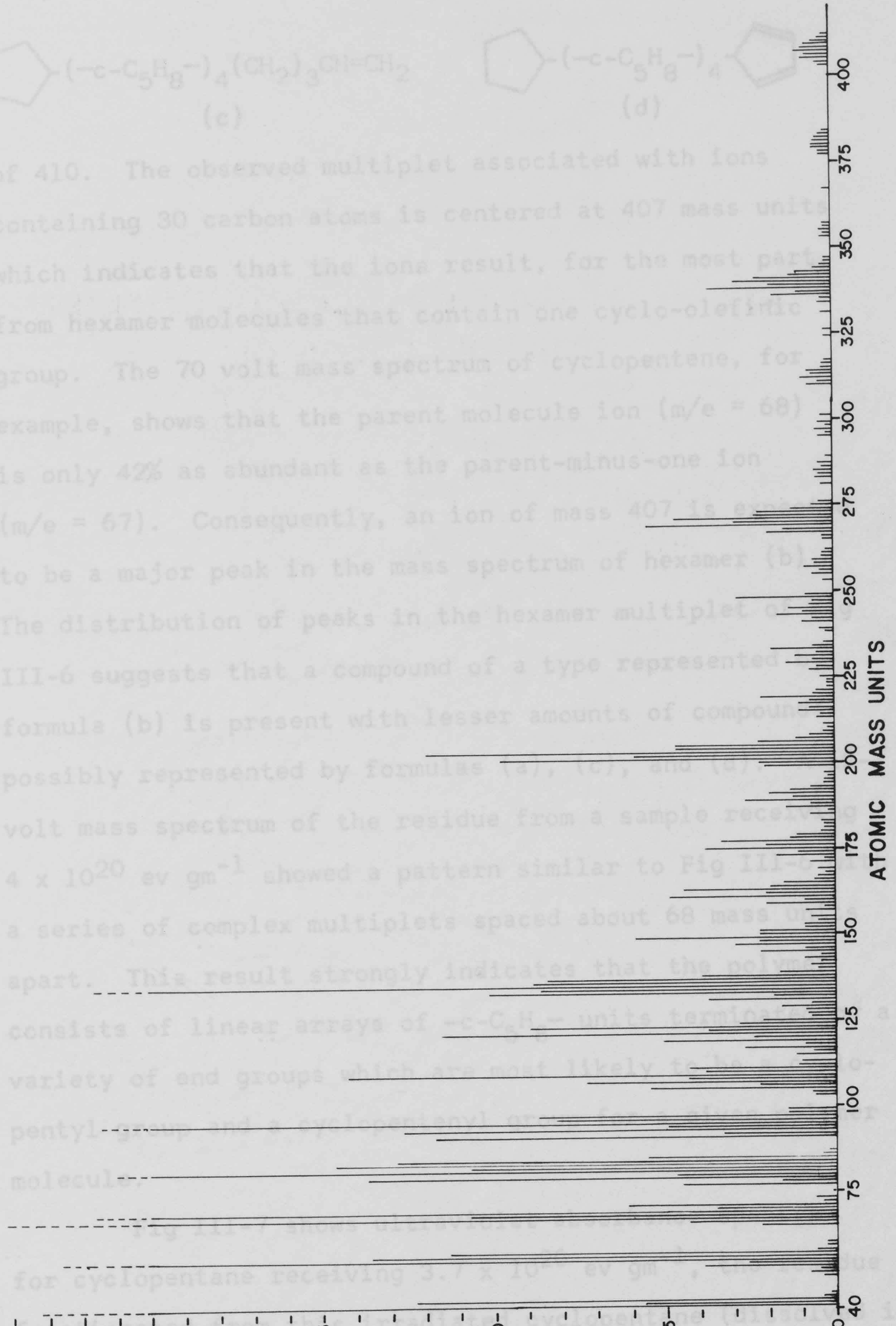
FIGURE III-6

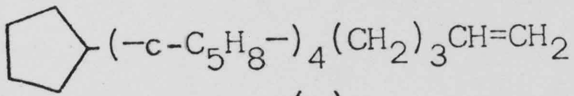
Mass Spectrum of Polymeric Residue from Irradiated Pure Liquid Cyclopentane

Dose: 3.88×10^{19} ev gm^{-1}

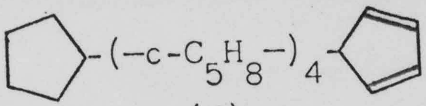
Ionizing Voltage: 70 volts

Probe Temperature: 165°C


INTENSITY
0
5
10
15
20
25
30
35
40
ATOMIC MASS UNITS
40
75
100
125
150
175
200
225
250
275
300
325
350
375
400



(c)



(d)

of 410. The observed multiplet associated with ions containing 30 carbon atoms is centered at 407 mass units which indicates that the ions result, for the most part, from hexamer molecules that contain one cyclo-olefinic group. The 70 volt mass spectrum of cyclopentene, for example, shows that the parent molecule ion (m/e = 68) is only 42% as abundant as the parent-minus-one ion (m/e = 67). Consequently, an ion of mass 407 is expected to be a major peak in the mass spectrum of hexamer (b). The distribution of peaks in the hexamer multiplet of Fig III-6 suggests that a compound of a type represented by formula (b) is present with lesser amounts of compounds possibly represented by formulas (a), (c), and (d). A 12-volt mass spectrum of the residue from a sample receiving 4×10^{20} ev gm^{-1} showed a pattern similar to Fig III-6 with a series of complex multiplets spaced about 68 mass units apart. This result strongly indicates that the polymer consists of linear arrays of $-c\text{-}C_5H_8-$ units terminated by a variety of end groups which are most likely to be a cyclopentyl group and a cyclopentenyl group for a given polymer molecule.

Fig III-7 shows ultraviolet absorbance spectra for cyclopentane receiving 3.7×10^{20} ev gm^{-1}, the residue fractionated from this irradiated cyclopentane (dissolved in

FIGURE III-7

Ultraviolet Absorption Spectra

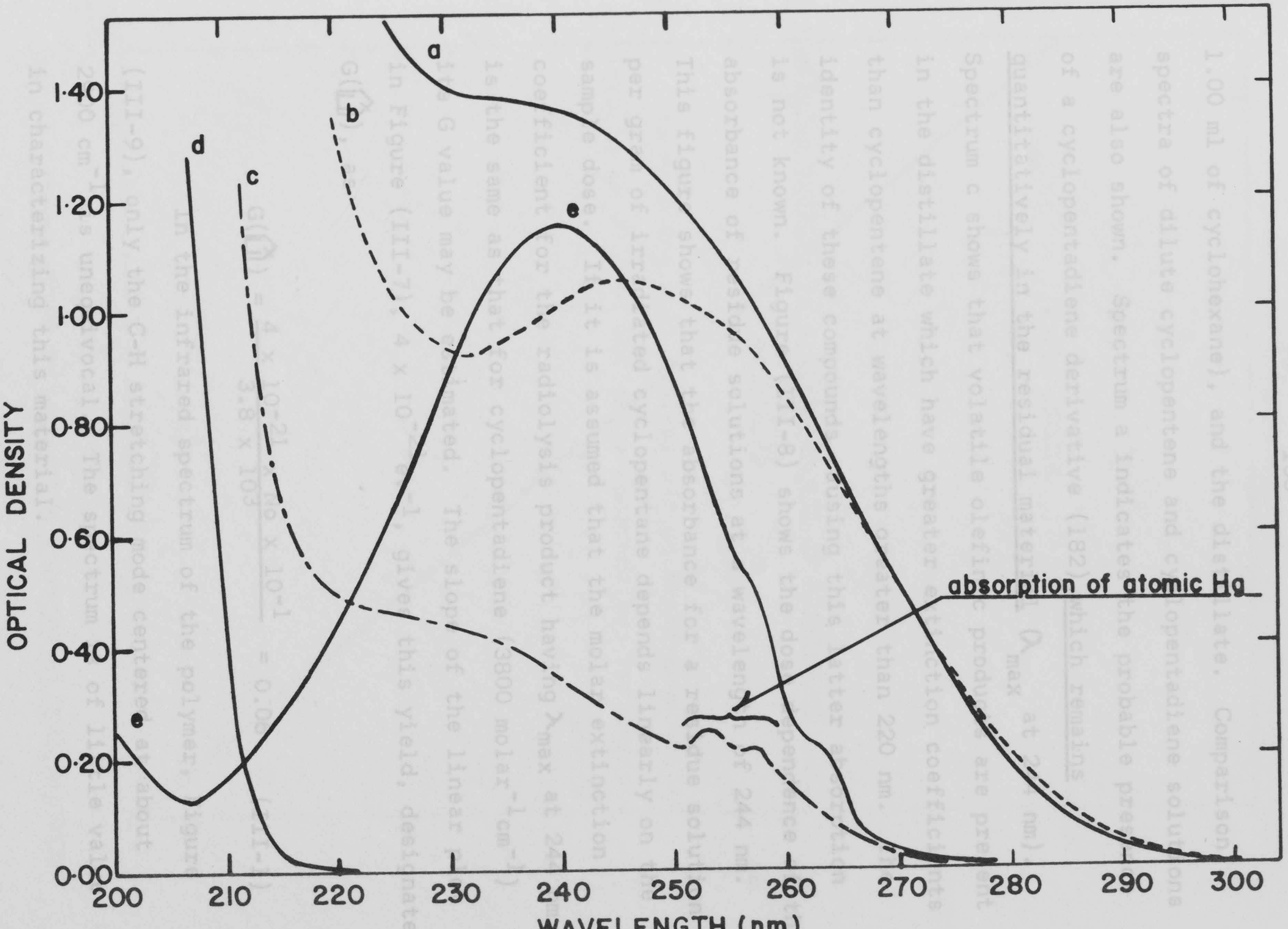
a. Irradiated cyclopentane; dose of 3.7×10^{20} ev gm^{-1}; 1.0 cm path length.

b. Non-volatile residue from 6.62 gm of irradiated cyclopentane; dose of 3.7×10^{20} ev gm^{-1}; 0.10 cm path length; residue dissolved in 1.00 ml of cyclohexane.

c. Volatile component from irradiated cyclopentane; dose of 3.7×10^{20} ev gm^{-1}; 1.0 cm path length.

d. 5.7×10^{-3} M cyclopentene in cyclopentane; 1.0 cm path length.

e. 3.0×10^{-3} M cyclopentadiene in cyclopentane; 0.10 cm path length.


OPTICAL DENSITY
1·40
1·20
1·00
0·80
0·60
0·40
0·20
0·00
WAVELENGTH (nm)
200
210
220
230
240
250
260
270
280
290
300
a
b
c
d
e
e
absorption of atomic Hg

1.00 ml of cyclohexane), and the distillate. Comparison spectra of dilute cyclopentene and cyclopentadiene solutions are also shown. Spectrum a indicates the probable presence of a cyclopentadiene derivative (182) <u>which remains quantitatively in the residual material</u> (λ_{max} at 244 nm). Spectrum c shows that volatile olefinic products are present in the distillate which have greater extinction coefficients than cyclopentene at wavelengths greater than 220 nm. The identity of these compounds causing this latter absorption is not known. Figure (III-8) shows the dose dependence of the absorbance of residue solutions at a wavelength of 244 nm. This figure shows that the absorbance for a residue solution per gram of irradiated cyclopentane depends linearly on the sample dose. If it is assumed that the molar extinction coefficient for the radiolysis product having λ_{max} at 244 nm is the same as that for cyclopentadiene (3800 molar^{-1}cm^{-1}) its G value may be estimated. The slope of the linear plot in Figure (III-7), 4 x 10^{-21}ev^{-1}, gives this yield, designated G(), as

G() $= \frac{4 \text{ x } 10^{-21} \text{ x No x } 10^{-1}}{3.8 \text{ x } 10^{3}} = 0.06 \qquad \text{(III-1)}$

In the infrared spectrum of the polymer, Figure (III-9), only the C-H stretching mode centered at about 2900 cm^{-1} is unequivocal. The spectrum is of little value in characterizing this material.

FIGURE III-8

Dose Dependence of the Absorbance of Residue Solutions at 244 nm

Absorbance based on the residue from one gram of irradiated cyclopentane dissolved in 1.00 ml of cyclohexane.

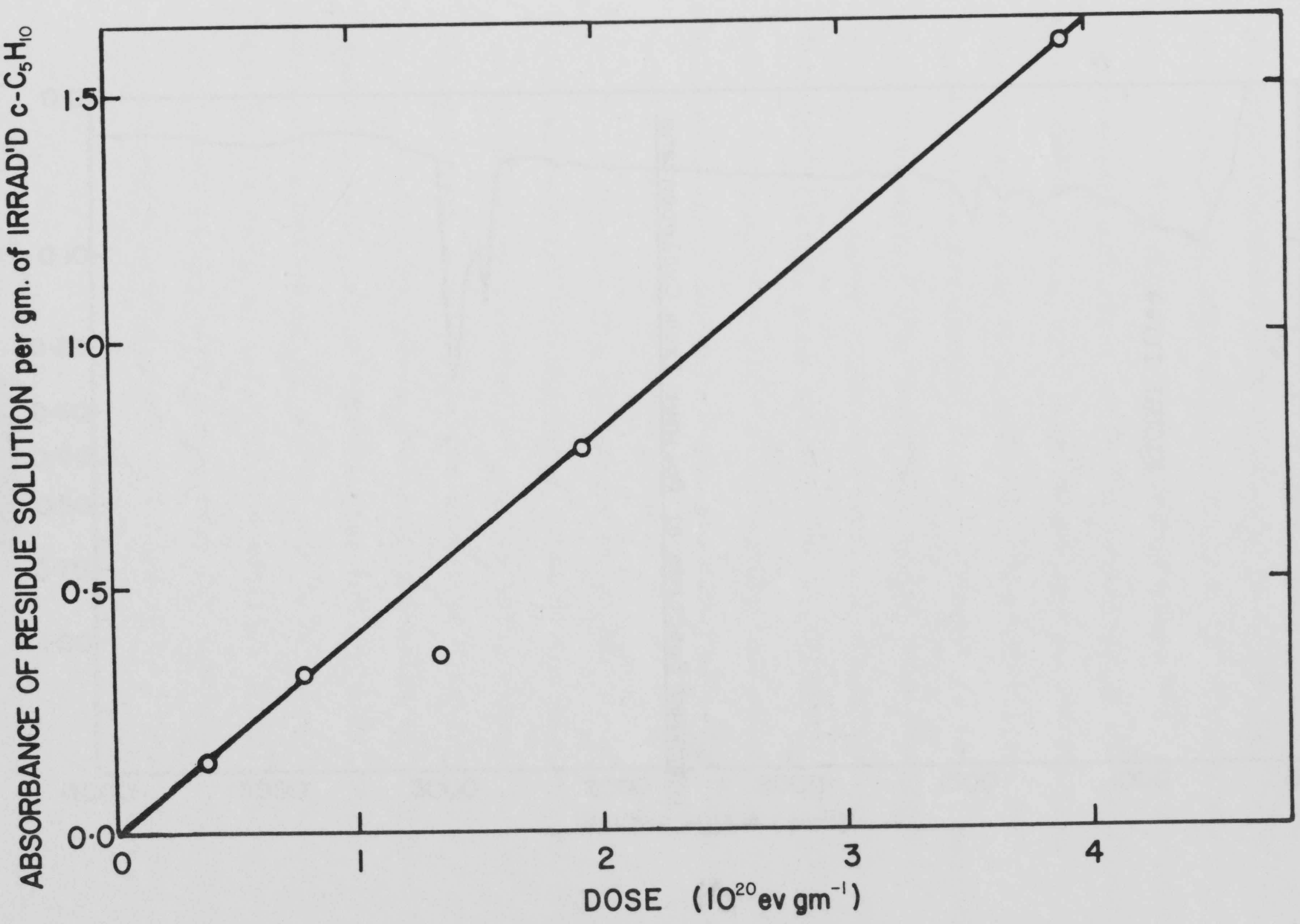
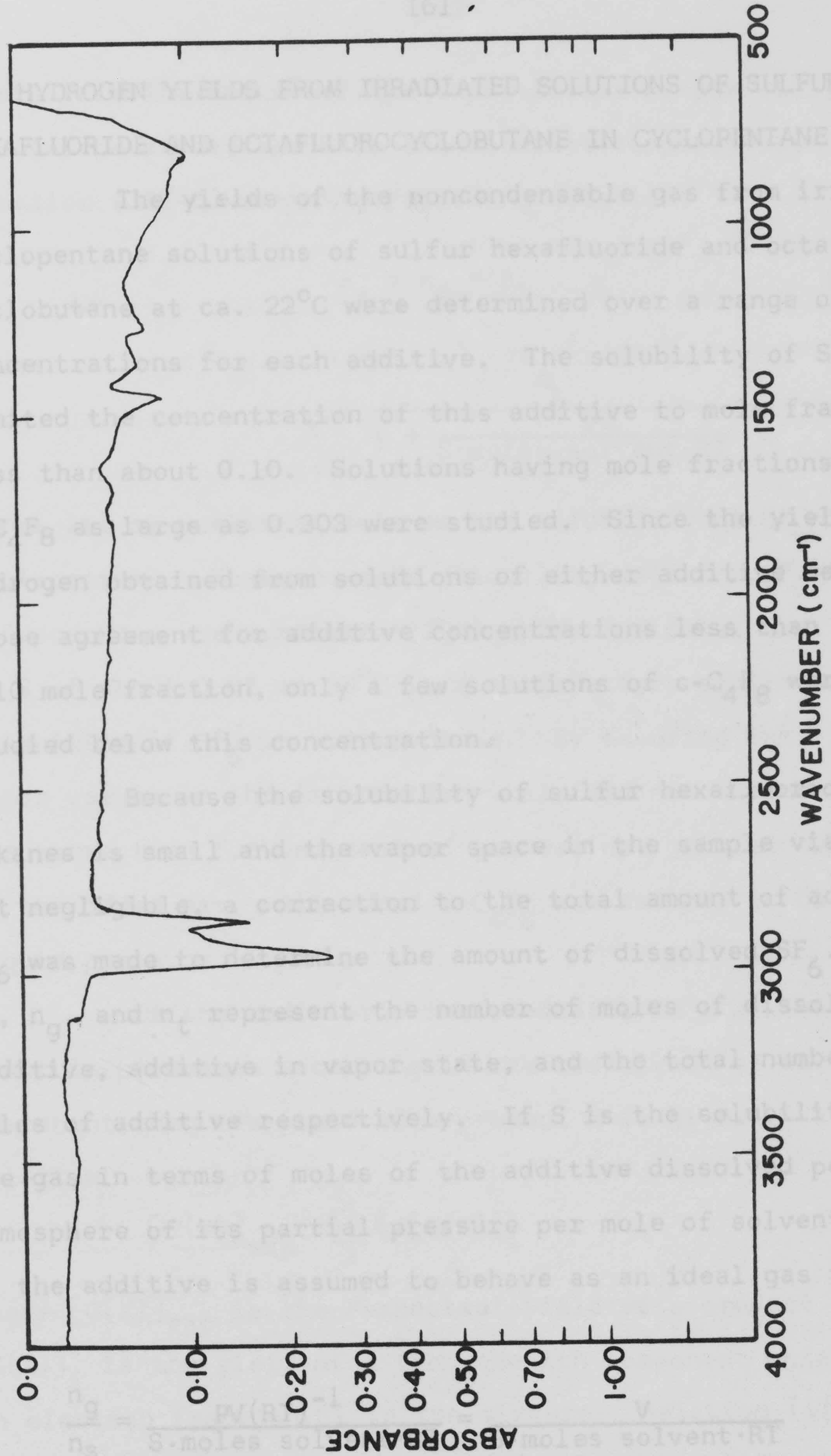

ABSORBANCE OF RESIDUE SOLUTION per gm. of IRRAD'D c-C_5H_{10}
1·5
1·0
0·5
0·0
0
1
2
3
4
DOSE (10^{20} ev gm^{-1})

FIGURE III-9

Infrared Spectrum of Polymer from Cyclopentane


ABSORBANCE
0·0
0·10
0·20
0·30
0·40
0·50
0·70
1·00
WAVENUMBER (cm⁻¹)
4000
3500
3000
2500
2000
1500
1000
500

B. HYDROGEN YIELDS FROM IRRADIATED SOLUTIONS OF SULFUR HEXAFLUORIDE AND OCTAFLUOROCYCLOBUTANE IN CYCLOPENTANE

The yields of the noncondensable gas from irradiated cyclopentane solutions of sulfur hexafluoride and octafluorocyclobutane at ca. 22°C were determined over a range of concentrations for each additive. The solubility of SF_6 limited the concentration of this additive to mole fractions less than about 0.10. Solutions having mole fractions of $c\text{-}C_4F_8$ as large as 0.303 were studied. Since the yields of hydrogen obtained from solutions of either additive were in close agreement for additive concentrations less than about 0.10 mole fraction, only a few solutions of $c\text{-}C_4F_8$ were studied below this concentration.

Because the solubility of sulfur hexafluoride in alkanes is small and the vapor space in the sample vials is not negligible, a correction to the total amount of added SF_6 was made to determine the amount of dissolved SF_6. Let n_s, n_g, and n_t represent the number of moles of dissolved additive, additive in vapor state, and the total number of moles of additive respectively. If S is the solubility of the gas in terms of moles of the additive dissolved per atmosphere of its partial pressure per mole of solvent and if the additive is assumed to behave as an ideal gas then

$$\frac{n_g}{n_s} = \frac{PV(RT)^{-1}}{S\cdot\text{moles solvent}\cdot RT} = \frac{V}{S\cdot\text{moles solvent}\cdot RT} \qquad \text{(III-2)}$$

where V is the volume of the vapor in the sample vial, R is the gas constant, and T is the absolute temperature. Combining Equation (III-2) with the following relation:

$$n_s + n_g = n_t \qquad \text{(III-3)}$$

gives

$$n_s = \frac{n_t}{1 + \dfrac{V}{S\cdot\text{moles solvent}\cdot RT}} \qquad \text{(III-4)}$$

There are no published data on the solubility of SF_6 in cyclopentane. However, some solubility data for SF_6 in other hydrocarbons are available (220) which indicates that a value of S of about 0.01 at 20°C is a satisfactory estimate for the solubility of SF_6 in cyclopentane. By ensuring that the vapor volume in the irradiation vials did not exceed 0.5 ml the correction for undissolved gas was not greater than 5% of the added gas. All added $c\text{-}C_4F_8$ was assumed to be in the liquid phase.

If the radiolytic intermediates in a mixture only react in processes occurring in the radiolysis of each pure component then the yield of a product X is given by the linear relation

$$[G(X)]_{exp} = \sum_i \epsilon i[G(X)]_i \qquad \text{(III-5)}$$

where $[G(X)]_{exp}$ is the "expected" yield of a product X and $[G(X)]_i$ is the yield of X from the ith component which has an electron fraction ϵi in the mixture. Relation (III-5) assumes that the energy absorbed by the ith component is directly proportional to its electron fraction. Often, however, reactive intermediates resulting from one component will react* with other components of the mixture at different rates or in different ways than they react with the component from which they are derived. If this latter behavior occurs, deviations from Equation (III-5) are expected. Conversely, deviations from yields calculated from Equation (III-5) indicate that the reactive intermediates of a mixed system react differently with at least one other component than they react with the component from which they are derived.

The hydrogen gas yields from irradiated binary cyclopentane solutions of SF_6 and c-C_4F_8 are given in Table (III-5) for several concentrations of the additives. Dose rates were in the range 6.60×10^{19} to 6.80×10^{19} ev ϵ-mole^{-1}hr^{-1}. Doses were between 7.98×10^{19} and 8.20×10^{19} ev per electron mole of mixture. Figure (III-10) shows the yields of hydrogen obtained for various mole fractions of the additives. This figure also includes curves for the "expected" hydrogen yield calculated on the basis of Equation (III-5) In applying this equation, X denotes H_2 while both $G(H_2)\ SF_6$ and $G(H_2)\ c\text{-}C_4F_8$ are zero. For these solutions

---

* Here the word "react" is used in a very general sense. Quenching the electronic excitation without chemical decomposition is an example of reaction in this regard.

TABLE III-5

Noncondensable Gas Yields from Cyclopentane Solutions of Fluorinated Additives

Electron Fraction Additive	Mole Fraction Additive	G(-196)	$G(CH_4)$	$G(H_2)$	Expected $G(H_2)$[b]	$\Delta(H_2)$	$\delta(H_2)$	$\frac{\delta(H_2)}{[\delta(H_2)]_{max}}$[c]
A. SF_6 Solutions								
2.90×10^{-5}	1.65×10^{-5}	5.12	0.029	5.09	5.35	0.26	0.26	0.077
4.95×10^{-5}	2.81×10^{-5}	5.04	0.03[a]	5.04	5.35	0.31	0.31	0.091
8.84×10^{-5}	5.05×10^{-5}	4.88	0.029	4.85	5.35	0.50	0.50	0.147
2.49×10^{-4}	1.42×10^{-4}	4.71	0.024	4.69	5.35	0.66	0.66	0.194
3.59×10^{-4}	2.04×10^{-4}	4.76	0.023	4.74	5.35	0.61	0.61	0.180
6.06×10^{-4}	3.46×10^{-4}	4.66	0.027	4.63	5.35	0.72	0.72	0.212
1.16×10^{-3}	6.60×10^{-4}	4.32	0.027	4.29	5.35	1.06	1.06	0.312
2.22×10^{-3}	1.27×10^{-3}	3.97	0.02[a]	3.95	5.35	1.40	1.40	0.412
2.46×10^{-3}	1.37×10^{-3}	4.04	0.02[a]	4.02	5.34	1.32	1.33	0.392
6.24×10^{-3}	3.51×10^{-3}	3.38	0.01[a]	3.37	5.31	1.94	1.95	0.574
1.45×10^{-2}	8.25×10^{-3}	3.02	0.01[a]	3.01	5.27	2.26	2.28	0.672
2.38×10^{-2}	1.36×10^{-2}	2.78	0.01[a]	2.77	5.22	2.45	2.51	0.738
3.53×10^{-2}	2.04×10^{-2}	2.46	0.01[a]	2.45	5.16	2.71	2.81	0.827
5.05×10^{-2}	2.80×10^{-2}	2.34	0.012	2.33	5.08	2.75	2.90	0.851

TABLE III-5 continued

Electron Fraction Additive	Mole Fraction Additive	G(-196)	$G(CH_4)$	$G(H_2)$	Expected[b] $G(H_2)$	$\Delta(H_2)$	$\delta(H_2)$	$\frac{\delta(H_2)}{[\delta(H_2)]_{max}}$ [c]
$7.43x10^{-2}$	$4.39x10^{-2}$	2.09	0.010	2.08	4.95	2.87	3.10	0.910
$1.40x10^{-1}$	$8.58x.0^{-2}$	1.77	0.01 [a]	1.76	4.60	2.84	3.30	0.970
$1.69x10^{-1}$	$1.06x10^{-1}$	1.69	0.00 [a]	1.69	4.45	2.76	3.32	0.976
B. C_4F_8 Solutions								
$7.60x10^{-3}$	$3.18x10^{-3}$	3.33	0.018	3.31	5.31	2.00	2.02	0.594
$3.98x10^{-2}$	$1.71x10^{-2}$	2.75	0.016	2.73	5.14	2.41	2.51	0.738
$1.27x10^{-1}$	$5.72x10^{-2}$	1.94	0.01 [a]	1.93	4.67	2.74	3.14	0.924
$3.01x10^{-1}$	$1.52x10^{-1}$	1.34	0.008	1.33	3.74	2.41	3.45	1.015
$3.51x10^{-1}$	$1.84x10^{-1}$	1.30	0.01 [a]	1.29	3.47	2.18	3.36	0.988
$4.48x10^{-1}$	$2.53x10^{-1}$	1.14	0.012	1.13	2.95	1.82	3.30	0.970
$4.98x.0^{-1}$	$3.03x10^{-1}$	0.967	0.009	0.96	2.68	1.72	3.40	1.000

---

[a] estimated methane yield

[b] expected $G(H_2)$ was calculated on the basis of the electron fraction $c\text{-}C_5H_{10}$ in the sample using $G(H_2)_o = 5.35$ for pure cyclopentane extrapolated to zero dose.

[c] $[\delta(H_2)]_{max}^{o}$ is taken as 3.40.

FIGURE III-10

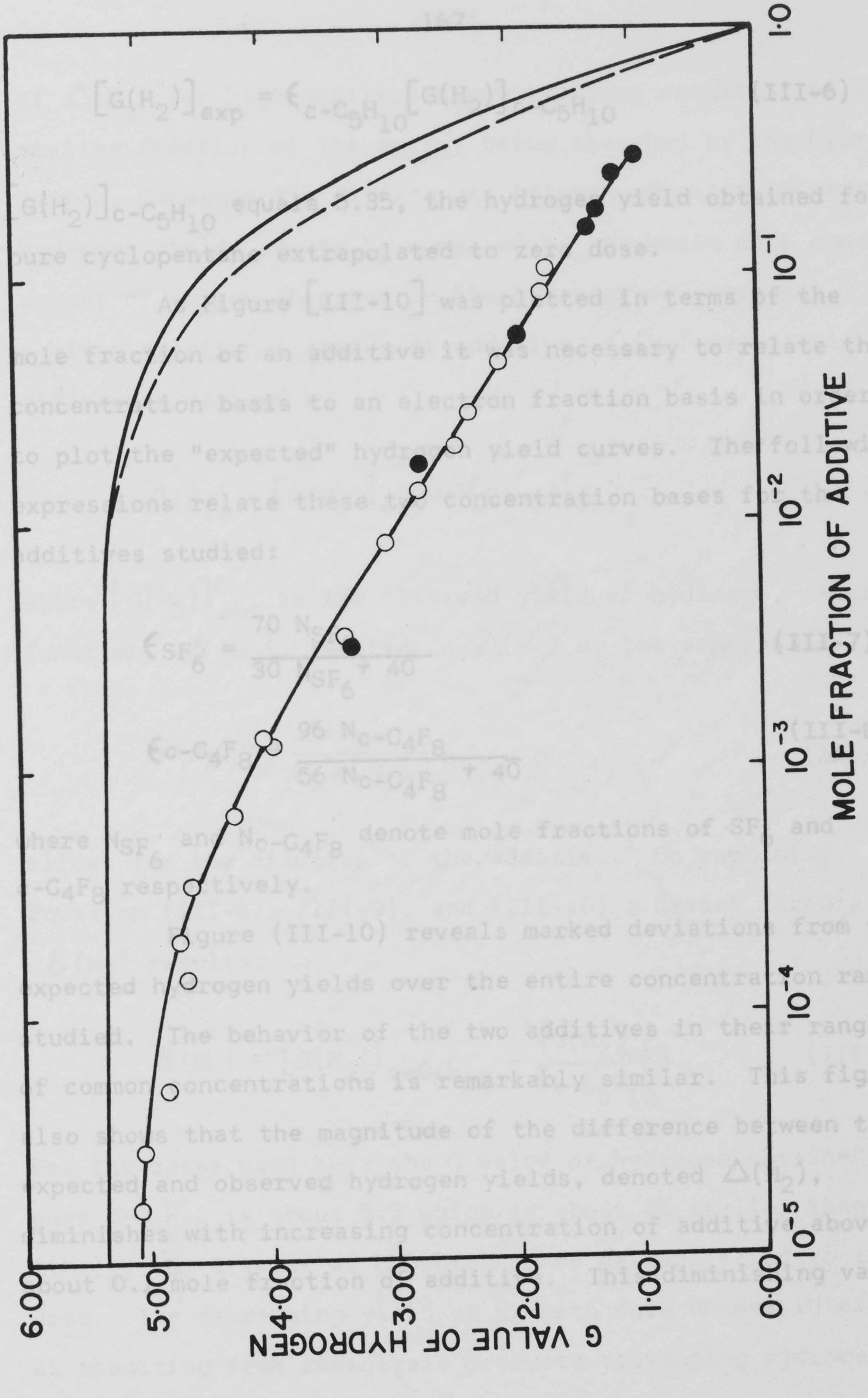
"Expected" and Observed Hydrogen Yields from
Cyclopentane - SF_6 Solutions
and
Cyclopentane - c-C_4F_8 Solutions

——— Expected hydrogen yield from SF_6 solutions

– – – – Expected hydrogen yield from c-C_4F_8 solutions

-○-○-○- Observed hydrogen yield from SF_6 solutions

-●-●-●- Observed hydrogen yield from c-C_4F_8 solutions


G VALUE OF HYDROGEN
6·00
5·00
4·00
3·00
2·00
1·00
0·00
MOLE FRACTION OF ADDITIVE
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1·0

$$\left[G(H_2)\right]_{exp} = \epsilon_{c\text{-}C_5H_{10}}\left[G(H_2)\right]_{c\text{-}C_5H_{10}} \qquad \text{(III-6)}$$

$\left[G(H_2)\right]_{c\text{-}C_5H_{10}}$ equals 5.35, the hydrogen yield obtained for pure cyclopentane extrapolated to zero dose.

As Figure [III-10] was plotted in terms of the mole fraction of an additive it was necessary to relate this concentration basis to an electron fraction basis in order to plot the "expected" hydrogen yield curves. The following expressions relate these two concentration bases for the additives studied:

$$\epsilon_{SF_6} = \frac{70\ N_{SF_6}}{30\ N_{SF_6} + 40} \qquad \text{(III-7)}$$

$$\epsilon_{c\text{-}C_4F_8} = \frac{96\ N_{c\text{-}C_4F_8}}{56\ N_{c\text{-}C_4F_8} + 40} \qquad \text{(III-8)}$$

where N_{SF_6} and $N_{c\text{-}C_4F_8}$ denote mole fractions of SF_6 and $c\text{-}C_4F_8$ respectively.

Figure (III-10) reveals marked deviations from the expected hydrogen yields over the entire concentration range studied. The behavior of the two additives in their range of common concentrations is remarkably similar. This figure also shows that the magnitude of the difference between the expected and observed hydrogen yields, denoted $\Delta(H_2)$, diminishes with increasing concentration of additive above about 0.1 mole fraction of additive. This diminishing value of $\Delta(H_2)$ for high additive concentrations results from the smaller fraction of the energy being absorbed by the hydrocarbon. Consequently differences between expected and observed hydrogen yields are to be compared on the basis of a constant amount of energy absorbed in the hydrocarbon component. At a given electron fraction of additive, $\Delta(H_2)$ represents the difference defined by

$$\Delta(H_2) = \left[G(H_2)\right]_{exp} - \left[G(H_2)\right]_{obs} \qquad \text{(III-9)}$$

where $\left[G(H_2)\right]_{obs}$ is the observed yield of hydrogen. Another function, $\delta(H_2)$, related to $\Delta(H_2)$ by the expression

$$\delta(H_2) = \frac{\Delta(H_2)}{\epsilon_{c\text{-}C_5H_{10}}} \qquad \text{(III-10)}$$

allows for the dilution of the additive. On combining Equation (III-6), (III-9), and (III-10) a direct formula for $\delta(H_2)$ results:

$$\delta(H_2) = \left[G(H_2)\right]_{c\text{-}C_5H_{10}} - \frac{\left[G(H_2)\right]_{obs}}{\epsilon_{c\text{-}C_5H_{10}}} \qquad \text{(III-11)}$$

For the doses used here the G value of hydrogen obtained with pure c-C_5H_{10} is about 5.2 which is about 4% smaller than $G(H_2)_o$, the G value of H_2 obtained by extrapolating to zero dose. The decreasing yield of H_2 with dose has been interpreted as resulting from radiolysis products scavenging hydrogen precursors through secondary reactions. When the concentration of an additive is greater than the concentration of inhibiting radiolysis products it will be assumed that $[G(H_2)]_o$ is to be used in the kinetic calculations instead of the actual yield of hydrogen for the particular dose, $[G(H_2)]_{c\text{-}C_5H_{10}}$. Equation (III-11) then becomes

$$\delta(H_2) = 5.35 - \frac{[G(H_2)]_{obs}}{\epsilon_{c\text{-}C_5H_{10}}} \qquad (III\text{-}12)$$

It is further assumed in this work that the consumption of an additive is negligibly small at all concentrations for the doses used. Figure (III-11) shows the values of $\delta(H_2)$ calculated for the various concentrations of additives studied. Values of $\Delta(H_2)$, $\delta(H_2)$ and $\frac{\delta(H_2)}{[\delta(H_2)]_{max}}$ are also given in Table (III-5). $[\delta(H_2)]_{max}$ was found to be 3.4.

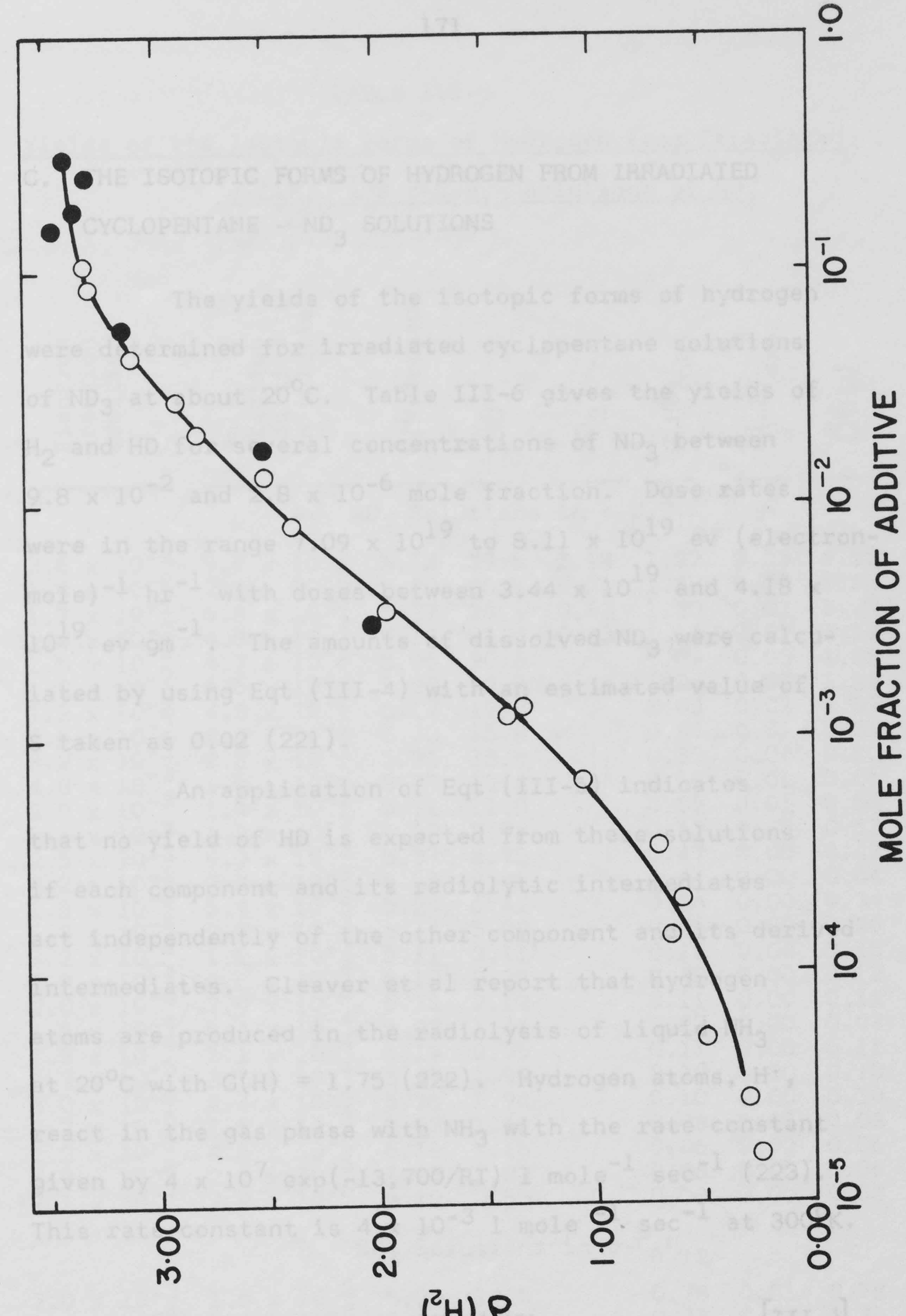
Samples of cyclopentane containing both SF_6 and a stoichiometric excess of ammonia produced, on irradiation, a yellowish white insoluble solid. This solid material produced an X-ray powder pattern identical to that of ammonium fluoride. Other components were also present in the solid. Mild heating of the precipitate in air (It was contained in a capillary tube) charred the sample easily. The odor of SO_2 and etching of the glass were apparent. Product yields were not measured in this system and further experiments with it were not pursued.

FIGURE III-11

The Differential Hydrogen Yields, $\delta(H_2)$, for Cyclopentane Solutions of SF_6 and $c\text{-}C_4F_8$

○ $SF_6\text{-}c\text{-}C_5H_{10}$ Solutions

● $c\text{-}C_4F_8\text{-}c\text{-}C_5H_{10}$ Solutions


G (H$_2$)
0·00
1·00
2·00
3·00
MOLE FRACTION OF ADDITIVE
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1·0

C. THE ISOTOPIC FORMS OF HYDROGEN FROM IRRADIATED CYCLOPENTANE - ND_3 SOLUTIONS

The yields of the isotopic forms of hydrogen were determined for irradiated cyclopentane solutions of ND_3 at about 20°C. Table III-6 gives the yields of H_2 and HD for several concentrations of ND_3 between 9.8×10^{-2} and 2.8×10^{-6} mole fraction. Dose rates were in the range 7.09×10^{19} to 8.11×10^{19} ev (electron-mole)$^{-1}$ hr^{-1} with doses between 3.44×10^{19} and 4.18×10^{19} ev gm^{-1}. The amounts of dissolved ND_3 were calculated by using Eqt (III-4) with an estimated value of S taken as 0.02 (221).

An application of Eqt (III-5) indicates that no yield of HD is expected from these solutions if each component and its radiolytic intermediates act independently of the other component and its derived intermediates. Cleaver et al report that hydrogen atoms are produced in the radiolysis of liquid NH_3 at 20°C with $G(H) = 1.75$ (222). Hydrogen atoms, $H^{\cdot}$, react in the gas phase with NH_3 with the rate constant given by $4 \times 10^7 \exp(-13,700/RT)$ l mole^{-1} sec^{-1} (223). This rate constant is 4×10^{-3} l mole^{-1} sec^{-1} at 300°K.

$$H\cdot + NH_3 \longrightarrow H_2 + NH_2 \qquad [III-1]$$

TABLE III-6

Yields of the Isotopic Forms of Hydrogen from Irradiated $c\text{-}C_5H_{10}$ and $c\text{-}C_6H_{12}$ Solutions of ND_3

Electron fraction additive	Mole fraction additive in solution	G(Hydrogen)	%HD	%D_2	G(HD) obs	G(HD) exp	δ(HD)
			A. ND_3 Solutions in $c\text{-}C_5H_{10}$				
2.6×10^{-2}	9.8×10^{-2}	5.13	29.6	1.18	1.52	0.05	1.52
1.9×10^{-2}	7.2×10^{-2}	5.29	26.1	0.76	1.38	0.03	1.38
1.7×10^{-2}	6.5×10^{-2}	5.17	26.1	0.68	1.30	0.03	1.29
1.4×10^{-2}	4.8×10^{-2}	5.13	22.4	0.43	1.15	0.02	1.14
1.5×10^{-2}	4.7×10^{-2}	5.25	20.8		1.09	0.03	1.08
1.2×10^{-2}	4.6×10^{-2}	5.37	23.2	0.45	1.24	0.02	1.23
1.2×10^{-2}	4.3×10^{-2}	5.17	19.7		1.03	0.02	1.02
7.5×10^{-3}	2.8×10^{-2}	5.30	15.8		0.84	0.01	0.84
8.2×10^{-3}	2.8×10^{-2}	5.21	15.8		0.82	0.01	0.82
4.8×10^{-3}	1.8×10^{-2}	5.37	12.4		0.66	0.01	0.66
3.9×10^{-3}	1.4×10^{-2}	5.11	11.0		0.56	0.01	0.56
3.3×10^{-3}	1.3×10^{-2}	5.32	9.96		0.53	0.00	0.53
2.5×10^{-3}	9.9×10^{-3}	5.37	8.75		0.47	0.00	0.47
2.2×10^{-3}	8.8×10^{-3}	5.25	8.46		0.44	0.00	0.44
1.5×10^{-3}	5.9×10^{-3}	5.24	6.42		0.34	0.00	0.34
6.7×10^{-4}	2.7×10^{-3}	5.14	5.00		0.26	0.00	0.26
3.2×10^{-4}	1.2×10^{-3}	5.11	3.11		0.16	0.00	0.16
2.3×10^{-4}	8.6×10^{-4}	5.19	2.38		0.12	0.00	0.12
2.0×10^{-4}	7.9×10^{-4}	5.12	2.12		0.11	0.00	0.11
1.6×10^{-4}	6.4×10^{-4}	5.07	1.41		0.07	0.00	0.07
1.3×10^{-4}	5.1×10^{-4}	5.19	2.05		0.11	0.00	0.11
8.7×10^{-5}	3.5×10^{-4}	5.27	1.99		0.10	0.00	0.10
6.0×10^{-5}	2.4×10^{-4}	5.26	1.94		0.10	0.00	0.10
3.7×10^{-5}	1.5×10^{-4}	5.02	1.52		0.08	0.00	0.08
1.2×10^{-5}	4.6×10^{-5}	5.19	1.16		0.06	0.00	0.06
6.7×10^{-6}	2.6×10^{-5}	4.97	1.22		0.06	0.00	0.06
*7.1×10^{-7}	2.8×10^{-6}	5.19	0.55		0.03	0.00	0.03
			B. ND_3 Solutions in $c\text{-}C_6H_{12}$				
3.0×10^{-3}	1.5×10^{-2}	5.35	14.5		0.78	0.01	0.78
3.8×10^{-4}	1.8×10^{-3}	5.44	5.62		0.31	0.00	0.31
1.4×10^{-5}	6.6×10^{-5}	5.48	1.76		0.10	0.00	0.10

* 10-ml sample

No direct measurement on the rate of the following reaction is presently available:

$$H\cdot + c\text{-}C_5H_{10} \longrightarrow H_2 + c\text{-}C_5H_9\cdot \qquad [III\text{-}2]$$

However, rate constants for hydrogen abstraction from paraffins by H· atoms appear to have frequency factors of about 1×10^{11} liter $mole^{-1}$ sec^{-1} and activation energies of about 7 kcal $mole^{-1}$ (224). Using these rate parameters the rate constant for reaction [III-2] was estimated to be approximately 10^6 liter $mole^{-1}$ sec^{-1} at 300° K. The ratio of the rates for reactions [III-1] and [III-2] is less than 10^{-8} when NH_3 and cyclopentane are in equal concentration at 300° K. If it is assumed that these gas phase data are applicable to the liquid phase reactions, deuterium abstraction from ND_3 by H· atoms or D· atoms in the cyclopentane solutions studied, makes a negligible contribution to hydrogen formation. Furthermore, any deuterium atoms resulting from the direct radiolysis of ND_3 react preferentially with cyclopentane to produce HD. Thus Eqt (III-5) should be modified to account for the amount of HD that is expected because of this deuterium atom yield from ND_3. G(D·) from ND_3 in the hydrocarbon solutions is not known but G(H·) reported by Cleaver et al for liquid NH_3 will be used as an approximation, any isotope effect for deuterium atom formation being neglected. The expected yield of HD is then given by

$$G(HD)_{exp} \approx \epsilon_{ND_3} G(H\cdot)_{\text{liquid } NH_3} \qquad \text{(III-13)}$$

The results in table III-6 show that the observed yields of HD, $G(HD)_{obs}$, are much larger than those expected on the basis of Eqt(III-13); reactivity transfer from the hydrocarbon to ammonia occurs. Let $\Delta(HD)$ denote the difference between $G(HD)_{obs}$ and the expected yield of HD, $G(DH)_{exp}$. As in Eqt (III-10) a quantity $\delta(HD)$ defined by

$$\delta(HD) = \frac{\Delta(HD)}{\epsilon_{c\text{-}C_5H_{10}}} \qquad \text{(III-14)}$$

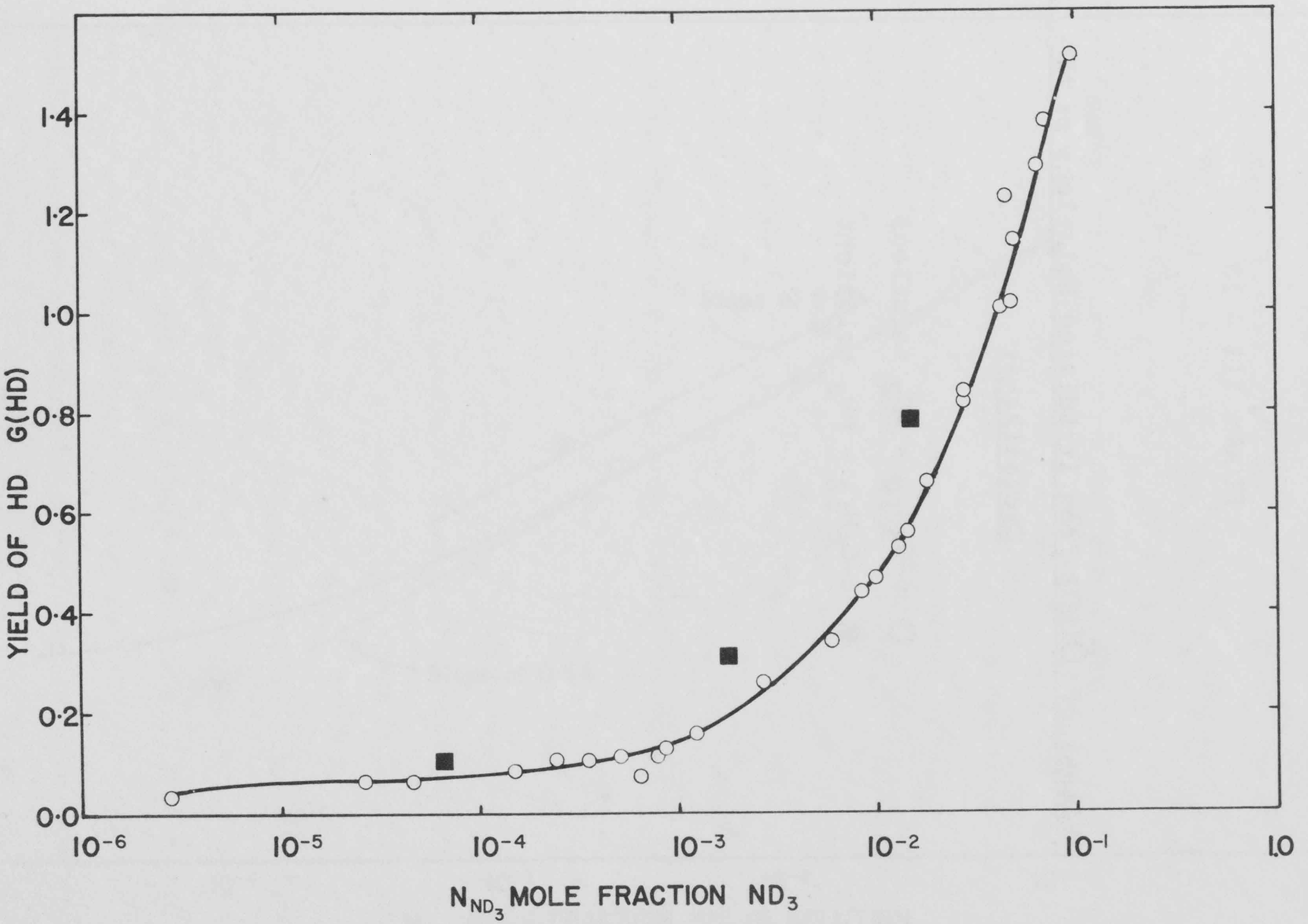
allows for the dilution effect of the ND_3. Values of $\delta(HD)$ for the ND_3 solutions are given in Table III-6; they are shown also in Fig (III-12) as a function of N_s, the mole fraction of ND_3 in the solution. Negligible differences occur between $\delta(HD)$ and $G(HD)_{obs}$ for all the concentrations of ND_3 used in this study. Figure (III-13) shows values of $\log_{10} \delta(HD)$ for various values of $\log_{10} N_s$. For values of N_s between 5×10^{-3} and 1×10^{-1} the slope of this plot is 0.54 which indicates that the HD yield depends approximately on the square root of the ND_3 concentration in this concentration range. Attempts to make solutions containing more than about 0.1 mole fraction ND_3 were not successful with the thin-bottomed sample cells because they did not withstand the ammonia pressure (ca. 10 atmospheres at 20°C).

FIGURE III - 12

Yields of HD from Irradiated Solutions of ND_3 in Cycloakanes

○ c-C_5H_{10} - ND_3 Solutions

■ c-C_6H_{12} - ND_3 Solutions



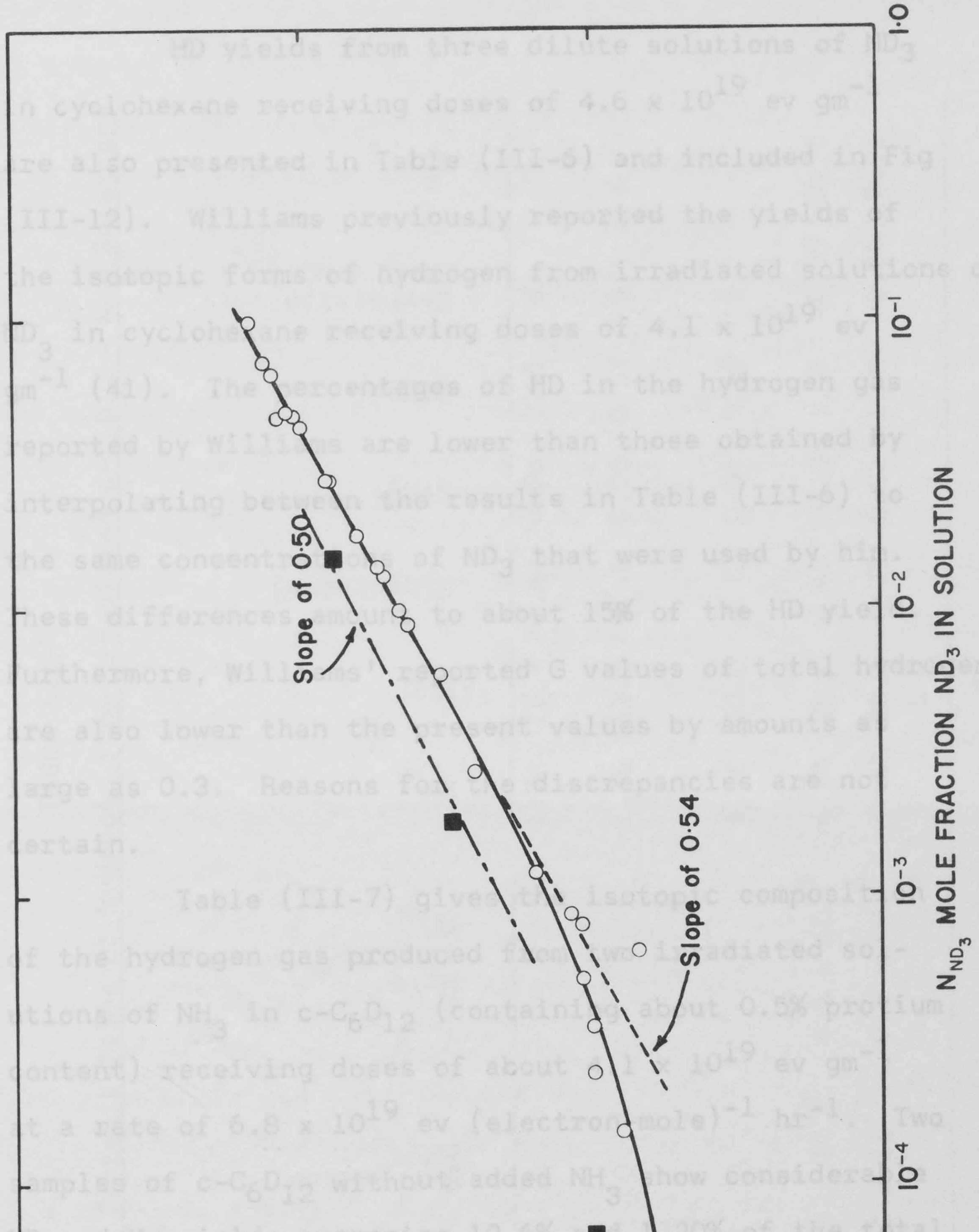
YIELD OF HD G(HD)
0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
10^-6
10^-5
10^-4
10^-3
10^-2
10^-1
1.0
N_ND3 MOLE FRACTION ND3

FIGURE III - 13

Values of δ(HD) from Irradiated Solutions of ND_3 in Cycloalkanes

○ c-C_5H_{10} - ND_3 solutions

■ c-C_6H_{12} - ND_3 solutions


YIELD OF HD G(HD)
10
1·0
0·1
0·01
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1·0
N_{ND_3} MOLE FRACTION ND_3 IN SOLUTION
Slope of 0·50
Slope of 0·54

HD yields from three dilute solutions of ND_3 in cyclohexane receiving doses of 4.6×10^{19} ev gm^{-1} are also presented in Table (III-6) and included in Fig (III-12). Williams previously reported the yields of the isotopic forms of hydrogen from irradiated solutions of ND_3 in cyclohexane receiving doses of 4.1×10^{19} ev gm^{-1} (41). The percentages of HD in the hydrogen gas reported by Williams are lower than those obtained by interpolating between the results in Table (III-6) to the same concentrations of ND_3 that were used by him. These differences amount to about 15% of the HD yield. Furthermore, Williams' reported G values of total hydrogen are also lower than the present values by amounts as large as 0.3. Reasons for the discrepancies are not certain.

Table (III-7) gives the isotopic composition of the hydrogen gas produced from two irradiated solutions of NH_3 in c-C_6D_{12} (containing about 0.5% protium content) receiving doses of about 4.1×10^{19} ev gm^{-1} at a rate of 6.8×10^{19} ev (electron-mole)$^{-1}$ hr^{-1}. Two samples of c-C_6D_{12} without added NH_3 show considerable HD and H_2 yields averaging 12.6% and 1.20% of the total hydrogen yield respectively. Nash and Hamill (225) observed similar percentages for these isotopic hydrogen yields from irradiated c-C_6D_{12} having 99.6% isotopic purity with respect to deuterium content. The present total hydrogen yield is about 13% higher than they reported. These workers showed that the yields of H_2

TABLE III-7

Yields of the Isotopic Forms of Hydrogen from Irradiated $c\text{-}C_6D_{12} - NH_3$ Solutions

Sample	ϵ-Fraction NH_3	Mole fraction NH_3	$\%H_2$	%HD	G(hydrogen)	$G(H_2)$	G(HD)	Correction $G(H_2 + HD)_{obs}$ *	$\delta(H_2 + HD)$*
1	0	0	1.26	12.7	4.84	0.06	0.61	0	--
2	0	0	1.16	12.5	4.60	0.05	0.57	0	--
Average of 1 & 2	0	0	1.21	12.6	4.72	0.06	0.59	0	--
3	9.5×10^{-4}	4.5×10^{-3}	4.14	26.1	4.43	0.18	1.16	-0.59	0.75
4	2.1×10^{-3}	9.8×10^{-3}	4.80	28.6	4.39	0.21	1.26	-0.56	0.91

* Lower limits; see footnote on page 179

and HD result mainly from hydrogen atoms. For the samples of c-C_6D_{12} without added NH_3 the high yields of products containing protium indicate large isotope effects favoring H· atom formation and/or H· atom abstraction.

For the concentrations of NH_3 employed, the direct radiolysis of NH_3 is insignificant. Consequently no corrections on the values of $G(H_2 + HD)_{obs}$ are required. The increased values of $G(H_2 + HD)_{obs}$ for the NH_3 solutions show that reactivity transfer from the hydrocarbon to NH_3 occurs. However, the extent of reactivity transfer is not simply the difference between $G(H_2 + HD)_{obs}$ and $G(H_2 + HD)_o$, the sum of the H_2 and HD yields in the absence of NH_3. The correction to be applied to $G(H_2 + HD)_{obs}$ is the value of $G(H_2 + HD)_o$ modified to take into account the extent of reactivity transfer to the ammonia, ie the correction is

$$G(H_2 + HD)_o \left\{ 1 - \frac{G\begin{pmatrix}\text{scavenged}\\ \text{hydrogen}\\ \text{precursor}\end{pmatrix}}{G(\text{total hydrogen})} \right\} \qquad \text{(III-15)}$$

The results in Fig (III-13) for the c-C_6H_{12} - ND_3 solutions indicate that when the mole fractions of ND_3 are 5×10^{-3} and 1×10^{-2} the values of δ(HD) are about 0.50 and 0.68 respectively. These values of δ(HD) represent the lower limit for the extent of reactivity transfer from c-C_6H_{12} to ND_3 at the respective concentrations of ND_3*.

---

* In the discussion of these results in section IV-D it is demonstrated that an isotope effect occurs in the formation of the hydrogen precursors which ensures that δ(HD) represents only a lower limit to the extent of reactivity transfer in the c-C_6H_{12} - ND_3 solutions.

The values of $\delta(H_2 + HD)$ for the $c\text{-}C_6D_{12}$ - NH_3 solutions are greater than the values of $\delta(HD)$ for the $c\text{-}C_6H_{12}$ - ND_3 solution at equal concentrations of the two kinds of ammonia. This difference between the two systems is discussed later. It will be assumed that the extent of reactivity transfer is the same in the $c\text{-}C_6D_{12}$ - NH_3 and $c\text{-}C_6H_{12}$ - ND_3 systems. Thus an upper limit for the corrected value of $G(H_2 + HD)_o$ to be applied in the $c\text{-}C_6D_{12}$ - NH_3 system was obtained by equating $G\left|\begin{matrix}\text{scavenged}\\ \text{hydrogen}\\ \text{precursor}\end{matrix}\right|$ to $\delta(HD)$ for the $c\text{-}C_6H_{12}$ - ND_3 system at the same concentration of the two kinds of ammonia. The calculated corrections to be applied to the value of $G(H_2 + HD)_{obs}$ are given in Table III-7. Consequently a lower limit to the value of $\delta(H_2 + HD)$ which represents the extent of reactivity transfer in these solutions is given by

$$\delta(H_2 + HD) \geqslant G(H_2 + HD)_{obs} - G(H_2 + HD)_o \times \left(1 - \frac{\delta(HD)_{c\text{-}C_6H_{12} - ND_3}}{4.72}\right) \quad \text{(III-16)}$$

The lower limiting values of $\delta(H_2 + HD)$, calculated from Eqt (III-16) using the approximate value of $\delta(HD)_{c\text{-}C_6H_{12} - ND_3}$ for the concentrations of NH_3 employed, are given in Table III-7.

D. RADIOLYSIS OF CYCLOPENTANE - BENZENE MIXTURES

Cyclopentane solutions containing concentrations of benzene in the range 2.1×10^{-3} to 8.9×10^{-1} mole fraction were irradiated at approximately 22° C to doses of $2.1 \pm 0.1 \times 10^{20}$ ev gm^{-1}. The dose rate was $7.7 \pm 0.1 \times 10^{19}$ ev $(\epsilon\text{-mole})^{-1}$ hr^{-1}. Among the products measured were hydrogen, pentene-1, cyclopentene, and cyclopentylcyclopentane. Table III-8 gives the yields of these products for various $c\text{-}C_5H_{10}$ - C_6H_6 mixtures. In these mixtures the expected yield of a product which also occurs in the radiolysis of pure cyclopentane is calculated by Eqt (III-5). The observed yields of hydrogen, pentene-1, cyclopentene, and cyclopentylcyclopentane show a reduction from the expected values even for the lowest concentration of benzene employed. The values of $\delta(H_2)$, δ(pentene-1), δ(cyclopentene), and δ(cyclopentylcyclopentane), which are given in Table III-9, were calculated from the following relation:

$$\delta(X) = G(X)_{c\text{-}C_5H_{10}} - \frac{\left[G(X)_{obs} - \epsilon_{C_6H_6} G(X)_{C_6H_6}\right]}{\epsilon_{c\text{-}C_5H_{10}}} \qquad \text{(III-17)}$$

where X represents a cyclopentane radiolysis product in the irradiated mixture. Hydrogen is the only product that results from both benzene and cyclopentane as pure components. $G(H_2)_{C_6H_6}$ the hydrogen yield from pure benzene, was found to be 0.04 at a dose of 2.0×10^{20} ev gm^{-1}. Values of $\delta(H_2)$ are shown in Fig III-14. Values of δ(pentene-1), δ(cyclo-

TABLE III-8

Some Product Yields from Irradiated Cyclopentane - Benzene Mixtures

Electron fraction benzene	Mole fraction benzene	$G(H_2)$	$G(c\text{-}C_5H_8)$ [a]	G(cyclopentylcyclopentane) [b]	G(pentene-1) [a]	G(cyclopentylcyclohexadienes) [c]	G(cyclopentylbenzene) [c]
2.2×10^{-3}	2.1×10^{-3}	--	--	1.06	--	--	0.02
3.9×10^{-3}	3.7×10^{-3}	--	--	1.05	--	0.01	0.04
6.5×10^{-3}	6.2×10^{-3}	4.61	2.54	--	0.77	--	--
8.1×10^{-3}	7.7×10^{-3}	--	--	0.91	--	0.02	0.05
1.1×10^{-2}	1.0×10^{-2}	4.38	2.30	0.80	0.72	0.02	0.05
1.8×10^{-2}	1.7×10^{-2}	3.97	1.97	0.72	0.65	0.03	0.06
3.9×10^{-2}	3.7×10^{-2}	3.43	1.68	0.47	0.60	0.05	0.07
6.1×10^{-2}	5.8×10^{-2}	2.92[d]	1.44	0.36	0.54	--	--
8.0×10^{-2}	7.7×10^{-2}	--	--	0.33	--	0.11	0.11
1.0×10^{-1}	9.6×10^{-2}	2.37	1.21	0.30	0.46	0.12	0.12
1.6×10^{-1}	1.6×10^{-1}	1.78	0.88	--	0.39	0.16	0.15
2.2×10^{-1}	2.1×10^{-1}	1.36	0.62	0.12	0.32	0.12	0.11
2.9×10^{-1}	2.8×10^{-1}	1.02	0.48	0.07	0.26	0.10	0.09
4.5×10^{-1}	4.3×10^{-1}	0.61	0.28	0.02	0.20	0.08	0.08
5.1×10^{-1}	5.0×10^{-1}	--	--	--	--	0.07	0.06
5.8×10^{-1}	5.7×10^{-1}	0.37	0.18	0.01	0.13	0.07	0.05
6.9×10^{-1}	6.8×10^{-1}	--	--	0.00	--	0.05	0.04
7.8×10^{-1}	7.8×10^{-1}	0.16	0.08	0.00	0.07	0.02	0.03
8.9×10^{-1}	8.9×10^{-1}	--	--	--	--	0.01	0.01
1.00	1.00	0.04	--	--	--	--	--

[a] Analysed on the squalane column without conversion to methane

[b] Analysed on the "Tris" column with conversion to methane

[c] Analysed on the Ucon column with conversion to methane

[d] This result assumes $G(CH_4) = 0.03$

Doses are in the range of 1.9×10^{20} to 2.0×10^{20} ev gm^{-1}; the dose rate is $7.72 \pm 0.04 \times 10^{19}$ ev (ϵ-mole)$^{-1}$ hr^{-1}.

TABLE III-9

Differential Yields of Cyclopentane Products from Irradiated Cyclopentane - Benzene Mixtures

Mole fraction benzene	Electron fraction cyclo-pentane	$\epsilon_B G(H_2)_B$ *	$\frac{G(H_2)_{obs} - \epsilon_B G(H_2)_B}{\epsilon_{c\text{-}C_5H_{10}}}$	$\delta(H_2)$ a	$\delta(c\text{-}C_5H_8)$ b	δ(cyclo-pentyl-cyclo-pentane) c	δ(pent-ene-1) d
2.1×10^{-3}	1.00	--	--	--	--	0.23	--
3.7×10^{-3}	1.00	--	--	--	--	0.24	--
6.2×10^{-3}	0.99	0.00	4.65	0.74	0.43	--	--
7.7×10^{-3}	0.99	--	--	--	--	0.38	--
1.0×10^{-2}	0.99	0.00	4.44	0.93	0.64	0.48	0.01
1.7×10^{-2}	0.98	0.00	4.04	1.31	0.96	0.55	0.08
3.7×10^{-2}	0.96	0.00	3.57	1.78	1.22	0.81	0.11
5.8×10^{-2}	0.94	0.00	3.10	2.25	1.44	0.91	0.16
7.7×10^{-2}	0.92	--	--	--	--	0.93	--
9.6×10^{-2}	0.90	0.00	2.64	2.71	1.62	0.96	0.23
1.6×10^{-1}	0.84	0.01	2.10	3.25	1.92	--	0.27
2.1×10^{-1}	0.78	0.01	1.73	3.62	2.18	1.1	0.33
2.8×10^{-1}	0.71	0.01	1.43	3.92	2.29	1.2	0.37
4.3×10^{-1}	0.55	0.02	1.06	4.29	2.5	1.2	0.40
5.7×10^{-1}	0.42	0.02	0.84	4.52	2.6	1.3	0.43
6.8×10^{-1}	0.31	--	--	--	--	1.3	--
7.8×10^{-1}	0.22	0.03	0.60	4.76	2.6	1.3	0.43
8.9×10^{-1}	0.11	--	--	--	--	--	--
1.00	0.00	0.04	--	--	--	--	--

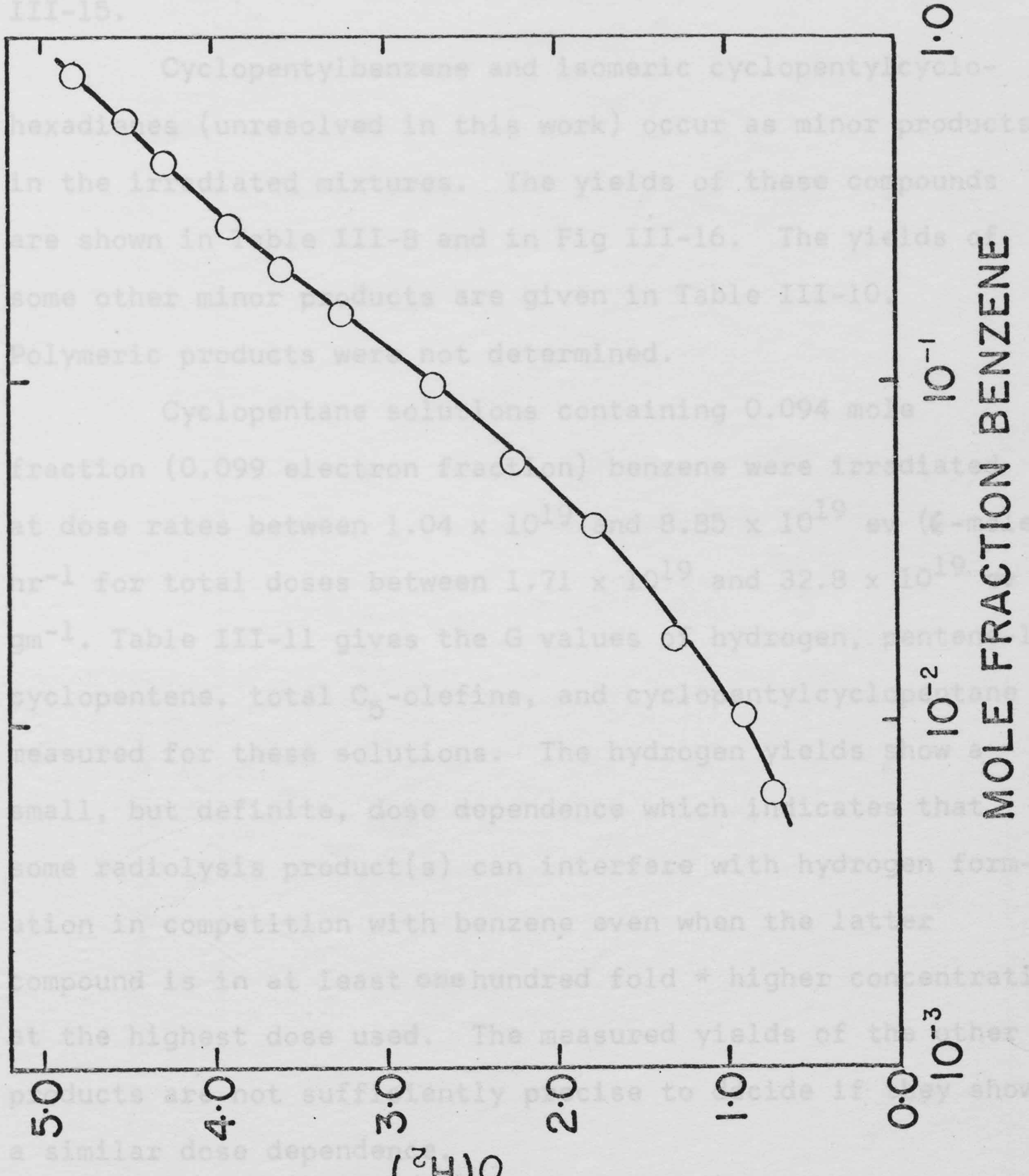
a $G(H_2)_{c\text{-}C_5H_{10}}$ is assumed to be 5.35, the initial H_2 yield in pure cyclopentane
b $G(c\text{-}C_5H_8)$ is assumed to be 2.96, the initial yield of $c\text{-}C_5H_8$ in pure cyclopentane
c G(cyclopentylcyclopentane) is assumed to be 1.29, the initial yield in pure $c\text{-}C_5H_{10}$
d G(pentene-1) is assumed to be 0.74, the initial yield in pure $c\text{-}C_5H_{10}$
* B represents benzene.

FIGURE III-14

Values of $\delta(H_2)$ for Cyclopentane - Benzene Mixtures pentene), and δ(cyclopentylcyclopentane) are shown in Fig III-15.

Cyclopentylbenzene and isomeric cyclopentylcyclohexadienes (unresolved in this work) occur as minor products in the irradiated mixtures. The yields of these compounds are shown in Table III-8 and in Fig III-16. The yields of some other minor products are given in Table III-10. Polymeric products were not determined.

Cyclopentane solutions containing 0.094 mole fraction (0.099 electron fraction) benzene were irradiated at dose rates between 1.04 x 10^{19} and 8.85 x 10^{19} ev (e-mole)$^{-1}$ hr^{-1} for total doses between 1.71 x 10^{19} and 32.8 x 10^{19} ev gm^{-1}. Table III-11 gives the G values of hydrogen, pentene-1, cyclopentene, total C_5-olefins, and cyclopentylcyclopentane measured for these solutions. The hydrogen yields show a small, but definite, dose dependence which indicates that some radiolysis product(s) can interfere with hydrogen formation in competition with benzene even when the latter compound is in at least one hundred fold * higher concentration at the highest dose used. The measured yields of the other products are not sufficiently precise to decide if they show a similar dose dependence.



Cyclopentane solutions containing 0.094 mole fraction benzene were irradiated to total doses between 2.6 x 10^{19} and

---

* This value assumes the G value for the radiolytically produced inhibitor is three.

pentene), and δ(cyclopentylcyclopentane) are shown in Fig III-15.

Cyclopentylbenzene and isomeric cyclopentylcyclohexadienes (unresolved in this work) occur as minor products in the irradiated mixtures. The yields of these compounds are shown in Table III-8 and in Fig III-16. The yields of some other minor products are given in Table III-10. Polymeric products were not determined.

Cyclopentane solutions containing 0.094 mole fraction (0.099 electron fraction) benzene were irradiated at dose rates between 1.04×10^{19} and 8.85×10^{19} ev (ϵ-mole)$^{-1}$ hr^{-1} for total doses between 1.71×10^{19} and 32.8×10^{19} ev gm^{-1}. Table III-11 gives the G values of hydrogen, pentene-1, cyclopentene, total C_5-olefins, and cyclopentylcyclopentane measured for these solutions. The hydrogen yields show a small, but definite, dose dependence which indicates that some radiolysis product(s) can interfere with hydrogen formation in competition with benzene even when the latter compound is in at least one hundred fold * higher concentration at the highest dose used. The measured yields of the other products are not sufficiently precise to decide if they show a similar dose dependence.

Cyclopentane solutions containing 0.094 mole fraction benzene were irradiated to total doses between 2.6×10^{19} and

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* This value assumes the G value for the radiolytically produced inhibitor is three.

FIGURE III-15

Values of δ(Pentene-1), δ(Cyclopentene) and δ(Cyclopentylcyclopentane) for Cyclopentane - Benzene Mixtures

A. ○ $\delta(H_2)$

B. □ δ(Pentene-1)

○ δ(Cyclopentylcyclopentane)

△ δ(Cyclopentene)

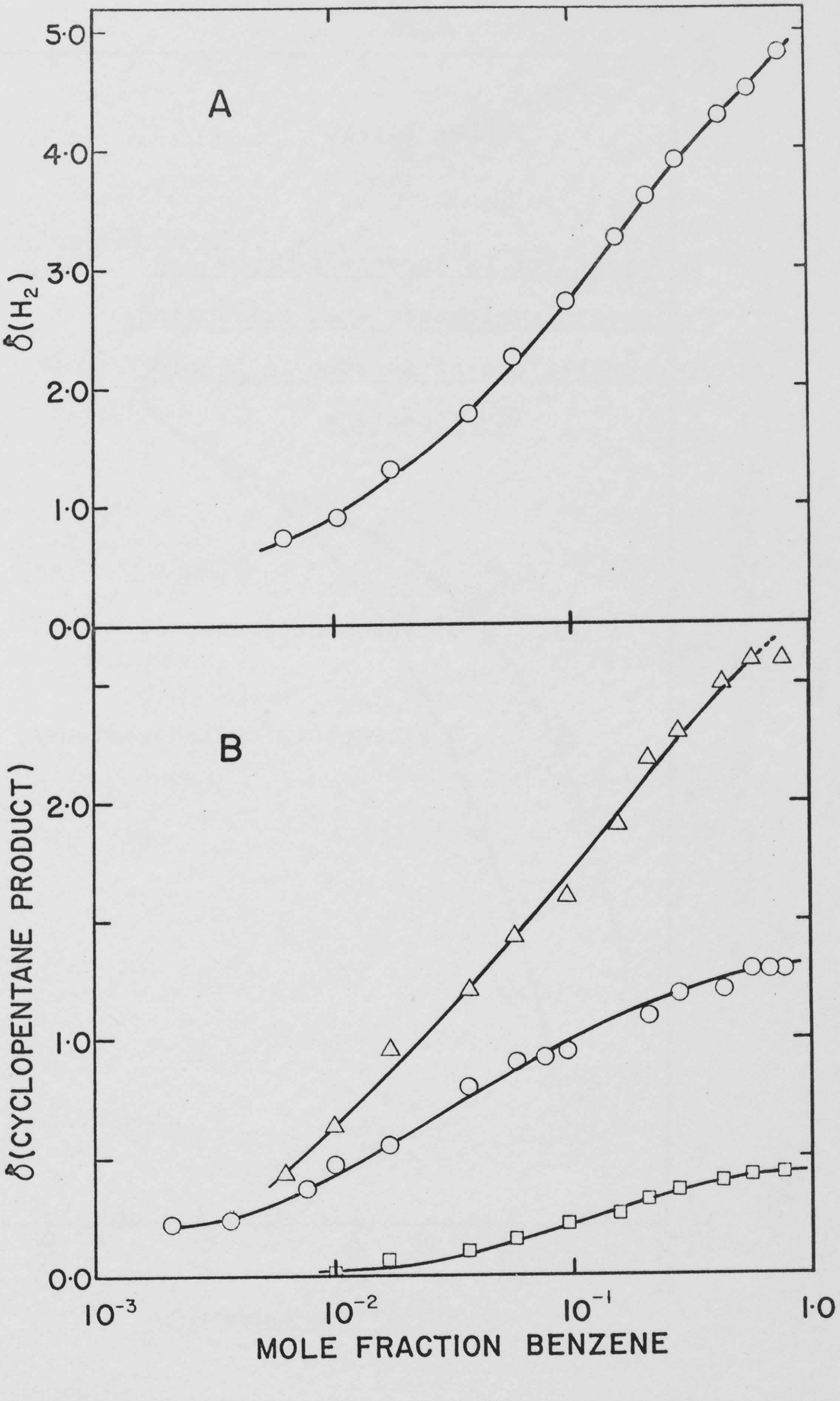

A
B
5·0
4·0
3·0
2·0
1·0
0·0
δ(H₂)
2·0
1·0
0·0
δ(CYCLOPENTANE PRODUCT)
10⁻³
10⁻²
10⁻¹
1·0
MOLE FRACTION BENZENE

FIGURE III-16

G Values for Cyclopentylbenzene and Cyclopentylcyclohexadienes for Various Concentrations of Benzene in Liquid Cyclopentane

○ G(cyclopentylbenzene)

△ G(cyclopentylcyclohexadienes)

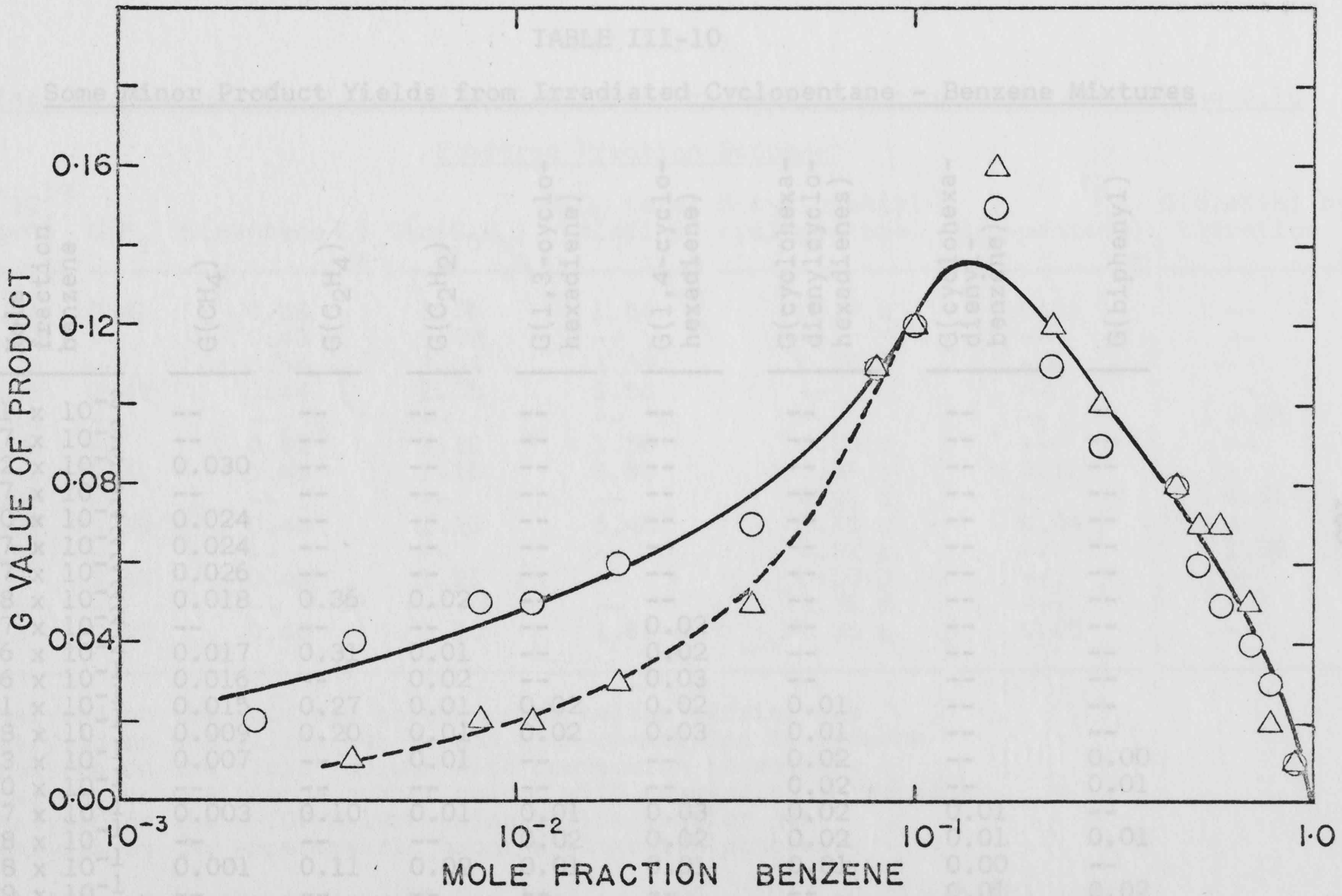

G VALUE OF PRODUCT
0·00
0·04
0·08
0·12
0·16
MOLE FRACTION BENZENE
10^{-3}
10^{-2}
10^{-1}
1·0

TABLE III-10

Some Minor Product Yields from Irradiated Cyclopentane - Benzene Mixtures

Mole fraction benzene	G(CH_4)	G(C_2H_4)	G(C_2H_2)	G(1,3-cyclohexadiene)	G(1,4-cyclohexadiene)	G(cyclohexadienylcyclohexadienes)	G(cyclohexadienylbenzene)	G(biphenyl)
2.1×10^{-3}	--	--	--	--	--	--	--	--
3.7×10^{-3}	--	--	--	--	--	--	--	--
6.2×10^{-3}	0.030	--	--	--	--	--	--	--
7.7×10^{-3}	--	--	--	--	--	--	--	--
1.0×10^{-2}	0.024	--	--	--	--	--	--	--
1.7×10^{-2}	0.024	--	--	--	--	--	--	--
3.7×10^{-2}	0.026	--	--	--	--	--	--	--
5.8×10^{-2}	0.018	0.36	0.02	--	--	--	--	--
7.7×10^{-2}	--	--	--	--	0.02	--	--	--
9.6×10^{-2}	0.017	0.31	0.01	--	0.02	--	--	--
1.6×10^{-1}	0.016	--	0.02	--	0.03	--	--	--
2.1×10^{-1}	0.015	0.27	0.01	0.02	0.02	0.01	--	--
2.8×10^{-1}	0.009	0.20	0.01	0.02	0.03	0.01	--	--
4.3×10^{-1}	0.007	--	0.01	--	--	0.02	--	0.00
5.0×10^{-1}	--	--	--	--	--	0.02	--	0.01
5.7×10^{-1}	0.003	0.10	0.01	0.01	0.03	0.02	0.01	--
6.8×10^{-1}	--	--	--	0.02	0.02	0.02	0.01	0.01
7.8×10^{-1}	0.001	0.11	0.02	0.01	0.01	0.01	0.00	--
8.9×10^{-1}	--	--	--	--	--	--	0.01	0.02
1.00	--	--	--	--	--	--	0.02	0.03

a Analysed on silica gel column with conversion to methane
b Analysed on Ucon column with conversion to methane

TABLE III-11

Effect of Dose on the Yields of Cyclopentane Products in Cyclopentane Containing 0.10 Electron Fraction Benzene

Dose 10^{19} ev gm^{-1}	$G(H_2)$	G(pentene-1) a	$G(c\text{-}C_5H_8)$ a	$G(C_5$ total olefin) b	G(cyclopentyl-cyclopentane)	G(n-pentane) e	G(olefin) by titration f
1.71	2.41	0.38	1.05	1.54	0.39 c	0.11	--
2.60	--	0.40	1.09	--	--	--	--
2.72	--	0.54	1.04	1.59	0.35 c	--	--
2.95	2.42	0.44	1.05	1.56	--	--	--
3.00	--	--	--	--	--	--	2.54
3.04	--	0.52	1.10	1.56	0.36 c	--	--
3.42	2.41	0.43	1.15	1.65	0.39 c	0.11	--
5.98	--	--	--	--	0.42 d	--	2.51
7.95	2.39	0.40	1.13	1.40	0.33 c	0.04	--
17.9	--	--	--	--	0.32 c	--	1.88
20.0	2.37	0.46	1.21	--	0.30 c	--	--
30.6	--	--	--	--	0.32 d	--	--
32.8	2.32	0.40	1.10	1.61	0.35 c	0.05	--

a Analysed on the squalane column using helium carrier gas
b Analysed on the silica gel column with conversion to methane
c Analysed on the "Tris" column with conversion to methane
d Analysed on a silicone rubber column with conversion to methane
e Analysed on the o-TCP column using helium carrier gas
f Analysed by the amperometric bromine titration procedure

Dose rates are in the range of 1.0×10^{19} to 8.85×10^{19} ev $(\epsilon\text{-mole})^{-1}$ hr^{-1}.

3.6 x 10^{19} ev gm^{-1} at dose rates varying between 8.85 x 10^{16} and 8.65 x 10^{19} ev (ϵ-mole)$^{-1}$ hr^{-1}. Table III-12 gives the yield of hydrogen, pentene-1, cyclopentene, and cyclopentylcyclopentane under these conditions. No significant effect of dose rate occurs for the hydrogen yields. G(cyclopentene) in these solutions show a small dose rate effect. A more substantial dose rate effect is apparent for the yields of cyclopentylcyclopentane; the G value of this product is only about 70% as large at a dose rate of 8.8 x 10^{16} ev (ϵ-mole)$^{-1}$ hr^{-1} when samples receive a total dose of about 3 x 10^{19} ev gm^{-1}.

TABLE III-12

Effect of Dose Rate on the Yields of Cyclopentane Products in Cyclopentane Containing 0.10 Electron Fraction of Benzene

Dose rate 10^{16} ev (ϵ-mole)$^{-1}$ hr^{-1}	Dose 10^{19} ev gm^{-1}	$G(H_2)$	$G(CH_4)$ a	$G(C_2H_6)$ b	$G(C_2H_4)$ b	G(pent-ene-1) c	$G(c\text{-}C_5H_8)$ c	$G(C_5$-olefin) b	G(cyclo-pentyl-cyclo-pentane) d
8.85	2.76	2.39	0.026	0.012	0.30	0.39	0.98	1.36	0.25
24.8	3.64	--	--	--	--	0.43	1.08	1.63	0.31
1040	2.60	--	--	--	--	0.40	1.09	--	0.31
8650	2.95	2.42	0.030	--	--	0.44	1.10	1.56	0.36

a Analysed on charcoal column with He carrier gas

b Analysed on Silica gel column with conversion to methane

c Analysed on squalane column with He carrier gas

d Analysed on "Tris" column with conversion to methane

DISCUSSION

A. PURE LIQUID CYCLOPENTANE

1. General

Table IV-1 summarizes the "zero dose" yields of several radioysis products obtained in this study as well as many results in the literature. Product yields obtained in the present work agree well with the results of Hughes and Hanrahan (183). Poor agreement exists for the most part with Lepley's results (177), the only other extensive study of liquid cyclopentane. Two possible reasons exist for the discordance with Lepley's results. In the first place, although Lepley used "gas chromatographically pure" cyclopentane, apparently no final purification was made before irradiation to remove possible traces of o-TCP stripped off the gas chromatograph column. Secondly, the lowest doses used in the work exceeded 3 x 10^{20}ev gm^{-1}.

Lepley measured several minor products having molecular weights between cyclopentane and cyclopentylcyclopentane. Hughes and Hanrahan claim that these minor products do not occur at their low doses (From reference(183) these doses appear to be greater than 7 x 10^{19}ev gm^{-1} for liquid product analyses.) and ascribe their presence in Lepley's work to secondary reactions at the high doses employed. The current work

TABLE IV-1

PRODUCT YIELDS FROM IRRADIATED LIQUID CYCLOPENTANE[1]

Product	This work a	Hughes & Hanrahan (183) a	Lepley (177) b	Hardwick (148) a	Muccini Schuler (89) c	Holroyd (103, 79,80)d	Stone (93) e	Yang & Marcus (92) f	Toma & Hamill (182)g
Hydrogen	5.35	5.20	3.77[j]	5.78		5.2	4.97	5.8	5.25
Methane	0.03	0.04	1.50						
Ethylene	0.45	0.40	1.10						
Ethane	0.03	0.08							
Propylene	0.28	0.16	0.48						
Propane	0.08	0.08	0.18						
Cyclopropane	0.12	0.10	0.13						
C_4	<0.01	trace							
n-Pentane	0.14	0.16	0.12						
Pentene-1	0.74	0.62	0.58	4.24					
Cyclopentene	2.97	3.10	0.87			3.4	3.0	3.0	2.92
Allylcyclopentane	0.08								
n-Pentylcyclopentane	0.06								

TABLE IV-1 (continued)

Product	This work a	Hughes & Hanrahan (183) a	Lepley (177) b	Hardwick (148) a	Muccini Schuler (89) c	Holroyd (103, 79,80)d	Stone (93) e	Yang & Marcus (92) f	Toma & Hamill (182)g
Cyclopentyl-cyclopentane	1.29	1.22	1.51		1.00	1.1	1.3	1.25	
3-Cyclopentyl-cyclopentene	0.11								
Polymer	0.7								
Total hydrocarbon radical yield				3.4		4.5 h			
Cyclopentyl radical					2.6	4.1 h			
Hydrogen atom				3.06		1.8±0.4 i			

a Zero dose value

b Dose of 3.1×10^{20} ev gm^{-1}

c Dose of about 3×10^{20} ev gm^{-1}

d Dose of about 3×10^{19} ev gm^{-1}; 28° C

e Dose of about 4×10^{19} ev gm^{-1}

f Dose of about 2×10^{20} ev gm^{-1}

TABLE IV-1 (continued)

g Dose of about 8 x 10^{19} ev gm^{-1}

h Dose of about 2 x 10^{20} ev gm^{-1}; alkyl radicals only; 10° C

i Doses of 2 x 10^{19} to 4 x 10^{19} ev ml^{-1}

j Dose of about 2 x 10^{21} ev gm^{-1}

k The yield of polymer is given in terms of the G value of cyclopentane converted to polymer, ie, $G(-c\text{-}C_5H_{10})_{polymer}$

l All numbers in this table are G values supports Lepley's suggestion that these compounds occur as primary radiolysis products. Yields of 3-cyclopentylcyclopentene, n-pentylcyclopentane, and allylcyclopentane were determined at lower doses than those used by Hughes and Hanrahan. That such compounds are to be expected is indicated by the results of Holroyd and Klein (179) on the primary radical yields in irradiated liquid cyclopentane. Their measured yields of some radicals, G(3-cyclopentenyl) = 0.17, and G(n-pentyl) = 0.14, are sufficiently large that if these radicals only combine with cyclopentyl radicals, higher yields of the products in question would result than the yields observed.

Holroyd (103) reports a relatively high value for the yield of cyclopentene, $G(c\text{-}C_5H_8) = 3.4$. This result was obtained from gas chromatograph analyses on a silica gel column. Experience with this column indicates that pentene-1 is usually poorly resolved, if at all, from cyclopentene.

2. Products from Ring Opening and Fragmentation of Cyclopentane

Decomposition of vibrationally and/or electronically excited cyclopentane molecules and ions produces reactive intermediates that are precursors to ring-opened C_5 and fragmentation products. Methane results mainly from methyl radicals, since Kuntz and Schuler (120) measured $G(CH_3\cdot)$ in liquid cyclopentane radiolysis to be 0.019. The mechanism of formation of other fragmentation products is not known with any certainty. Ethane and propane may result in part from H_2^--transfer reactions of ethylene ions and propylene ions with cyclopentane:

$$C_2H_4^+ + c\text{-}C_5H_{10} \longrightarrow C_2H_6 + c\text{-}C_5H_8^+ \qquad [IV\text{-}1]$$

$$\Delta H_r^o = -28 \text{ kcal mole}^{-1}$$

$$C_3H_6^+ + c\text{-}C_5H_{10} \longrightarrow C_3H_8 + c\text{-}C_5H_8^+ \qquad [IV\text{-}2]$$

$$\Delta H_r^o = -20 \text{ kcal mole}^{-1}$$

A $C_3H_6^+$ ion is the most abundant ion in the conventional mass spectrum of cyclopentane. This ion may be produced in the liquid phase radiolysis as well, although its formation from ground state cyclopentane ion is endothermic by at least 18 kcal mole^{-1}.

Pentamethylene diradical can be produced on ring cleavage of excited cyclopentane. Pentene-1 can be partly produced by isomerization of this diradical:

$$\cdot CH_2(CH_2)_3CH_2\cdot \longrightarrow CH_2{=}CH(CH_2)_2CH_3 \qquad [IV\text{-}3]$$

The yield of the diradical is not known.

A material balance for fragmentation products requires that the total yield of C_2 products equals

G(C_3 products) + 2 G(CH_4). Since G(C_2H_4) + G(C_2H_6) + G(ethylcyclopentane) $\approx$ 0.53, and G(c-C_3H_6) + G(C_3H_8) + G(allylcyclopentane) + 2 G(CH_4) $\approx$ 0.62 the material balance for fragmentation products is satisfactory.

3. Cyclopentene, Cyclopentylcyclopentane, and Polymer

Some excited cyclopentane molecules, formed directly or upon ion-electron recombination, undergo C-H bond cleavage to generate cyclopentyl radicals and hydrogen atoms (possibly "hot"). ESR spectroscopy gives direct proof for the presence of cyclopentyl radicals in irradiated cyclopentane (66). The ratio of rate constants for disproportionation (k_d) and combination (k_c) of cyclopentyl radicals in liquid cyclopentane is not known; $\frac{k_d}{k_c}$ in vapor phase c-C_5H_{10} is 1.0 at 300° K (67). This vapor phase value of $\frac{k_d}{k_c}$ will be used for the liquid phase reactions. This choice is not unreasonable because the ratio $\frac{k_d}{k_c}$ for cyclohexyl radicals in liquid cyclohexane at 296° K is 1.1 (226).

Holroyd and Klein (179) give G(cyclopentyl) = 4.1 for the yield of cyclopentyl radical <u>outside of spurs</u> in liquid cyclopentane receiving a dose of 2×10^{20} ev gm^{-1}. A small portion of this yield is consumed in forming allylcyclopentane (0.1)*, n-pentylcyclopentane (0.1), and 3-cyclopentylcyclopentene (0.2). An unknown fraction of the cyclopentyl radicals are consumed in polymer formation

---

* Numbers in parentheses are G values for consumed cyclopentyl radicals. Disproportionation reactions accompanying the combination reactions are crudely taken into account by multiplying the yield of the combination product by 1.5 to obtain the consumption of cyclopentyl radical.

but this is believed to be small. The G value for cyclopentyl radicals that are available for disproportionation and combination <u>among themselves</u> is about (4.1 - 0.3) or 3.8. A fraction α of these combine where

$$\alpha = \frac{1}{1 + \frac{k_d}{k_c}} = \frac{1}{2.0} = 0.50 \qquad \text{(IV-1)}$$

The yield of cyclopentylcyclopentane resulting from radical combination outside of spurs is $\frac{1}{2}$x0.50x 3.8 or about 1.0. The G value of cyclopentylcyclopentane produced by processes other than combination of cyclopentyl radicals outside of spurs is

$$G(\text{cyclopentylcyclopentane})_{\text{total}} - 1 = 0.3$$

Stone (93) observed a residual yield of cyclopentylcyclopentane in cyclopentane containing 0.0038 molar iodine as a radical scavenger. A limiting G(cyclopentylcyclopentane) of 0.17 was found in these fully scavenged solutions at doses of about 4 x 10^{19} ev gm^{-1}. The cause of the discrepancy between the observed limit of 0.17 and the estimated value 0.3 is not known; some possible reasons for it are:

1) The experimental result of Holroyd and Klein, and that of Stone were not obtained at the same dose. Consistent results require that all information on yields be obtained at the same dose; preferably "zero" dose.

2) $\frac{k_d}{k_c}$ for cyclopentyl radicals in liquid cyclopentane at 300° K may be less than 1.0. If $\frac{k_d}{k_c}$ were

0.70 no discrepancy would exist, other factors remaining the same.

3) G(cyclopentyl) may be greater than 4.1. No discrepancy would exist if G(cyclopentyl) were 4.8, other factors remaining the same.

4) Iodine may inhibit some non-radical processes normally contributing to the residual yield.

An observed residual yield of the dimer in scavenger studies may be attributed to the combination of radicals initially produced in the same spur (radical pair dimerization) (227) or to ion - molecule reactions (direct dimerization) (73). Intermolecular insertion of cyclopentane carbene could, in principle, produce the dimer. However, this carbene converts quantitatively by an intramolecular reaction to cyclopentene (228). Moreover, the yield of carbenoid intermediates in cycloalkane radiolysis is probably less than 0.1 (Appendix C).

The yield of cyclopentene from the mutual disproportionation of radicals outside of spurs is $\frac{1}{2}$ of 0.50 x 3.8 or about 1.0. Cyclopentene is also generated in disproportionation reactions which parallel the combination reactions which produce, for example, allylcyclopentane, n-pentylcyclopentane, and 3-cyclopentylcyclopentene. Radical - radical reactions involving allyl radical favor combination over disproportionation (229); a negligible amount of cyclopentene is assumed to result from the disproportionation reactions between cyclopentyl and allyl radicals. G(3-cyclopentenyl) in liquid cyclopentane is 0.17 (179). Since the yield of 3-cyclopentylcyclopentene is 0.11 the remaining amount of the 3-cyclopentenyl radicals, 0.06, disproportionates with cyclopentyl radicals to give an additional cyclopentene yield of 0.12 (cyclopentadiene was not an observed product). G(n-pentyl) in liquid cyclopentane is said to be 0.14 (179). Approximately half these n-pentyl radicals form n-pentylcyclopentane; the remainder could generate a maximum cyclopentene yield of 0.07 through radical disproportionations. Summing these yields of cyclopentene from radical sources outside the spurs gives G(cyclopentene) as (0.2 + 1.0). By difference, disproportionation of radical pairs in the spurs such as reactions [IV-4] and [IV-5],

$$[\text{c-C}_5\text{H}_9^{\cdot} + \text{H}\cdot] \longrightarrow \text{c-C}_5\text{H}_8 + \text{H}_2 \qquad [\text{IV-4}]$$

$$[\text{c-C}_5\text{H}_9^{\cdot} + \text{c-C}_5\text{H}_9^{\cdot}] \longrightarrow \text{c-C}_5\text{H}_8 + \text{c-C}_5\text{H}_{10} \qquad [\text{IV-5}]$$

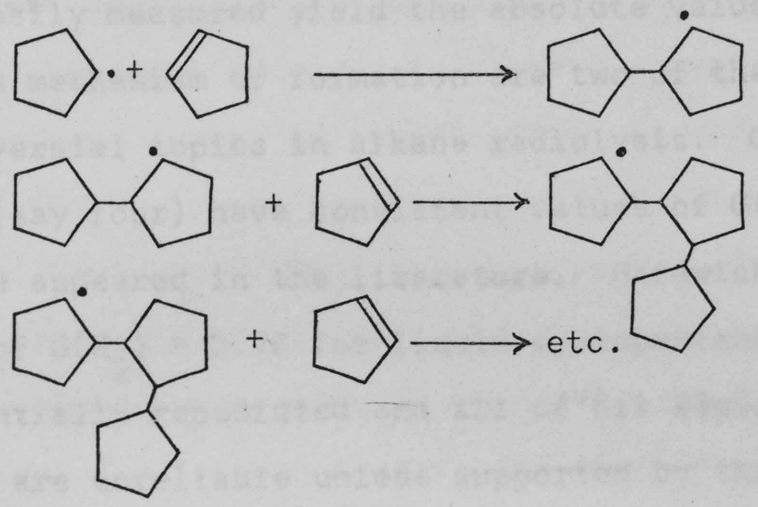
and non-radical reactions such as [IV-6] and [IV-7],

$$\text{c-C}_5\text{H}_{10}^{+} + e^{-} \longrightarrow \text{c-C}_5\text{H}_8 + \text{H}_2 \text{ (or 2 H}\cdot) \qquad [\text{IV-6}]$$

$$\text{c-C}_5\text{H}_{10}^{*} \longrightarrow \text{c-C}_5\text{H}_8 + \text{H}_2 \text{ (or 2 H}\cdot) \qquad [\text{IV-7}]$$

gives G(cyclopentene) from non-radical processes and the reaction of cyclopentyl radicals in spurs is (3.0 - 1.2) = 1.8. $\text{c-C}_5\text{H}_{10}^{*}$ is assumed to be an excited molecule produced directly from fast electrons in the radiolysis. As noted previously, cyclopentane carbene isomerizes to cyclopentene but the carbene is present in negligible amounts.

The mechanism of polymer formation is unknown at this time. Reactions of cyclopentyl radicals with cyclopentene, generated during the radiolysis, to produce polymer would be dose dependent at low doses, its yield increasing with dose.



[IV-8a]

[IV-8b]

[IV-8c]

The radical addition scheme [IV-8a, b, etc.] with the additional polymer termination reactions of combination and disproportionation with cyclopentyl radicals would produce a distribution of polymers having progressively smaller contributions from larger polymers. Such a distribution does not occur. Lower yields of trimer occur than of higher polymers. The dose independent yield of the substituted conjugated olefin component in the polymer conflicts with the radical chain mechanism for its formation. Ionic polymerization was suggested for the formation, in methane, of dose independent yields of products containing up to twenty carbon atoms (230,231). The yield of the cyclopentane polymer is not satisfactorily known over a wide enough dose range nor is the material sufficiently characterized to speculate further on the mechanism of its formation.

4. Hydrogen and the Hydrogen Material Balance

Although hydrogen occurs with the largest and most easily measured yield the absolute value of this yield and its mechanism of formation are two of the most controversial topics in alkane radiolysis. Only within recent years (say four) have consistent values of $G(H_2)$ for cyclopentane appeared in the literature. Hardwick's early high value of $G(H_2) = 5.78$ for liquid cyclopentane has been substantially repudiated and all of his reported $G(H_2)$ values are unreliable unless supported by the results of several more recent workers.

A variety of intermediates and mechanisms are believed to produce the final observed hydrogen yield. Some of these are:

a) thermal hydrogen atoms,

b) hot hydrogen atoms,

and c) directly produced molecular hydrogen.

Ion recombination in pure cyclopentane can produce all of these kinds of hydrogen sources. One aspect of this work is a study of the contribution that ions make as precursors for these hydrogen sources. Further discussion of this contribution is delayed until a model of ion scavenging is developed in Section IV-B-1.

Some of the stable radiolysis products have the same relative hydrogen content as cyclopentane, which has an empirical formula CH_2. Others are either relatively hydrogen deficient or else contain a greater percentage of hydrogen than does cyclopentane. For each product there is a G value, denoted Equivalent $G(H_2)$, which expresses the yield of hydrogen required to convert a hypothetical compound with the same number of carbon atoms, x, and an empirical formula $(CH_2)_x$ to the observed yield of product. For example, Equivalent $G(H_2)$ for cyclopentene is -1 times G(cyclopentene). Table IV-2 gives the Equivalent $G(H_2)$ for all the significant products measured. Products having Equivalent $G(H_2)$ equal to zero are omitted from Table IV-2. The Equivalent $G(H_2)$ of a homogeneous polymer, consisting of n $(-C_5H_8-)$ residues linked in a linear array and terminated by cyclopentyl groups is

$$\text{Equivalent } G(H_2)_{\text{polymer}} = -\frac{n+1}{n+2} G(-c\text{-}C_5H_{10})_{\text{polymer}} \qquad \text{(IV-2)}$$

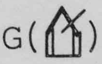
where $G(-c\text{-}C_5H_{10})_{\text{polymer}}$ is the G value for cyclopentane being converted to polymer. $G(-c\text{-}C_5H_{10})_{\text{polymer}}$ is about 0.7. For the polymer obtained from liquid cyclopentane a suitable value of n is four which gives Equivalent $G(H_2)_{\text{polymer}} = -0.6$. However, the ultraviolet absorption spectrum of the polymer shows that an additional hydrogen deficiency occurs in this material. Since G() is about 0.06 the Equivalent $G(H_2)_{\text{polymer}}$ is reduced further by 2(0.06) or 0.12, bringing the total value to about -0.7 for the polymer.

TABLE IV-2

Equivalent $G(H_2)$ for the Radiolysis Products

PRODUCT	EQUIVALENT $G(H_2)$
Hydrogen	5.35
Methane	0.03
Ethane	0.03
Propane	0.08
n-Pentane	0.14
Cyclopentene	-2.97
Allylcyclopentane	-0.08
Cyclopentylcyclopentane	-1.29
3-Cyclopentylcyclopentene	-0.22
Polymer	-0.7
SUM	+0.4

A hydrogen material balance requires that the sum of the Equivalent $G(H_2)$ for all radiolysis products be zero. This sum, given in Table IV-2, indicates that products deficient in hydrogen and having a combined Equivalent $G(H_2)$ of about -0.4 appear to be unaccounted for. However, it is not known if this deficiency results from the occurrence of undetected products or from a lack of sufficient accuracy in determining the measured product yields.

B. KINETIC MODELS FOR CHEMICAL SCAVENGING IN THE LIQUID PHASE

In this section two models are developed for treating the chemical effects of the various additives used in irradiated liquid cyclopentane. These moldels are tested in the subsequent sections of this chapter.

1. A Kinetic Model for the Scavenging of Ionic Intermediates Produced in Pairs

The passage of ionizing radiation through a sample leaves regions of deposited energy along the wakes of energetic electrons set in motion by the incident radiation. These regions are inhomogeneously distributed in the bulk of the sample and have higher concentrations of reactive species than if these same species were distributed homogeneously. These regions or "spurs" are generally isolated from each other for radiations of low linear energy transfer (LET) such as the ^{60}Co gamma radiation used in this work. The deposited energy lies in molecules of increased thermal energy and in reactive intermediates consisting of ion pairs, neutral radicals, and electronically excited molecules. The subsequent discussion in this section will be concerned with ion scavenging. Although spurs having more than one ion pair certainly occur (232) the interaction between counter ions is taken pairwise; higher order interactions will be ignored.

Some compounds, for example ND_3, when added in small amounts to cyclopentane, interfere with the composition and yields of radiolytic products even when they apparently do not enter normal atom and radical processes. This suggests that the chemical effects of such additives may occur via reactions with ionic intermediates. A simple diffusion model for the scavenging of charged intermediates interacting pairwise will now be developed on the basis of a two-state Markov chain involving dependent Bernoulli trials *. Freeman (235) developed a similar model and applied it to published data on the scavenging of positive ions and electrons in irradiated saturated hydrocarbon solutions.

The probability that a reactive intermediate, R, will encounter n scavenger molecules in a diffusive displacement, after which it has ν new neighbours, is given by the a priori probabilistic expression

$$\frac{\nu!}{(\nu-n)!\,n!}(N_s)^n\,(1-N_s)^{\nu-n} \qquad \text{(IV-3)}$$

where N_s is the mole fraction of scavenging compound, S, in solution. If the reactant R does not react with certainty when encountering a single molecule of scavenger the encounter efficiency, f, should be introduced to modify the actual concentration of S to an effective concentration fN_s. It is assumed that f is independent of n. However, in the subsequent development f

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* The concepts used in the present approach are discussed (for non-chemical applications) by, for example, Cox and Miller(233) and T. C. Fry (234).

will be taken as unity. The probability that R does <u>not react</u> with an S in a diffusive jump is consequently $(1-N_s)^{\nu}$, ie, n is taken as zero in Eqt (IV-3). But each diffusive displacement corresponds to the successive transformation of an initial two-state <u>column</u> vector P by the stationary Markovian transition matrix T. P is defined as

$$P = \downarrow (1-N_s)^{\nu_o}, \; 1 - (1-N_s)^{\nu_o} \downarrow \qquad \text{(IV-4)}$$

where the state component $(1-N_s)^{\nu_o}$ represents the probability that a reactive intermediate has no scavenger as a nearest neighbour in its generation site and $1 - (1-N_s)^{\nu_o}$ is the chance it has at least one. ν_o is the number of nearest neighbors in the initial encounter, it is expected to be greater than ν since all nearest neighbours are "new" for this initial state. Thus, this initial-state vector considers the possibility that an intermediate may be generated in a state such that scavenging is possible without it making a diffusive displacement.

The circumstances in electron scavenging are more complex than for positive ions. The electron upon being ejected from a molecule may encounter scavenger molecules before it becomes "thermalized". The probability of the capture of epithermal electrons by the chemical scavengers used in this work (SF_6 and $c\text{-}C_4F_8$) is expected to be small. In the following development it is assumed that:

a) electron scavenging occurs only if the electron becomes thermalized first,

b) ν_0 and ν are the same for positive ions and electrons,

and c) for mathematical simplicity ν_0 and ν are sufficiently similar that ν may be substituted for ν_0.

$$\text{Now} \quad T = \begin{vmatrix} (1-N_s)^{\nu} & 0 \\ 1-(1-N_s)^{\nu} & 1 \end{vmatrix} \qquad \text{(IV-5)}$$

Each element a_{ij} of T is a conditional probability such that

a_{11} = probability that the <u>unreacted state</u> exists after the ℓth diffusive jump given that the <u>unreacted state</u> existed after the $(\ell-1)$th jump,

a_{12} = probability that the <u>unreacted state</u> exists after the ℓth jump given that the <u>reacted state</u> existed after the $(\ell-1)$th jump,

a_{21} = probability that the <u>reacted state</u> exists after the ℓth jump if the <u>unreacted state</u> existed after the $(\ell-1)$th jump, and

a_{22} = probability that the <u>reacted state</u> exists after the ℓth jump if the <u>reacted state</u> existed after the $(\ell-1)$th jump. ℓ is an integer such that $1 \leq \ell \leq m$ where m is the number of diffusive jumps a scavengable intermediate makes in its lifetime.

The state vector describing the probabilistic condition of a reactive intermediate, R, after m diffusive displacements is then given by the matrix equation:

$$P^m = T^m P \tag{IV-6}$$

where $T^m = TT^{m-1} = TTT^{m-2}$, etc. (IV-7)

$$= \begin{vmatrix} (1-N_s)^{\nu} & 0 \\ 1-(1-N_s)^{\nu} & 1 \end{vmatrix}^m \tag{IV-8}$$

$$= \begin{vmatrix} (1-N_s)^{\nu m} & 0 \\ 1-(1-N_s)^{\nu m} & 1 \end{vmatrix} \tag{IV-9}$$

$$P^m = \begin{vmatrix} (1-N_s)^{\nu m} & 0 \\ 1-(1-N_s)^{\nu m} & 1 \end{vmatrix} \begin{pmatrix} (1-N_s)^{\nu} \\ 1-(1-N_s)^{\nu} \end{pmatrix} \tag{IV-10}$$

$$= \begin{pmatrix} (1-N_s)^{\nu(m+1)} \\ 1-(1-N_s)^{\nu(m+1)} \end{pmatrix} \tag{IV-11}$$

Consequently the probability that the state of R can be described as unreacted after m diffusive jumps is $(1-N_s)^{\nu(m+1)}$, and reacted, by the state component $1-(1-N_s)^{\nu(m+1)}$.

To describe the kinetics of competitive scavenging of the primary ions the following sequence of elementary reactions is assumed. Species enclosed by square brackets are assumed to be in spurs.

$$RH \rightsquigarrow [RH^+, e^-], \qquad [IV\text{-}9]$$

$$\left[RH^{+} + e^{-}\right] \longrightarrow RH^{+} + e^{-} \quad \text{(free ions)} \tag*{[IV-10]}$$

$$\left[RH^{+} + e^{-}\right] \longrightarrow \text{products (I)} \tag*{[IV-11]}$$

$$RH^{+} + e^{-} \longrightarrow \text{products (I)} \tag*{[IV-12]}$$

$$\left[RH^{+} + S_1\right] \longrightarrow \left[S(+) + \text{products (II)}\right] \tag*{[IV-13]}$$

$$RH^{+} + S_1 \longrightarrow S(+) + \text{products (II)} \tag*{[IV-14]}$$

$$\left[e^{-} + S_2\right] \longrightarrow \left[S(-)\right] \tag*{[IV-15]}$$

$$e^{-} + S_2 \longrightarrow S(-) \tag*{[IV-16]}$$

S_1 and S_2 are positive ion and electron scavengers, respectively. e^{-} denotes a thermalized electron. The identity of the primary positive ion is assumed to be RH^{+}, the parent molecule ion. S(+) and S(-) are the charged species which result from reaction of an intermediate with an appropriate scavenger. The fates of S(+) and S(-) may be affected by secondary reactions such as charge transfer, exchange, decomposition, etc., but ultimately charge neutralization limits the lifetime of the charges.

Turning now to the competitive scavenging of ions described by reactions [IV-10] to [IV-16] an expression is developed for calculating the fraction of primary ion pairs scavengable at various concentrations of scavenger. Whether

RH^+ or e^- or both are scavenged depends on the chemical characteristics of S. The model is crude in view of the many approximations required to make the mathematics tractable.

The steady-state drift velocity $\left(\frac{dy}{dt}\right)_{drift}$ of a particle in a viscous medium under the influence of a force $\vec{F}_y$ is (236):

$$\left(\frac{d\vec{y}}{dt}\right)_{drift} = \frac{\vec{F}_y}{f} \qquad \text{(IV-12)}$$

where f is the frictional factor for the particle. The drift velocity of an ion, $\left(\frac{d\vec{y}}{dt}\right)_{drift,1}$ is consequently

$$\left(\frac{d\vec{y}}{dt}\right)_{drift,1} = \frac{Z_1 e\vec{E}_2}{f_1} \qquad \text{(IV-13)}$$

where $Z_1 e\vec{E}_2$ is the electrical force on an ion of charge $Z_1 e$ in the field of a counter ion, $\vec{E}_2$. For a singly charged ion, Z_1 is +1 or -1 depending on whether the ion is positively or negatively charged respectively. e is the magnitude of the electronic charge. E_2 denotes the value of the electric field at the ion due to the charge on its <u>counter ion</u> located a distance y away, ie,

$$\vec{E}_2 = \frac{Z_2 e}{\epsilon y^2} \qquad \text{(IV-14)}$$

where $Z_2 e$ is the charge on the <u>counter ion</u>, either +1 or -1, depending on whether the counter ion is positively or negatively charged respectively. Only singly charged ions are considered and

$$Z_1 + Z_2 = 0 \qquad \text{(IV-15)}$$

ϵ is the static dielectric constant of the solution. The electrical mobility of an ion, μ, is defined as the drift velocity in unit field. Thus, for example,

$$\mu_1 = \frac{\left(\frac{d\vec{y}}{dt}\right)_{drift,1}}{E_2} = \frac{Z_1 e}{f_1} \qquad \text{(IV-16)}$$

The relative drift speed, $\left(\frac{dy}{dt}\right)_{rel}$, for an ion pair is then

$$\left(\frac{dy}{dt}\right)_{rel} = \left|\left(\frac{d\vec{y}}{dt}\right)_{drift,1}\right| + \left|\left(\frac{d\vec{y}}{dt}\right)_{drift,2}\right|$$

$$= (\mu_1 + \mu_2)\,\frac{e}{\epsilon y^2} \qquad \text{(IV-17)}$$

The time for geminate recombination τ_{gr} is consequently

$$\tau_{gr} = \int_{y}^{y_{min}} \left(\frac{dy}{dt}\right)_{rel}^{-1} dy \qquad \text{(IV-18)}$$

$$= \frac{\epsilon}{e\,(\mu_+ + \mu_-)} \int_{y_{min}}^{y} y^2\, dy \qquad \text{(IV-19)}$$

$$= \frac{1}{3} \cdot \frac{\epsilon}{e\,(\mu_+ + \mu_-)} \left(y^3 - y^3_{min}\right) \qquad \text{(IV-20)}$$

y_{min} is a separation distance, less than which, chemical scavenging cannot compete with mutual neutralization of ion pairs. The Nernst relation (IV-16) is assumed to hold for any separation greater than y_{min} even for the thermalized electron.

According to the theory of Brownian motion (237) the mean square diffusive displacement λ^2 of a microscopic particle in thermal equilibrium with the medium is

$$\lambda^2 = \frac{6\,kT\tau_1}{f} \qquad \text{(IV-21)}$$

where k is the Boltzmann constant, T is the absolute temperature, τ_1 is the mean time for a single diffusive displacement, and f is the frictional factor for the particle displacement. For a singly charged particle within an electric field the frictional factor is related to the mobility by Eqt (IV-22):

$$\frac{1}{f} = \frac{\mu}{e} \qquad \text{(IV-22)}$$

Considering for the moment only a positive ion, then

$$\frac{1}{\tau_1} = \frac{6\,kT\mu_+}{e\lambda_+^2} \qquad \text{(IV-23)}$$

and m_+, the number of diffusive displacements made by the positive ion before geminate recombination is

$$m_+ = \frac{\tau_{gr}}{(\tau_1)_+} = \frac{2\epsilon kT}{e^2} \cdot \frac{1}{\lambda_+^2}\left(\frac{\mu_+}{\mu_+ + \mu_-}\right)(y^3 - y_{min}^3) \qquad \text{(IV-24)}$$

Similarily, for the negative ion,

$$m_- = \frac{\tau_{gr}}{(\tau_1)_-} = \frac{2\,\epsilon kT}{e^2} \cdot \frac{1}{\lambda_-^2}\left(\frac{\mu_-}{\mu_+ + \mu_-}\right)(y^3 - y_{min}^3) \qquad \text{(IV-25)}$$

Substituting the appropriate relation, either (IV-24) or (IV-25) for m in Eqt (IV-11) gives the probability $P(N_s)$ of one of the partners of the ion pair with separation, y, being scavenged by S before neutralization:

$$P(N_s) = 1 - (1-N_s)^b \qquad \text{(IV-26)}$$

where $$b = \nu\left[\frac{2\epsilon kT}{\lambda_1^2 e^2}\left(\frac{\mu_1}{\mu_1 + \mu_2}\right)(y^3 - y_{min}^3) + 1\right] \qquad \text{(IV-27)}$$

and subscript 1 refers to the ion capable of being scavenged by S and 2 refers to the counter ion.

To determine the fraction of ions of a particular charge sign that are scavenged at a given concentration of scavenger N_s, one integrates over the complete range of separation distances, the product of $P(N_s)$ with $N(y,0)$, the fraction of ion pairs separated by y after the electron thermalization. However, Onsager (238) suggested that some ion pairs may escape geminate recombination at any separation distance, y, by Brownian motion with a probability given by

$$\phi_{esc} = \exp(-\frac{E}{kT}) \qquad \text{(IV-28)}$$

where E is the "height" of a hypothetical barrier equivalent to the electrostatic potential of the ion in the field of its counter ion, ie,

$$E = \frac{e^2}{\epsilon y} \qquad \text{(IV-29)}$$

These escaping or "free" ions become homogeneously distributed in the medium. The scavenging probability of such free ions is described by ordinary chemical kinetics. Considering reactions [IV-12] and [IV-14] the fraction of positive ions χ_+ scavenged by homogeneous kinetics, is

$$\chi_+ = \frac{k_{14}[S_1]}{k_{14}[S_1] + k_{12}[(e^-)_{free}]}\int_{y_{min}}^{\infty} N(y,0)\,\phi_{esc}\,dy \qquad \text{(IV-30)}$$

As the concentration of homogeneously distributed positive and negative ions is usually several orders of magnitude less than the concentration of scavenger in the experiments of interest, χ_+ or χ_- reduces to

$$\chi_+ \text{ or } \chi_- = \int_{y_{min}}^{\infty} N(y,0)\, \phi_{esc}\, dy \qquad \text{(IV-31)}$$

which is just the fraction of ions which are 'free'. For those ions, initially separated by a distance y, that normally undergo geminate recombination the fraction scavenged is $[1 - \phi_{esc}]\cdot[1 - (1-N_s)^b]$. The fraction of the total ion yield that is scavenged when S has the mole fraction N_s is *

$$\frac{G(S\ +)}{G(\text{total ion})} = \chi_+ + \int_{y_{min}}^{\infty} [1 - \phi_{esc}][1 - (1-N_s)^b] N(y,0)\, dy \qquad \text{(IV-32)}$$

$$= 1 - \int_{y_{min}}^{\infty} N(y,0)\, (1-N_s)^b\, dy$$

$$+ \int_{y_{min}}^{\infty} N(y,0)\, \phi_{esc}\, (1-N_s)^b\, dy \qquad \text{(IV-33)}$$

In general, for an arbitrary N(y,0) the integrals in Eqt (IV-32) are evaluated graphically or numerically.

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* Only positive ion scavenging is considered in examples when developing the equations; similar equations apply to negative ions.

The experimental results on ion scavenging suggest that the distribution of separation distances may be approximated by the normalized function

$$N(y,0) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}, \quad y \gtrsim y_{min} \tag{I-17}$$

where $\frac{3}{2}\, y_{min}^{\frac{3}{2}}$ is the normalizing factor. Using this distribution the integrals in Eqt (IV-32) were evaluated graphically by the procedure outlined in Appendix D-2. Using Eqt (D-13) of Appendix D, Eqt (IV-33) becomes

$$\frac{G(S|+|)}{G(\text{total ion})} - \frac{3}{2}\, y_{min}^{\frac{3}{2}} \int_{y_{min}}^{\infty} y^{-\frac{5}{2}} \phi_{esc}\, (1-N_s)^b\, dy$$

$$= (1 - P) + P(Qy_{min}^3)^{\frac{1}{2}} \left[\sqrt{\pi} + \int_0^{u_{min}} u^{-2} \left[\exp(-u^2) - 1 \right] du \right] \tag{IV-34}$$

where $P \equiv \exp\left(\left[1 - \frac{2\, \epsilon kT}{e^2} \frac{1}{\lambda_1^2} \left(\frac{\mu_1}{\mu_1 + \mu_2} \right) y_{min}^3 \right] \nu \ln(1-N_s) \right)$, (IV-35)

$$Q \equiv \frac{-2\, \epsilon kT}{e^2} \frac{1}{\lambda_1^2} \left(\frac{\mu_1}{\mu_1 + \mu_2} \right) \nu \ln(1-N_s), \tag{IV-36}$$

$$u = (Qy^3)^{\frac{1}{2}}, \tag{IV-37}$$

and $u_{min} = (Qy_{min}^3)^{\frac{1}{2}}$ (IV-38)

If the concentration of S is sufficiently small such that

$P \approx 1$ and $\int_0^{u_{min}} u^{-2} \left[\exp(-u^2) - 1 \right] du$ is small then

$$\frac{G(+)}{G(\text{total ion})} - \frac{3}{2}\, y_{min}^{\frac{3}{2}} \int_{y_{min}}^{\infty} y^{-\frac{5}{2}} \phi_{esc}\, (1-N_s)^b\, dy$$

$$\approx K\left[-\ln(1-N_s)\right]^{\frac{1}{2}} \qquad \text{(IV-39)}$$

$$\approx K\sqrt{N_s}\,,\quad N_s \ll 1 \qquad \text{(IV-40)}$$

where K is a proportionality factor involving the quantities y_{min}, ϵ, ν, μ_1, μ_2, $\overline{\lambda}_1^2$, and T. The integral on the left hand side of Eqt (IV-39) is equivalent to the fraction of ions that are free ions when $N_s = 0$. Consequently, for hydrocarbons, this integral is small for all values of N_s.

It is of interest to determine the rate at which the population of ion pairs decays in time even in the absence of scavengers. This decay would be observed, for example, after the absorption of a very short pulse of ionizing radiation. The formulation of ion pair recombination by migration under coulomb attraction is considered in the first instance. Decay by electron tunnelling is mentioned later.

Eqt (IV-18) gives the time required for geminate recombination of ion pairs separated by a distance y. Consequently after a time τ_{gr}, the distance separating all extant ion pairs <u>originally exceeded</u>

$$y = \left(\frac{3e\,(\mu_+ + \mu_-)}{\epsilon}\,\tau_{gr} + y_{min}^3\right)^{\frac{1}{3}} \qquad \text{(IV-41)}$$

Of all ion pairs the fraction which undergoes geminate recombination in time t is then

$$\int_{y_{min}}^{y(t)} (1 - \phi_{esc})\, N(y,0)\, dy, \qquad \text{(IV-42)}$$

where y(t) is given by Eqt (IV-41) with τ_{gr} taken as t.

The rate at which "free ions" of a particular charge type disappear is given satisfactorily by ordinary homogeneous kinetics:

$$- \frac{d\left[\text{free ion}\right]}{dt} = k \left[\text{free ion}\right]^2 \qquad \text{(IV-43)}$$

where $\left[\text{free ion}\right]$ is the (homogeneous) molar concentration of free ions of either charge (not the sum of both types) and k is a bimolecular rate constant. Let f be the fraction of free ions recombined at a time t after electron thermalization. Let a be their initial concentration taken as if these ions are homogeneously distributed. Then integration of Eqt (IV-43) leads to

$$\frac{f}{1 - f} = akt \text{ or } f = \frac{akt}{1 + akt} \qquad \text{(IV-44)}$$

The fraction of all ions which recombine homogeneously in time t is then

$$\frac{akt}{1 + akt} \int_{y_{min}}^{\infty} \phi_{esc}\, N(y,0)\, dy \qquad \text{(IV-45)}$$

Debye developed the following expression for the rate constant of encounter-controlled reaction between oppositely charged ions in a liquid of low dielectric constant(239):

$$k = \frac{4\pi e^2 N_o^2}{\epsilon\, 1000\, RT}\left[D(+) + D(-)\right] \qquad \text{(IV-46)}$$

where N_o is Avogadro's number, R is the gas constant, and D(+) and D(-) are the diffusion coefficients for the positively and negatively charged reactants respectively. Since $D = \frac{\mu RT}{eN_o}$, Eqt (IV-46) becomes

$$k = \frac{4\pi e(\mu_+ + \mu_-)\, N_o}{\epsilon\, 1000}\ \text{liter mole}^{-1}\ \text{sec}^{-1} \qquad \text{(IV-47)}$$

Hummel and Allen (240) determined μ_+ and μ_- of the charged species in X-irradiated n-hexane at 24° C finding μ_+, 0.7×10^{-3} and μ_-, $1.3 \times 10^{-3}\ \text{cm}^2\ \text{V}^{-1}\ \text{sec}^{-1}$. Using these values of the ion mobilities

$$\begin{aligned} k &= 6.3 \times 4.8 \times 10^{-10} \times 2.0 \times 10^{-3} \times 300 \times 6.0 \times 10^{20} \\ &= 1.1 \times 10^{12}\ \text{liter mole}^{-1}\ \text{sec}^{-1} \end{aligned}$$

A value of k suitable for cyclopentane radiolysis is then about 1×10^{12} liter mole^{-1} sec^{-1}.

The value of a depends on the dose received by the sample. The number of free ions of a given charge type produced by a dose $\mathcal{D}$ in ev gm^{-1} is $\frac{1}{100}$ G(free ion)$\mathcal{D}$. On a molarity basis the expression becomes

$$a = \frac{10\rho\, G(\text{free ion})}{N_o}\mathcal{D} \qquad \text{(IV-48)}$$

where ρ is the density of the liquid alkane. If G(free ion) in irradiated alkane is taken as 0.1 (240) then a in cyclopentane at room temperature is about $1 \times 10^{-24}\mathcal{D}$ molar. If a short pulse of radiation supplies a dose of 1×10^{18} ev gm^{-1} the initial concentration of free ions in cyclopentane would be about 1×10^{-6} M. Hence $ak = 1 \times 10^{6}$ sec^{-1} so the values of akt after 10^{-11} sec and 10^{-7} sec would be about 10^{-5} and 10^{-1} respectively. Consequently at times less than 10^{-7} sec after the pulse only a negligible fraction of the free ions would have recombined.

On combining Eqt (IV-42) and Eqt (IV-45) the fraction of all ion pairs surviving a time t is

$$1 - \int_{y_{min}}^{y(t)} (1 - \phi_{esc})\, N(y,0)\, dy - \frac{akt}{1 + akt} \int_{y_{min}}^{\infty} \phi_{esc}\, N(y,0)\, dy \qquad \text{(IV-49)}$$

Eqt (IV-49) will be applied in Section IV-C-3 of this chapter after considering a suitable value of y_{min} and the form of $N(y,0)$.

At small values of y the frequency of parent ion recapture may be so large that the chance of ion scavenging for such separations is insignificant even at high concentrations of scavenger. Also, Eqt (IV-12) may no longer be valid. It is possible that the rate of geminate recombination, at small values of y, occurs for the most part by electron tunnelling. An estimate of tunnelling frequencies was obtained by developing a simple model for such a process occurring with trapped electrons under the influence of a coulombic electric field. This model, outlined in Appendix E, is of limited use at the present time because there is no information on the energies of "solvated" electrons in liquid alkanes. However, the model suggests that the frequency of tunnelling is markedly dependent on the separation distance, y. A suitable value of y_{min} to be used with the initial distribution of separation distances, N(y,0), may be one where the tunnelling frequency at y_{min} becomes greater than the frequency of diffusive displacement of ions. Eqt (IV-21) gives this jump frequency as

$$\frac{1}{\tau_1} = \frac{6\,kT\mu_-}{e\,\lambda_-^2} \qquad \text{(IV-50)}$$

Taking the root mean square jump distance as 3 Å, $\mu_- = 1.3 \times 10^{-3}$ cm^2 V^{-1} sec^{-1}* and T as 298° K gives a diffusive jump frequency of 1.5×10^{12} sec^{-1} or a mean time for a single diffusive jump of 7×10^{-13} sec. On the basis of the tunnelling model developed in Appendix E tunnelling frequencies of this magnitude occur for electrons in traps of ½ ev depth when y is 12 Å or at y equal to 16 Å when a trap depth of $\frac{1}{8}$ ev is considered.

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* It is not definitely known at this time whether this value, obtained by Hummel and Allen (240) for the negative species in irradiated n-hexane, applies to an electron or a negative ion resulting from electron scavenging. As noted above the concentration of free ions, which forms the basis of mobility measurements, is extremely small and such ions have a comparatively long lifetime. Consequently traces of impurities which can scavenge electrons would vitiate the conclusion that the measured mobility is to be associated with the electron.

In developing the ion scavenging model the only question considered was, "What is the probability that an ion encounters at least one scavenger molecule before charge neutralization?" This is all that is necessary if one only requires a knowledge of the reacted or unreacted state of the initial ion after m diffusive displacements. However, in some scavenging experiments the fate of the charged species leaving the first encounter with scavenger may be very important. For example, in the radiolysis of cyclopentane - ND_3 solutions, it is postulated that the amount of HD in the product hydrogen is related to the extent that protons transfer from alkane ions to ND_3 giving ND_3H^+ ions. If an ND_3H^+ ion now encounters one or more ND_3 molecules before neutralization then the questions of ion solvation and the possibility of isotopic exchange should be considered. The scavenger model can be extended to estimate the fraction of initial hydrocarbon ions which encounter more than one scavenger molecule in m diffusive displacements. This probability, P_c, is

$$P_c = 1 - P_o - P_1 \qquad \text{(IV-51)}$$

where P_o is the probability of RH^+ encountering no S in m diffusive jumps and P_1 is the probability of RH^+ encountering exactly one S in m diffusive jumps. P_o is $(1-N_s)^{\nu(m+1)}$, as before. Using Eqt (IV-3), P_1 is given by the expression

$$P_1 = \frac{(m+1)!}{(m)!1!} \frac{\nu !}{(\nu - 1)!\,1!} (N_s)(1-N_s)^{\nu - 1} (1-N_s)^{\nu(m)}$$

or $$P_1 = \nu(m+1)(N_s)(1-N_s)^{\nu(m+1)-1} \qquad \text{(IV-52)}$$

Expression (IV-52) makes the crude assumption that the unscavenged ion and the scavenged ion(or scavenger ion) have the same mobility parameters. Combining the expressions for P_o and P_1, P_c is given by

$$P_c = 1 - (1-N_s)^{\nu(m+1)} - \nu(m+1)N_s\,(1-N_s)^{\nu(m+1)-1} \qquad \text{(IV-53)}$$

The fraction of all scavengable ions which encounter more than one S when averaging over the population of ion pairs, is

$$\int_{y_{min}}^{\infty}\left[1 - (1-N_s)^{\nu(m+1)} - \nu(m+1)N_s\,(1-N_s)^{\nu(m+1)-1}\right] \times \left[1-\phi_{esc}\right]N(y,0)\,dy + \int_{y_{min}}^{\infty}\phi_{esc}\,N(y,0)\,dy \qquad \text{(IV-54)}$$

It is assumed in expression (IV-54) that all free ions encounter more than one S molecule for all concentrations of S considered. The fraction of all <u>scavenged</u> ions which encounter one or more additional scavenger molecules is

$$\left\{\int_{y_{min}}^{\infty}(1-\phi_{esc})\,N(y,0)\left[1 - (1-N_s)^{\nu(m+1)} - \nu(m+1)N_s \times (1-N_s)^{\nu(m+1)-1}\right]dy + \int_{y_{min}}^{\infty}\phi_{esc}\,N(y,0)\,dy\right\}$$

(This expression is continued on the next page.)

$$\div \left\{ \int_{y_{min}}^{\infty} (1 - \phi_{esc})\, N(y,0) \left[1 - (1-N_s)^{\nu(m+1)} \right] dy + \int_{y_{min}}^{\infty} \phi_{esc}\, N(y,0)\, dy \right\} \qquad \text{(IV-55)}$$

$$= 1 - \frac{\nu N_s \int_{y_{min}}^{\infty} (m + 1)(1 - \phi_{esc})\, N(y,0)(1-N_s)^{\nu(m+1)-1}\, dy}{\int_{y_{min}}^{\infty} (1 - \phi_{esc})\, N(y,0)\left[1 - (1-N_s)^{\nu(m+1)} \right] dy + F} \qquad \text{(IV-56)}$$

where F is the integral

$$\int_{y_{min}}^{\infty} \phi_{esc}\, N(y,0)\, dy. \qquad \text{(IV-31)}$$

2. A Kinetic Model for Scavenging Electronically Excited Species in the Liquid Phase by Suitable Reagents

The effects of additives on the product yields in alkane radiolysis have been interpreted in terms of such diversified (and ambiguous) processes as radical scavenging, ion scavenging, energy transfer, etc. Often simple kinetic models for such processes may be developed which illustrate the behavior of the alkane-additive systems in, more or less, detail. Although agreement of the experimental observations with the predictions of a kinetic model never constitutes proof of a mechanism, poor agreement indicates that the model must be altered or possibly eliminated. The model developed in section IV-B-1 considered a scavengable species whose lifetime depended on a separation distance and the characteristics of motion in a coulomb field. Although that model is still to be applied, other models should be developed for comparison purposes. A greatly altered form of the ion scavenging model considers the mean lifetime of all scavengable species to be the same. This second model, to be developed here, is not suitable for the scavenging of ions having a distribution of separation distances. However, it is useful for treating the scavenging behavior of neutral excited species whose mean lifetimes, in the absence of scavenger, depend on the rate constant for a unimolecular decay.

Consider the following set of elementary reactions which are assumed to result from the absorption of a single radiation pulse of short duration:

$$RH \rightsquigarrow RH^{*} \qquad [IV\text{-}17]$$

$$RH^{*} \xrightarrow{\lambda'} \text{products} \qquad [IV\text{-}18]$$

$$RH^{*} + S \longrightarrow RH + S^{*} \qquad [IV\text{-}19]$$

For the purposes of this study, RH^{*} is a potential proton or electron donor with a mean lifetime $\frac{1}{\lambda'}$. RH^{*} can decompose unimolecularly possibly giving a variety of products. S^{*} is, for example, a protonated S, or S^{-} with a counter charge within a molecular diameter or so. S^{*} may not be distinguishable from an electronically excited state of S or SH.

Assume that the rate of reaction [IV-18] can be described by a first order decay constant, λ', covering several possible modes of unimolecular decay. The scavenging reaction will be described by a rate, σ, which is dependent on the scavenger concentration. According to the model developed in section IV-B-1 the probability that the initial state of a scavengable intermediate can be described as reacted is given by the expression $1 - (1 - fN_s)^{\nu_o}$ with N_s denoting the mole fraction of scavenger in the irradiated sample. However, only those intermediates <u>not</u> scavenged in their initial cage have the option of either surviving a natural lifetime or being scavenged through further random encounters with scavenger, S. The time required to complete a reaction with a scavenger molecule in any encounter is assumed to be negligible compared to the natural mean lifetime of RH^{*}, $\frac{1}{\lambda'}$, or to the mean time for a diffusive displacement of RH^*.

Consider the fraction of intermediates, $(1 - fN_s)^{\nu_0}$, which are not scavenged in their initial cages. Their rate of disappearance is described by the equation

$$-\frac{dn^{iu}_{RH^*}(t)}{dt} = \left[\lambda' + \sigma\right] n^{iu}_{RH^*}(t) \qquad \text{(IV-57)}$$

where $n^{iu}_{RH^*}$ is the number of RH^* initially unscavenged which are present a time t after their formation. If $n^{iu}_{RH^*}(0)$ is the total number of the intermediates that escaped scavenging in their initial cages, then the probability $\rho^{iu}_{RH^*}(t)$ that an initially unscavenged RH^* survives a time t is

$$\rho^{iu}_{RH^*}(t) = \frac{n^{iu}_{RH^*}(t)}{n^{iu}_{RH^*}(0)} \qquad \text{(IV-58)}$$

Integration of Eqt (IV-57) and using Eqt (IV-58) gives **

$$\rho^{iu}_{RH^*}(t) = \exp\left|-\lambda' t - \int_0^t \sigma \, dt\right| \qquad \text{(IV-59)}$$

Thus $\rho^{iu}_{RH^*}(t)$ is the product of two factors. One, $\exp(-\lambda' t)$, is the probability that a given initially unscavenged RH^* lives for a time t without decaying unimolecularly. The second factor, $\exp\left[-\int_0^t \sigma \, dt\right]$, is the probability that RH^*,

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** It is assumed in the first instance that σ may be dependent on t.

having escaped its initial cage, is not scavenged in the time t. The later probability is $(1 - fN_s)^{\nu m}$. f, the encounter efficiency, is assumed to be independent of time. Now

$$m = \frac{t}{\tau_1} = \frac{6\,Dt}{\overline{\lambda^2}} \qquad \text{(IV-60)}$$

where D is the diffusion coefficient of RH^* and $\overline{\lambda^2}$ is the mean square diffusive jump distance of RH^*, consequently

$$\exp\left(-\int_0^t \sigma\, dt\right) = \exp\left(\frac{\nu 6D}{\overline{\lambda^2}}\left[\ln(1 - fN_s)\right] t\right) \qquad \text{(IV-61)}$$

or

$$\int_0^t \sigma\, dt = -\frac{6\nu D}{\overline{\lambda^2}}\left[\ln(1 - fN_s)\right] t \qquad \text{(IV-62)}$$

and

$$\sigma = -\frac{6\nu D}{\overline{\lambda^2}} \ln(1 - fN_s) \qquad \text{(IV-63)}$$

Now $\sigma\rho^{iu}_{RH^*}(t)$ represents the time rate of change of the probability of scavenging an RH^* at a time t after having escaped scavenging in its initial cage. The probability that a given initially unscavenged RH^* will be scavenged in its lifetime is consequently

$$\int_0^\infty \sigma\rho^{iu}_{RH^*}(t)\, dt = \frac{G(S^*)}{G(RH^*)^{iu}} \qquad \text{(IV-64)}$$

where $\frac{G(S^*)}{G(RH^*)^{iu}}$ is the fraction of the initially unscavenged RH^* which reacts with S in their lifetimes. Substituting Eqts (IV-59), (IV-62), and (IV-63) into Eqt(IV-64) gives

$$\frac{G(S^*)}{G(RH^*)^{iu}}$$

$$= -\frac{6\nu D}{\lambda^2}\ln(1 - fN_s)\int_0^\infty \exp\left(-\lambda' t + \frac{6\nu D}{\lambda^2}\left[\ln(1-fN_s)\ t\right]\right) dt \qquad \text{(IV-65)}$$

$$= \frac{-\frac{6\nu D}{\lambda^2}\ln(1 - fN_s)}{\lambda' - \frac{6\nu D}{\lambda^2}\ln(1 - fN_s)} \qquad \text{(IV-66)}$$

The probability of an initially produced RH* being scavenged by S is then

$$\frac{G(S^*)}{G(\text{total } RH^*)}$$

$$= 1 - (1 - fN_s)^{\nu_0} - (1 - fN_s)^{\nu_0}\left\{\frac{\frac{6\nu D}{\lambda^2}\ln(1 - fN_s)}{\lambda' - \frac{6\nu D}{\lambda^2}\ln(1 - fN_s)}\right\} \qquad \text{(IV-67)}$$

Eqt (IV-67) will be applied later.

C. CYCLOPENTANE SOLUTIONS OF SULPHUR HEXAFLUORIDE AND OCTAFLUOROCYCLOBUTANE

1. The Mechanism of the Suppression of the Hydrogen Yields

The results obtained with the fluorinated additives indicate an interaction with the precursor(s) of radiolytic H_2. Furthermore, the similarity of their inhibiting effects suggests that their mode of action is alike. Several sources of H_2 from irradiated pure cyclopentane are conceivable which, in principle, could be suppressed by these fluorinated additives. Three sources are

a) electronically excited neutral molecules,

b) hydrogen atoms,

and c) hydrocarbon positive ions and electrons which give H_2 or, at least different H_2 precursors, on recombination.

There is no information on the efficiencies of SF_6 and $c\text{-}C_4F_8$ for quenching electronically excited species. A kinetic model for the quenching of an electronically excited species in liquid phase as developed in section IV-B-2 is applied to the SF_6 and $c\text{-}C_4F_8$ results in the next section.

The rate constant for the gas phase reaction of thermal hydrogen atoms with SF_6, Eqt [IV-20],

$$H\cdot + SF_6 \xrightarrow{k_1} HF + SF_5\cdot \qquad [IV\text{-}20]$$

was measured by Fenimore and Jones (241) to be $k_1 = 2 \times 10^{12} \times \exp(-30{,}000/RT)$ l mole^{-1} sec^{-1}. At 300° K, k_1 is approximately 10^{-10} l mole^{-1} sec^{-1}. As noted in section III-C-1 the rate of reaction [III-2] is approximately 10^6 l mole^{-1}

$$H\cdot + c\text{-}C_5H_{10} \xrightarrow{k_2} H_2 + c\text{-}C_5H_9\cdot \qquad [III\text{-}2]$$

sec^{-1} at 300° K. Although the limiting suppression of hydrogen was not reached experimentally with the concentrations of SF_6 attained in the present work such a limit is expected, on the basis of the c-C_4F_8 results, to occur with a mole ratio of c-C_5H_{10} to SF_6 equal to about four. With such a mole ratio of the components the rate of reaction [III-2] is still about 10^{16} times greater at room temperature than reaction [IV-20].

While the rate constant for reaction [IV-20] appears small at 300° K, its slowness cannot be ascribed to a lack of exothermicity (the heat of reaction is about -46 kcal mole^{-1}). On the other hand, the reaction of H· with c-C_4F_8 is endothermic * (about +16 kcal mole^{-1}) and the reaction is expected to be slow. The following metathesis reaction is exothermic by about 14 kcal mole^{-1} yet CF_4 is known to be inert to hydrogen atoms (245):

$$H\cdot + CF_4 \longrightarrow HF + CF_3\cdot \qquad [IV\text{-}21]$$

$$\Delta H_r^o = -14 \text{ kcal mole}^{-1}$$

Although the rate constants for reactions [IV-20] and [III-2] were estimated for gas phase reactions at temperatures well removed from the range in which they were measured, the conclusion remains that virtually no thermal hydrogen atoms

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* The first bond dissociation energies of SF_6 (242), CF_4 (243), and c-C_4F_8 (244) are stated to be 86 , 122, and 152 kcal mole^{-1} respectively.

react with either SF_6 or c-C_4F_8 in liquid phase cyclopentane. The fluorinated additives might be expected to react with "hot" hydrogen atoms to reduce the H_2 yield. $\delta(H_2)$ is then expected to be approximately proportional to the atomic ratio of fluorine to hydrogen in the solutions. However, the observed values of $\delta(H_2)$ are not related to this atomic ratio. The selective scavenging of "hot" hydrogen atoms is not operative.

Hydrocarbon positive ions and electrons are important precursors to hydrogen atoms, radicals, electronically excited hydrocarbon species, and ultimately, radiolytic H_2. The photoionization of SF_6 (246) indicates that the lowest ionization threshold occurs at 15.35 ev and is probably associated with the following process:

$$SF_6 + h\nu \longrightarrow SF_6^+ + e^- \qquad [IV-22]$$

As the ionization potential of c-C_5H_{10} is about 10.5 ev (91) charge transfer to SF_6 is unlikely. The lowest appearance potential of any positive ion of c-C_4F_8 occurs at 12.25 ev in an electron impact spectrum (244) so charge transfer from cyclopentane ion is also excluded in this system.

The following H_2-transfer reaction is exothermic:

$$C_5H_{10}^+ + SF_6 \longrightarrow C_5H_8^+ + SF_4 + 2HF \qquad [IV-23]$$

$$\Delta H_r^o = -51 \text{ kcal mole}^{-1}$$

H_2-transfer to c-C_4F_8 to produce $CHF_2(CF_2)_2CF_2H$ is also expected to be exothermic (ΔH_r^o = -15 kcal mole^{-1}). However, no data are available on the occurrence of these reactions.

Single step H_2-transfer reactions of hydrocarbon positive ions were observed with cyclopropane, propylene, ethylene, and acetylene (80). Table IV-3 gives calculated gas phase reaction heats for H_2-transfers from the cyclopentane ion to a variety of compounds. It is interesting to note that while the H_2-transfer from $c\text{-}C_5H_{10}^+$ to $c\text{-}C_5H_{10}$ to give n-pentane and $c\text{-}C_5H_8^+$ is exothermic (-26 kcal $mole^{-1}$) this reaction must be relatively slow at 20° C because n-pentane is only a minor product in the radiolysis of pure liquid cyclopentane, $\left[G(C_5H_{12})\right]_o \approx 0.14$. Similarly, H_2-transfer to cyclobutane to produce n-butane is almost as exothermic as the H_2-transfer to cyclopropane but only the latter of these two reactions was observed in a tandem mass spectrometric study of the impact of cyclohexane positive ions on the two hydrocarbons (247). Oxygen does not appear to react with the cyclohexane ion (78) although the reaction is exothermic ($\sim$-30 kcal $mole^{-1}$).

There is, of course, no relation between a reaction heat and the rate of the corresponding reaction. Furthermore, the reaction path is immaterial to the calculations of this heat; the result is the same whether the process occurs in one or several steps. It follows that the occurrence of a large yield of a product containing two hydrogen atoms originating from a hydrocarbon ion is not proof of a single step transfer process. The factors involved in single step H_2-transfers are not presently understood. π-bond character appears to be common to all good acceptors yet irradiated benzene - cyclopentane solutions produced only minor amounts

TABLE (IV-3)

Reaction Heats for H_2-Transfers or 2H·-Transfers from the Cyclopentane Molecule Ion to Various Acceptors

Typical reactions:

$$c\text{-}C_5H_{10}^{+} + X \qquad c\text{-}C_5H_8^{+} + H_2X$$

$$c\text{-}C_5H_{10}^{+} + X \qquad c\text{-}C_5H_8^{+} + Y + H_2Z \text{ (or 2HZ)}$$

Acceptor, X	Ionization potential, ev	Products	ΔH_r^o, kcal mole^{-1}
$c\text{-}C_5H_{10}$	10.5	$n\text{-}C_5H_{12}$	-26
$c\text{-}C_3H_6$	10.0	C_3H_8	-46
$c\text{-}C_4H_8$	10.5	$n\text{-}C_4H_{10}$	-45
$c\text{-}C_5H_8$ *	9.0	$c\text{-}C_5H_{10}$	-35
benzene	9.2	1,3-cyclohexadiene	-3
CCl_4	11.7	$CHCl_3$ + HCl	-31
$CHCl_3$	11.4	CH_2Cl_2 + HCl	-29
O_2	12.1	H_2O_2	-32
CO_2	13.8	HCOOH	-2
CO_2	13.8	CO + H_2O	+1
NO_2	9.8	NO + H_2O	-54
N_2O	12.9	N_2 + H_2O	-87
SO_2	12.3	SO + H_2O	+23
Cl_2	11.5	2HCl	-53
Br_2	10.6	2HBr	-20
I_2	9.3	2HI	-20

TABLE (IV-3)(Continued)

Acceptor, X	Ionization potential, ev	Products	ΔH^o_r, kcal mole^{-1}
$(CN)_2$	13.6	2HCN	-51
SF_6	15.4	$SF_4 + 2HF$	-51
XeF_2	11.5	$Xe + 2HF$	-111
B_4H_{10}	--	$2B_2H_6$	-10

Notes

1. Thermochemical data was obtained from the "JANAF Thermochemical Tables," U. S. Dept. of Commerce, Washington, 1961, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Res. Proj. #44, Carnegie Press, Pittsburgh, Pa., 1953, and V. I. Vedeneev et al., "Bond Energies, Ionization Potentials, and Electron Affinities," Edward Arnold, London, 1966.

2. For purposes of calculation all reactants and products are assumed to be in the ideal gas state at a pressure of one atmosphere.

* This reaction is closely related to positive charge transfer.

of the cyclohexadienes, which could also arise by other processes (see also reference 247). Results in Table IV-3 indicate that H_2-transfer to benzene is practically thermoneutral. This latter fact may explain the slowness of the H_2-transfer to benzene. It is assumed here, without any further information being available, that single step H_2-transfers to the fluorinated additives are negligibly slow.

The following hydrogen atom transfer reaction involving SF_6 is highly exothermic:

$$C_5H_{10}^+ + SF_6 \longrightarrow C_5H_9^+ + HF + SF_5\cdot \qquad [IV\text{-}24]$$

$$\Delta H_r^o = -63 \text{ kcal mole}^{-1}$$

However, the analogous reaction with c-C_4F_8 is endothermic (+32 kcal mole^{-1}) and it is not expected to occur in the gas or liquid phase. Because the SF_6 and c-C_4F_8 systems behave similarly it is assumed that H atom-transfer reactions are absent in the SF_6 solutions as well. To summarize, it is unlikely that the fluorinated additives react with hydrocarbon positive ions to suppress hydrogen formation.

A highly efficient electron attachment process occurs in the gas phase with SF_6 to produce SF_6^- with an autoionization lifetime of about 25μsec (164). Also long lived negative parent molecule ions exist for some cyclic perfluorocarbons such as perfluoromethylcyclohexane (162, 163) and probably also for c-C_4F_8 (164). The electron affinity of SF_6 is about 34 kcal mole^{-1} (242). The rate constants for gas phase attachment of an electron to SF_6 and CF_3-c-C_6F_{11} were determined by Mahan and Young (163) to be 1.9×10^{14} and 6×10^{14} l mole^{-1} sec^{-1} respectively at 300° K. Dissociative recombination rate constants for positive ions and electrons in Ar, Xe, N_2, and O_2 for example, are of the order of 10^{15} l mole^{-1} sec at 300° K (248). For a gaseous system, with the concentrations of fluorinated additives used here, the attachment of electrons to SF_6 or c-C_4F_8 greatly exceeds electron - positive ion recombination rates. The suppression of hydrogen yields by these additives is consistent with an electron scavenging mechanism if the recombination of the parent hydrocarbon molecule ion with a scavenged electron species gives less radiolytic hydrogen than the positive ion-electron neutralization. The similarity between the scavenging behavior of certain fluorine compounds (165) and that of such accepted electron scavengers as CCl_4 and N_2O, supports the hypothesis that the inhibiting effects of SF_6 and c-C_4F_8 occur by electron scavenging. A kinetic treatment of electron scavenging is given in section IV-C-3.

2. The Fluorinated Additives as Scavengers for Electronically Excited Cyclopentane Molecules

In this section the kinetic model for the scavenging of neutral excited species is applied. It is demonstrated that calculations based on this model are in poor agreement with the observed effects of the fluorinated additives.

Assume that an electronically excited hydrocarbon molecule, RH^*, is a major source of hydrogen or hydrogen precursors and that it can be deactivated by the fluorinated additives. Then $\frac{\delta(H_2)}{[\delta(H_2)]\ max} = \frac{\delta(H_2)}{3.4}$ is the fraction of RH^* being deactivated by the additive with mole fraction N_s at which concentration the hydrogen suppression amounts to $\delta(H_2)$. Equation (IV-68) gives the relation between $\frac{\delta(H_2)}{3.4}$ and N_s:

$$\frac{\delta(H_2)}{3.4} = 1 - (1-fN_s)^{\nu_o} - (1-fN_s)^{\nu_o} \frac{\frac{6\nu D}{\overline{\lambda^2}} \ln(1-fN_s)}{\lambda' - \frac{6\nu D}{\overline{\lambda^2}} \ln(1-fN_s)} \qquad \text{(IV-68)}$$

where all of the symbols were previously defined. In the calculations using Eqt (IV-68) the following values were used for some of the quantities: $\nu_o = 8.0$, $\nu = 4.0$, $\overline{\lambda^2} = 9.0 \times 10^{16}\ cm^2$, and $D = 3.0 \times 10^{-5}\ cm^2\ sec^{-1}$. The remaining quantities of Eqt (IV-68), f and λ' were used in the following four combinations:

a) $f = 1.00$, $\lambda' = 5.0 \times 10^{9}$ sec^{-1}

b) $f = 1.00$, $\lambda' = 1.0 \times 10^{9}$ sec^{-1}

c) $f = 1.00$, $\lambda' = 1.0 \times 10^{8}$ sec^{-1}

d) $f = 0.10$, $\lambda' = 1.0 \times 10^{8}$ sec^{-1}

Table IV-4 summarizes a typical calculation with the prescribed values of ν_o, ν, $\overline{\lambda}^2$, and D, and the conditions $f = 0.10$ and $\lambda' = 1.0 \times 10^{8}$ sec^{-1}. Figure IV-1 shows the calculated scavenging curves for the above combinations a) to d) as well as the observed values of $\frac{\delta(H_2)}{3.4}$ for both of the fluorinated additives. Clearly, no calculated curve satisfactorily fits the observed data. Altering the scavenging efficiency factor, f from 1.0 to 0.1 but maintaining $\lambda' = 1.0 \times 10^{8}$ sec^{-1} did not affect the shape of the scavenging curve; the result was a curve almost coincident with the scavenger plot for $f = 1.00$ and $\lambda' = 1.0 \times 10^{9}$ sec^{-1}. It is concluded that sulfur hexafluoride and octafluorocyclobutane do not influence the yield of hydrogen from the irradiated cyclopentane solutions by a mechanism involving the deactivation of neutral electronically excited cyclopentane molecules.

3. Application of the Ion Scavenging Model

The calculations of the previous section ruled out scavenging of an electronically excited species as the cause of the hydrogen suppression by the fluorinated additives. Thus, only one of the reasons considered for the hydrogen suppression remains, namely the scavenging of

TABLE IV-4

Calculation of the Fraction of Excited Molecules Deactivated for Various Values of N_s*

N_s	fN_s	$\ln(1-fN_s)$	$(1-fN_s)^{\nu_o}$	$\frac{6\nu D}{\lambda^2}\ln(1-fN_s)$	$\lambda' - \frac{6\nu D}{\lambda^2}\ln(1-fN_s)$	Fraction of RH* deactivated
1.0×10^{-1}	1.0×10^{-2}	-1.0×10^{-2}	0.92	-8.0×10^{9}	8.1×10^{9}	0.99
4.0×10^{-2}	4.0×10^{-3}	-4.0×10^{-3}	0.97	-3.2×10^{9}	3.3×10^{9}	0.97
1.0×10^{-2}	1.0×10^{-3}	-1.0×10^{-3}	0.99	-8.0×10^{8}	9.0×10^{8}	0.89
4.0×10^{-3}	4.0×10^{-4}	-4.0×10^{-4}	1.00	-3.2×10^{8}	4.2×10^{8}	0.76
1.0×10^{-3}	1.0×10^{-4}	-1.0×10^{-4}	1.00	-8.0×10^{7}	1.8×10^{8}	0.44
4.0×10^{-4}	4.0×10^{-5}	-4.0×10^{-5}	1.00	-3.2×10^{7}	1.3×10^{8}	0.25
1.0×10^{-4}	1.0×10^{-5}	-1.0×10^{-5}	1.00	-8.0×10^{6}	1.1×10^{8}	0.07

* $f = 0.10$; $\lambda' = 1.0 \times 10^{8}\ \text{sec}^{-1}$; $\frac{6\nu D}{\lambda^2} = 8.0 \times 10^{11}\ \text{sec}^{-1}$.

FIGURE IV-1

Fraction of RH^* Scavenged at Various Concentrations of the Fluorinated Additives in Cyclopentane

A. Calculated Curves

$\frac{6\nu D}{\lambda^2}$ for SF_6 is taken as 8.0×10^{11} sec^{-1} at 20° C

———— $\lambda' = 5 \times 10^{9}$ sec^{-1} for RH^*, f = 1.00

— - — - $\lambda' = 1 \times 10^{9}$ sec^{-1} for RH^*, f = 1.00

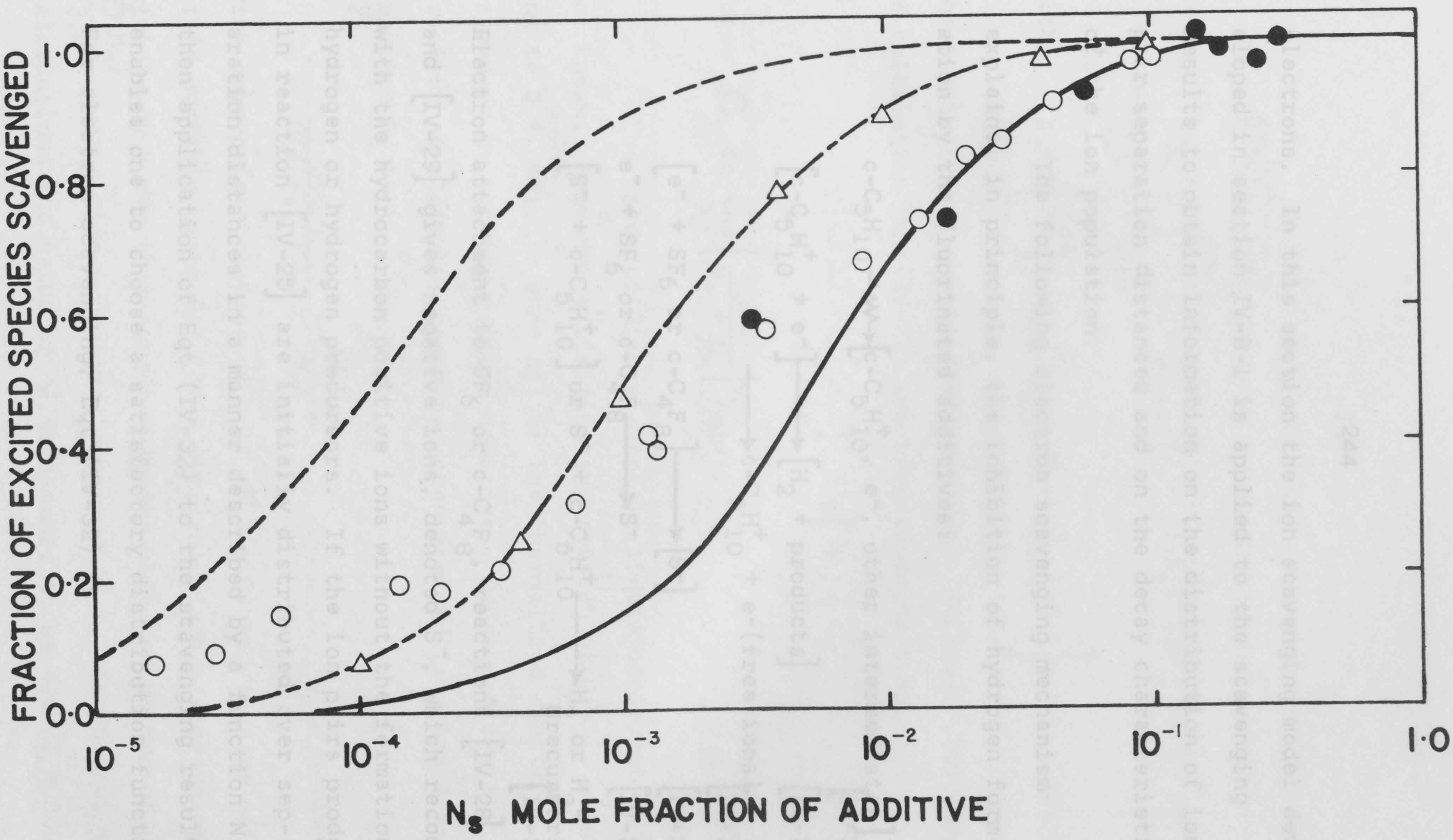
- - - - - - $\lambda' = 1 \times 10^{8}$ sec^{-1} for RH^*, f = 1.00

△ $\lambda' = 1 \times 10^{8}$ sec^{-1} for RH^*, f = 0.10

B. Observed Scavenging of a Hydrogen Precursor

○ SF_6 - c-C_5H_{10} solutions

● c-C_4F_8 - c-C_5H_{10} solutions


FRACTION OF EXCITED SPECIES SCAVENGED
1·0
0·8
0·6
0·4
0·2
0·0
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1·0
N_s MOLE FRACTION OF ADDITIVE

electrons. In this section the ion scavenging model developed in section IV-B-1 is applied to the scavenging results to obtain information on the distribution of ion pair separation distances and on the decay characteristics of the ion population.

The following electron scavenging mechanism explains, in principle, the inhibition of hydrogen formation by the fluorinated additives:

$$\text{c-C}_5\text{H}_{10} \rightsquigarrow \left[\text{c-C}_5\text{H}_{10}^+,\ e^-,\ \text{other intermediates}\right] \qquad [\text{IV-25}]$$

$$\left[\text{c-C}_5\text{H}_{10}^+ + e^-\right] \longrightarrow \left[\text{H}_2 + \text{products}\right] \qquad [\text{IV-26}]$$

$$\longrightarrow \text{c-C}_5\text{H}_{10}^+ + e^-\text{(free ions)} \qquad [\text{IV-27}]$$

$$\left[e^- + \text{SF}_6 \text{ or c-C}_4\text{F}_8\right] \longrightarrow \left[\text{S}^-\right] \qquad [\text{IV-28}]$$

$$e^- + \text{SF}_6 \text{ or c-C}_4\text{F}_8 \longrightarrow \text{S}^- \qquad [\text{IV-29}]$$

$$\left[\text{S}^- + \text{c-C}_5\text{H}_{10}^+\right] \text{ or } \text{S}^- + \text{c-C}_5\text{H}_{10}^+ \longrightarrow \text{H}_2 \text{ or H}_2\text{-precursors} \qquad [\text{IV-30}]$$

Electron attachment to SF_6 or $c-C_4F_8$, reactions [IV-28] and [IV-29] gives negative ions, denoted S^-, which recombine with the hydrocarbon positive ions without the formation of hydrogen or hydrogen precursors. If the ion pairs produced in reaction [IV-25] are initially distributed over separation distances in a manner described by a function N(y,0) then application of Eqt (IV-32) to the scavenging results enables one to choose a satisfactory distribution function. For electron scavenging, Eqt (IV-32) is

$$\frac{G(S^-)}{G(\text{total ion})} = \chi_- + \int_{y_{min}}^{\infty} (1 - \phi_{esc}) \left[1 - (1-N_s)^b \right] N(y,0)\, dy \qquad \text{(IV-32)}$$

with $$b = \nu \left[\frac{2\epsilon k T}{\lambda_-^2} \left(\frac{\mu_-}{\mu_+ + \mu_-} \right) (y^3 - y^3_{min}) + 1 \right] \qquad \text{(IV-27)}$$

where all of the symbols were previously defined. For purposes of calculation Eqt (IV-27) was rearranged to give

$$b = \nu \left[\frac{2\epsilon k T}{e^2} \Omega_- \left[\left(\frac{y}{y_{min}} \right)^3 - 1 \right] + 1 \right] \qquad \text{(IV-69)}$$

where Ω_- is $\frac{1}{\lambda_-^2} \left(\frac{\mu_-}{\mu_+ + \mu_-} \right) y^3_{min}$ (IV-70)

The value of G(total ion) in liquid cyclopentane is not known. However, a limiting suppression of $G(H_2)$, amounting to 3.4, results when all of the thermalized electrons are scavenged by the fluorinated additive. Consequently, the fraction of electrons scavenged when the additive has a mole fraction N_s is

$$\frac{G(S^-)}{G(\text{total ion})} = \frac{\delta(H_2)}{3.4} \qquad \text{(IV-71)}$$

With appropriate choices of both an N(y,0) and a value of b it is possible using Eqt (IV-32) to calculate a scavenging efficiency curve that agrees with the observed values of $\frac{\delta(H_2)}{3.4}$ over a wide concentration range of S. Throughout the calculations the value of ν is assumed to be 4.0, T = 300° K, and $\epsilon = 1.96$. For a given distribution function, N(y,0), a value of Ω_- is chosen which gives the best fit with the observed values of $\frac{\delta(H_2)}{3.4}$. A typical calculation for a particular N(y,0) and a fixed value of b at a single concentration of S is given in Appendix D-2.

Freeman (112) suggested a distribution for ion pair separation distances which has all thermalized electrons separated from their counter ions by at least 18 Å in liquid cyclopentane at 20° C. This minimum initial separation distance is denoted y_o. This distribution which is not a continuous function but is, however, a delta function distribution, was used in the calculations in three ways:

a) Following Freeman's arguments, ion pairs may drift together to a minimum separation of $y_{min} = 10$ Å at which distance chemical scavenging cannot compete with parent ion - electron recombination. The solid curve in Fig IV-2 shows the best fitting curve calculated in this way. In this case the values of Ω_- and $\left(\frac{\mu_-}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_-^2}$ are 7.0×10^{-6} cm and 7.0×10^{15} cm^{-2} respectively.

b) In this case, Freeman's distribution was used but y_{min} was treated as a variable parameter. The dash-dot curve of Fig IV-2 was calculated with $y_{min} = 17$ Å and $\Omega_- = 1.5 \times 10^{-4}$ cm; the value of $\left(\frac{\mu_-}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_-^2}$ is 3.0×10^{16} cm^{-2}.

c) The calculated results for cases a) and b) indicate that an optimum fit with the observed data requires a value of y_{min} greater than 17 Å and a value of Ω_- greater

FIGURE IV-2

Fraction of Electrons Scavenged at Various Concentrations of the Fluorinated Additives

A. Calculated Curves

———————— Freeman's distribution with y_{min} = 10 Å
$\Omega_{\text{optimum}} = 7.0 \times 10^{-6}$ cm

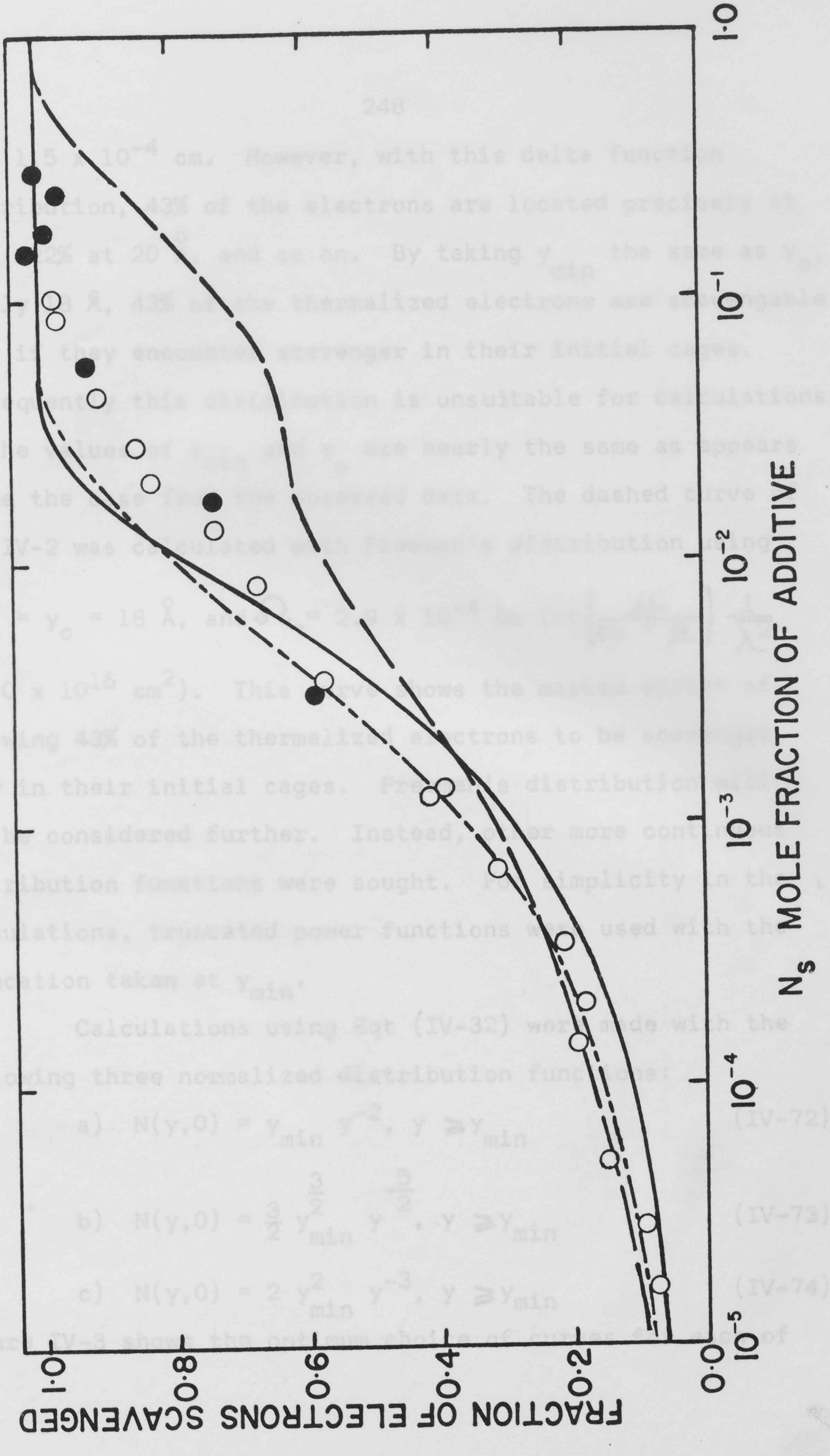
— — — — — Freeman's distribution with y_{min} = 17 Å
$\Omega_{\text{optimum}} = 1.5 \times 10^{-4}$ cm

- - - - - - - Freeman's distribution with $y_{min} = y_o$ = 18 Å, $\Omega_{\text{optimum}} = 2.9 \times 10^{-4}$ cm

B. Observed Scavenging of a Hydrogen Precursor

○ SF_6 - c-C_5H_{10} solutions

● c-C_4F_8 - c-C_5H_{10} solutions


FRACTION OF ELECTRONS SCAVENGED
0·0
0·2
0·4
0·6
0·8
1·0
N_s MOLE FRACTION OF ADDITIVE
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1·0

than 1.5 x 10^{-4} cm. However, with this delta function distribution, 43% of the electrons are located precisely at 18 Å, 22% at 20 Å, and so on. By taking y_{min} the same as y_o, namely 18 Å, 43% of the thermalized electrons are scavengable only if they encounter scavenger in their initial cages. Consequently this distribution is unsuitable for calculations if the values of y_{min} and y_o are nearly the same as appears to be the case from the observed data. The dashed curve of Fig IV-2 was calculated with Freeman's distribution using $y_{min} = y_o = 18$ Å, and $\Omega_- = 2.9 \times 10^{-4}$ cm (or $\left(\frac{\mu_-}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_-^2} = 5.0 \times 10^{16}$ cm^2). This curve shows the marked effect of allowing 43% of the thermalized electrons to be scavenged only in their initial cages. Freeman's distribution will not be considered further. Instead, other more continuous distribution functions were sought. For simplicity in the calculations, truncated power functions were used with the truncation taken at y_{min}.

Calculations using Eqt (IV-32) were made with the following three normalized distribution functions:

a) $N(y,0) = y_{min}\, y^{-2},\ y \geq y_{min}$ (IV-72)

b) $N(y,0) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}},\ y \geq y_{min}$ (IV-73)

c) $N(y,0) = 2\, y_{min}^{2}\, y^{-3},\ y \geq y_{min}$ (IV-74)

Figure IV-3 shows the optimum choice of curves for each of

FIGURE IV-3

Fraction of Electrons Scavenged at Various Concentrations of the Fluorinated Additives

A. Calculated Curves:

– – – – – – – $N(y,0) = y_{min}\, y^{-2},\ y \geq y_{min}$

$\Omega_{optimum} = 1.5 \times 10^{-5}$ cm

——————— $N(y,0) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}},\ y \geq y_{min}$

$\Omega_{optimum} = 2.5 \times 10^{-5}$ cm

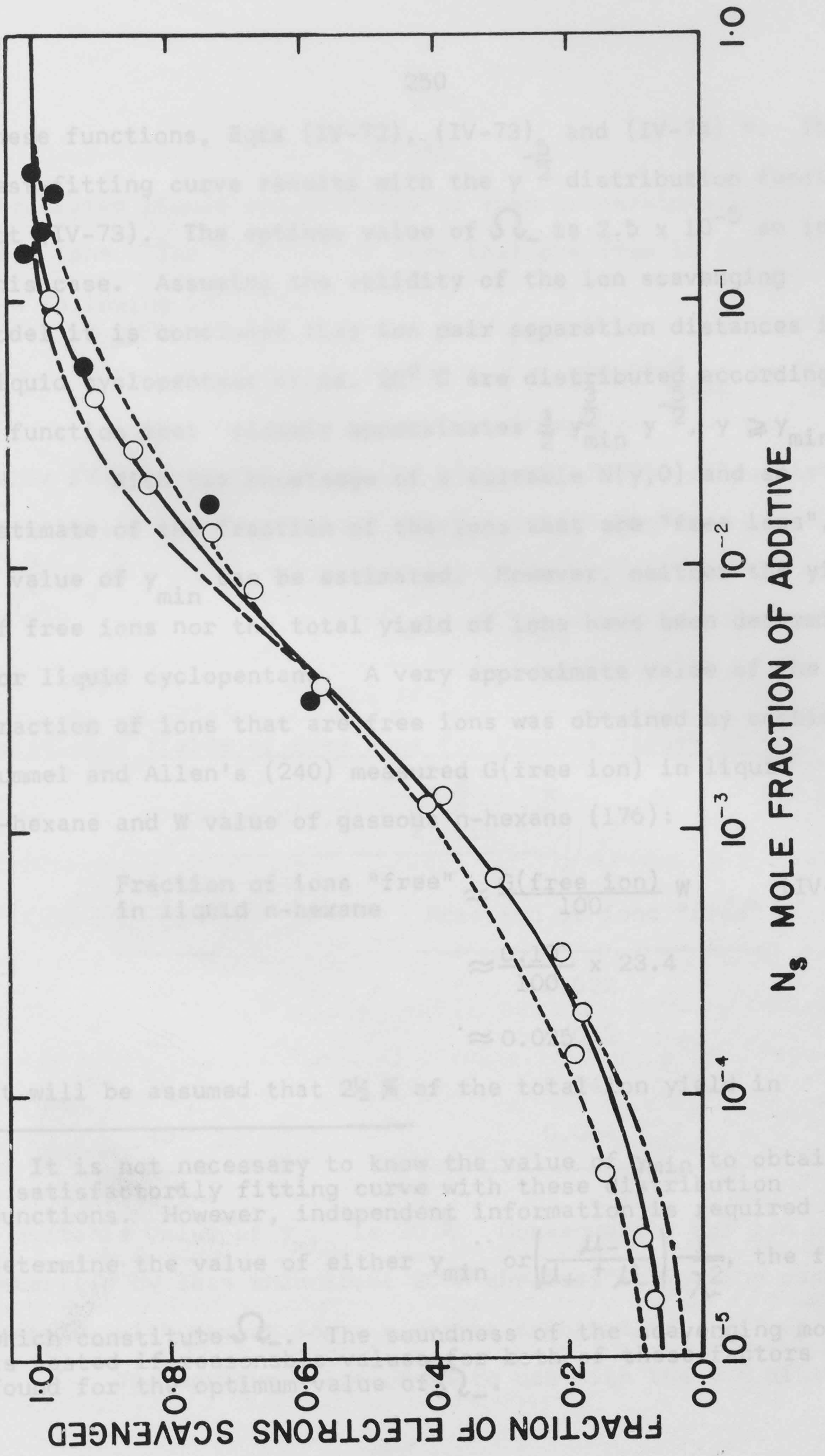
– — – — – — $N(y,0) = 2\, y_{min}^{2}\, y^{-3},\ y \geq y_{min}$

$\Omega_{optimum} = 5.0 \times 10^{-5}$ cm

B. Observed Values of $\frac{\delta(H_2)}{3.4}$:

○ SF_6 - c-C_5H_{10} solutions

● c-C_4F_8 - c-C_5H_{10} solutions



FRACTION OF ELECTRONS SCAVENGED
0·0
0·2
0·4
0·6
0·8
1·0
N_s MOLE FRACTION OF ADDITIVE
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1·0

these functions, Eqts (IV-72), (IV-73) and (IV-74) *. The best-fitting curve results with the $y^{-\frac{5}{2}}$ distribution function, Eqt (IV-73). The optimum value of Ω_- is 2.5×10^{-5} cm in this case. Assuming the validity of the ion scavenging model it is concluded that ion pair separation distances in liquid cyclopentane at ca. 20° C are distributed according to a function that closely approximates $\frac{3}{2}\,y_{min}^{\frac{3}{2}}\;y^{-\frac{5}{2}},\; y \geqslant y_{min}$.

With the knowledge of a suitable $N(y,0)$ and an estimate of the fraction of the ions that are "free ions", a value of y_{min} can be estimated. However, neither the yield of free ions nor the total yield of ions have been determined for liquid cyclopentane. A very approximate value of the fraction of ions that are free ions was obtained by combining Hummel and Allen's (240) measured G(free ion) in liquid n-hexane and W value of gaseous n-hexane (176):

$$\begin{aligned} \text{Fraction of ions "free" in liquid n-hexane} &\approx \frac{G(\text{free ion})}{100}\,W \qquad \text{(IV-75)} \\ &\approx \frac{0.10}{100} \times 23.4 \\ &\approx 0.025 \end{aligned}$$

It will be assumed that 2½ % of the total ion yield in

---

* It is not necessary to know the value of y_{min} to obtain a satisfactorily fitting curve with these distribution functions. However, independent information is required to determine the value of either y_{min} or $\left(\frac{\mu_-}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_-^2}$, the factors which constitute Ω_-. The soundness of the scavenging model is tested if reasonable values for both of these factors are found for the optimum value of Ω_-.

irradiated liquid cyclopentane at room temperature become free ions. The fraction of ions that are free is given by the following integral:

$$\text{Fraction of ions "free"} = \int_{y_{min}}^{\infty} N(y,0)\,\phi_{esc}\,dy \qquad \text{(IV-76)}$$

Table IV-5 gives values of the integral (IV-76) calculated graphically for four values of y_{min} using $N(y,0) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}$.

TABLE IV-5

Calculated Yields of Free Ions for Various Values of y_{min}

Using $N(y,0) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}$

y_{min}, Å	Fraction of ions "free"
20	0.022
25	0.032
30	0.041
40	0.064

A suitable value of y_{min} is 20 Å. Consequently for ion pairs separated by less than about 20 Å chemical scavenging cannot compete with parent ion - electron combination.

The optimum value of Ω to use with the $y^{-\frac{5}{2}}$ distribution function is 2.5×10^{-5} cm. Since y_{min} is about 20 Å , $\left(\frac{\mu_-}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_-^2}$ is estimated to be about 3.1×10^{15} cm^{-2} in liquid cyclopentane at room temperature. It is not possible with the available data from the cyclopentane results to determine separately either of the ionic mobilities or the mean square displacement per diffusive jump of the electron. However estimates of the ionic mobilities can be made.

Adamczewski's review (249) of the extensive published results on radiation induced conductivity in saturated hydrocarbons shows that the mobility of the negative ion is inversely proportional to the viscosity of the medium and that the ratio $\frac{\mu_-}{\mu_+}$ is about 1.5 ± 0.3 for the hydrocarbons having viscosities in the range 0.3 to 3 cp.* For cyclopentane, which has a viscosity of 0.43 cp at 20° C (250) the data in Fig 3 (b) of reference (249) suggests that μ_- for the thermalized electron may be about $1.0 \pm 0.2 \times 10^{-3}$ $cm^2\ V^{-1}\ sec^{-1}$. Hummel and Allen's value of $\mu_- = 1.3 \times 10^{-3}$ $cm^2\ V^{-1}\ sec^{-1}$ for n-hexane at 24° C with a viscosity of 0.30 cp (251) supports this estimated value of μ_- for the negative species in liquid cyclopentane. Assuming $(\mu_-)_{c\text{-}C_5H_{10}} = 1.0 \times 10^{-3}$ $cm^2\ V^{-1}\ sec^{-1}$, $(\mu_+)_{c\text{-}C_5H_{10}}$ is estimated to be about $\frac{1.0 \times 10^{-3}}{1.5} = 7 \times 10^{-4}$ $cm^2\ V^{-1}\ sec^{-1}$.

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* It was previously noted in the footnote on page 223 that these measured negative ion mobilities might not be associated with thermalized electrons but rather they may be for negative ions formed from impurities in the hydrocarbons. Since there is no information presently available to indicate otherwise, it will be assumed here that these reported mobilities are associated with thermalized electrons.

An approximate value of $(\mu_+ + \mu_-)_{c\text{-}C_5H_{10}}$ at room temperature is 1.7×10^{-3} cm^2 V^{-1} sec^{-1} and a suitable value of $\frac{\mu_-}{\mu_+ + \mu_-}$ for cyclopentane is 0.6. This last result is to be compared with the same ratio for the ions in n-hexane; using Hummel and Allen's measured values of μ_+ and μ_-, $\left(\frac{\mu_-}{\mu_+ + \mu_-}\right)_{n\text{-hexane}}$ $= 0.65$. Since $\left[\left(\frac{\mu_-}{\mu_+ + \mu_-}\right)\frac{1}{\overline{\lambda_-^2}}\right]_{c\text{-}C_5H_{10}}$ is approximately 3×10^{15} cm^2 and $\left(\frac{\mu_-}{\mu_+ + \mu_-}\right)_{c\text{-}C_5H_{10}}$ is about 0.6; $(\overline{\lambda_-^2})^{\frac{1}{2}}$ is about $\sqrt{2} \times 10^{-8}$ cm, ie the mean free path of the electron is estimated to be about $\frac{1}{4}$ of the diameter of a cyclopentane molecule. The frequency of diffusive displacements of the thermalized electron in liquid cyclopentane, $\left(\frac{1}{\tau_1}\right)_-$ is given by the following relation:

$$\left(\frac{1}{\tau_1}\right)_- = \frac{6\,D_-}{\overline{\lambda_-^2}} = \frac{6\,\mu_- RT}{e\,\overline{\lambda_-^2} N_o} \tag{IV-77}$$

where all of the symbols were previously defined. Using the crude estimates made for μ_- and $\overline{\lambda_-^2}$ this frequency is about 9×10^{11} sec^{-1}.

It was previously pointed out that the ion scavenging model implies that chemical scavenging of an electron in liquid cyclopentane cannot compete with electron recapture by a positive ion when the separation distance is less than about 20 Å. It is suggested that for separation distances less than 20 Å electron tunnelling takes place at a higher frequency than the frequency of diffusive displacements of the thermalized electron well separated from its counter ion. A simple model for this quantum mechanical tunnelling in a coulomb field is developed in Appendix E. There it is demonstrated (see Fig E-1) that electrons separated by 20 Å from their counter ions in a medium with a dielectric constant of 1.96, recombine by tunnelling at a frequency of 9×10^{11} $\sec^{-1}$ only if they are in traps less than $\frac{1}{8}$ ev in depth.

Having a suitable form of N(y,0), a value of y_{min}, and a crude estimate of $(\mu_+ + \mu_-)$ for the ions in liquid cyclopentane one can use Eqts (IV-49) and (IV-41) to determine the fraction of all ions surviving a time t after an instantaneous pulse of radiation. For example, the fraction of all ion pairs existing at time t originally had a separation exceeding a distance y(t) given by

$$y(t) = \left(\frac{3\, e(\mu_+ + \mu_-)}{\epsilon} t + y^3_{min}\right)^{\frac{1}{3}} \qquad \text{(IV-78)}$$

Table IV-6 gives values of y(t) determined for several values of t between 10^{-2} and 10^{-5} sec with $(\mu_+ + \mu_-) = 1.7 \times 10^{-3}$ $cm^2\ V^{-1}\ sec^{-1}$, $\epsilon = 1.96$, and $y_{min} = 2.0 \times 10^{-7}$ cm. The fraction of ions that are free was taken as 0.02,ie

$$\int_{y_{min}}^{\infty} N(y,0)\,\phi_{esc}\, dy = 0.02 \qquad \text{(IV-79)}$$

and the following approximation was made for the remaining integral in Eqt (IV-49):

$$\int_{y_{min}}^{y(t)} (1 - \Phi_{esc})\, N(y,0)\, dy \approx 0.98 \int_{y_{min}}^{y(t)} N(y,0)\, dy \qquad \text{(IV-80)}$$

Table IV-6 includes the calculation of the fraction of extant ion pairs for various times using $N(y,0) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}$ and $ak = 10^{6}$ sec^{-1}*. These results are also shown in Fig IV-4. The half-life of the total ion population is estimated to be about 7×10^{-11} sec after a pulse; free ions have a mean lifetime of about 10^{-6} sec after a pulse of about 10^{18} ev gm^{-1}. No direct experimental results are presently available to compare with this predicted decay behavior of the ion population.

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* The procedure used to estimate a value of ak is discussed on pages 220 and 221.

TABLE IV-6

Fraction of Ions Extant for Various Times after an Instantaneous Pulse of Radiation

t (sec)	y(t) (Å)	$0.98\int_{y_{min}}^{y(t)} N(y,0)dy$ [a]	$0.02\left(\frac{akt}{1+akt}\right)$ [b]	Fraction of ions extant at time t
1×10^{-12}	20.2	0.02	0.00	0.98
3×10^{-12}	20.8	0.06	0.00	0.94
1×10^{-11}	22.8	0.16	0.00	0.84
3×10^{-11}	26.7	0.34	0.00	0.66
1×10^{-10}	36.7	0.58	0.00	0.42
3×10^{-10}	49.3	0.73	0.00	0.27
1×10^{-9}	73.0	0.85	0.00	0.15
1×10^{-8}	156	0.96	0.00	0.04
1×10^{-7}	335	0.97	0.00	0.03
1×10^{-6}	722	0.98	0.01	0.01
1×10^{-5}	1550	0.98	0.01_8	0.00_6

a $N(y,0) = \frac{3}{2} y_{min}^{\frac{3}{2}} y^{-\frac{5}{2}}$ and $y_{min} = 2.0 \times 10^{-7}$ cm

b $ak = 10^6$ sec^{-1}

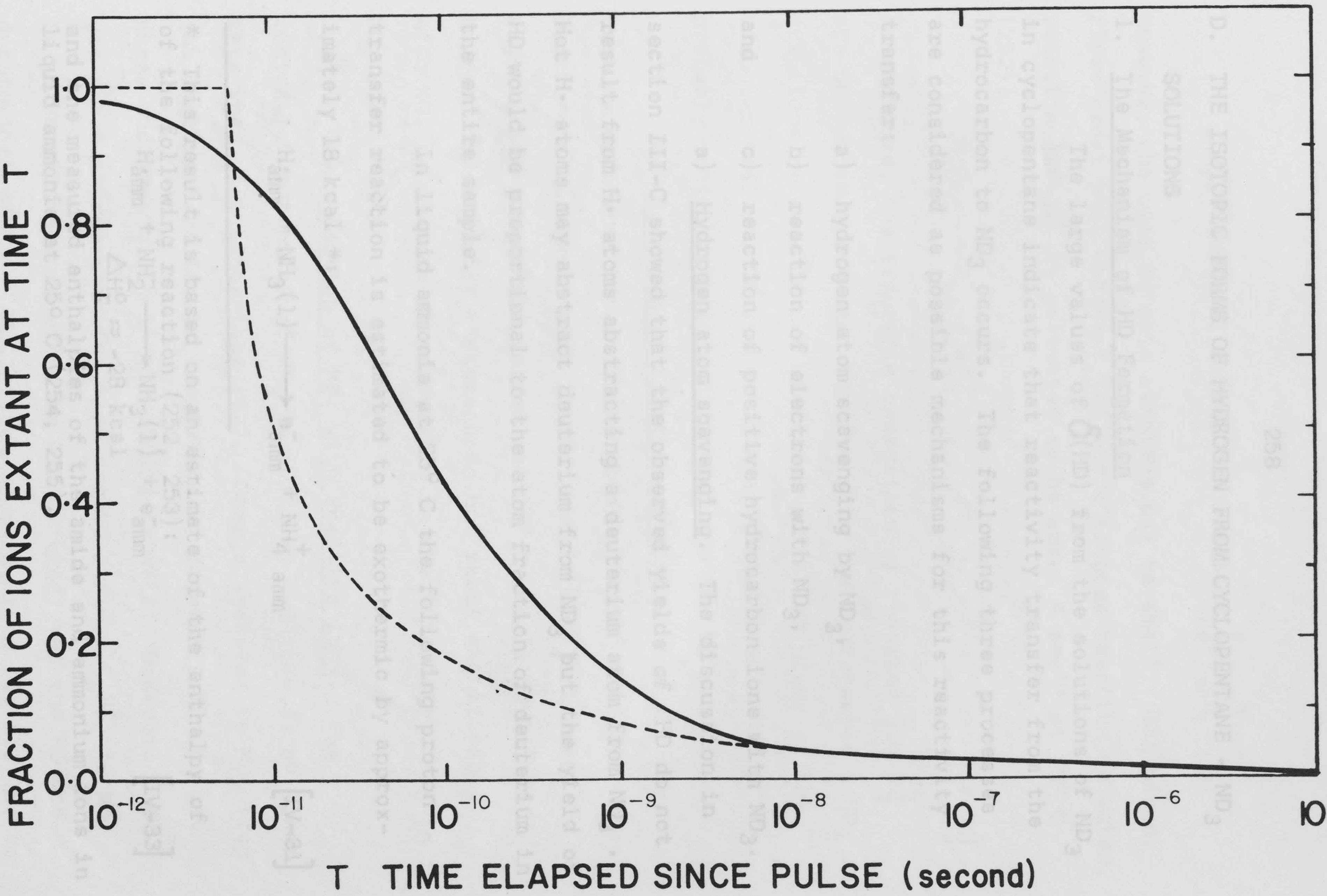
FIGURE IV-4

Fraction of Ion Pairs Extant at Various Times after an Instantaneous Pulse of Radiation

Dose = 1.0×10^{18} ev gm^{-1}

——— Calculated for cyclopentane at 20° C on the basis of $N(y,0) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}$, $y \geq y_{min} = 20$ Å

– – – – – – Calculated by Freeman for cyclohexane at 20° C on the basis of his suggested distribution (personal communication)


FRACTION OF IONS EXTANT AT TIME T
1·0
0·8
0·6
0·4
0·2
0·0
10^{-12}
10^{-11}
10^{-10}
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
T TIME ELAPSED SINCE PULSE (second)

D. THE ISOTOPIC FORMS OF HYDROGEN FROM CYCLOPENTANE - ND_3 SOLUTIONS

1. The Mechanism of HD Formation

The large values of δ(HD) from the solutions of ND_3 in cyclopentane indicate that reactivity transfer from the hydrocarbon to ND_3 occurs. The following three processes are considered as possible mechanisms for this reactivity transfer:

a) hydrogen atom scavenging by ND_3,

b) reaction of electrons with ND_3,

and c) reaction of positive hydrocarbon ions with ND_3.

a) Hydrogen atom scavenging. The discussion in section III-C showed that the observed yields of HD do not result from H· atoms abstracting a deuterium atom from ND_3. Hot H· atoms may abstract deuterium from ND_3, but the yield of HD would be proportional to the atom fraction of deuterium in the entire sample.

In liquid ammonia at 25° C the following proton transfer reaction is estimated to be exothermic by approximately 18 kcal *:

$$H\cdot_{amm} + NH_3(l) \longrightarrow e^-_{amm} + NH^+_{4\ amm} \qquad [IV\text{-}31]$$

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* This result is based on an estimate of the enthalpy of of the following reaction (252, 253):

$$H_{amm} + NH_2^- \longrightarrow NH_3(l) + e^-_{amm} \qquad [IV\text{-}33]$$

$$\Delta H^o_r \approx -28 \text{ kcal}$$

and the measured enthalpies of the amide and ammonium ions in liquid ammonia at 25° C (254, 255).

$$\Delta H_r^o \approx -18 \text{ kcal mole}^{-1} \text{ for reaction } [\text{IV-31}]$$

However, the rate of this reaction may be small. The pseudo first order rate constant for the analogous reaction in water, reaction [IV-32] is estimated to be about 4 sec^{-1} at 25° C (252):

$$H^{\cdot}_{aq} \longrightarrow H^{+}_{aq} + e^{-}_{aq} \qquad [\text{IV-32}]$$

Furthermore, the favorable energetics of reaction [IV-31] are undoubtedly affected adversely in the hydrocarbon - ND_3 solutions because of the decreased solvating power of the nonpolar medium. Consequently hydrogen atom scavenging probably contributes insignificantly to the HD production.

b) Reaction of Electrons with ND_3. Ammonia does not capture electrons in an alkane glass at -196° C (256). The solvated electron in pure liquid ammonia does not react significantly with the solvent at 20° C over a period of hours. Consequently electrons do not react significantly with ND_3 to produce HD precursors in the irradiated c-C_5H_{10} - ND_3 solutions.

c) Reaction of ND_3 with Positive Ions. The ionization potential of NH_3 is 10.15 ev (257), 0.37 ev lower than that of cyclopentane (91). Charge transfer to ND_3 from the cyclopentane ion is energetically favorable in the gas phase and presumably in the liquid as well. However, the gas phase charge transfer from ground state c-$C_6H_{12}^+$ to ND_3 is an endothermic reaction by 0.3 ev (258) yet the HD production in the c-C_6H_{12} - ND_3 system appears, from Fig III-12, to be slightly more efficient than the HD production in the $c\text{-}C_5H_{10} - ND_3$ solutions. Consequently charge transfer from cyclopentane ion to ND_3 is an unlikely process for HD production.

As previously stressed, a reaction with favorable energetics does not necessarily occur at a fast rate. For example, Yang and Marcus (258) found no reactivity transfer from water to cyclopentane in a vapor-phase radiolysis experiment yet the ionization potential of water is about 2 ev higher than that of cyclopentane. Thus charge transfer appears to be relatively slow in these systems even for energetically favorable reactions.

Carbonium ions can react with ammonia either by a Lewis acid-base reaction,

$$R^+ + NH_3 \longrightarrow RNH_3^+ \qquad [IV\text{-}34]$$

or by a Brønsted acid-base reaction,

$$R^+ + NH_3 \longrightarrow R(-H) + NH_4^+ \qquad [IV\text{-}35]$$

where R(-H) is an olefin. For example, the proton affinity of cyclopentene is estimated to be about -172 kcal mole^{-1} * while that of ammonia is about -202 kcal mole^{-1} (262). Thus a proton transfer from cyclopentyl carbonium ion to ammonia is exothermic by about 30 kcal mole^{-1}. However, congruent

---

* This value of the proton affinity of cyclopentene is based on an ionization potential of the cyclopentyl radical of 7.79 ev (259), $\Delta H_f^o(c\text{-}C_5H_8)$ = 7.9 kcal mole^{-1} (260), a BDE$(c\text{-}C_5H_9\text{-}H)$ = 93 kcal mole^{-1} (261), and $\Delta H_f^o(c\text{-}C_5H_{10})$ = -18.5 kcal mole^{-1} (260).

carbonium ions occur with only minor yields, if at all, in liquid-phase alkane radiolysis (131). Also, since a maximum of 20% of the cyclopentane ions fragment in the liquid-phase radiolysis, fragment carbonium ions and any resulting ammonium ions are produced only in monor yields, if at all. Consequently ammonium ion formation via a reaction of ND_3 with carbonium ions is probably an insignificant process for HD formation in the irradiated $c\text{-}C_5H_{10}$ - ND_3 solutions.

Busler et al (263) pointed out that the proton affinity of the cyclohexyl radical is less than that of ammonia. These workers suggest that the following reaction occurs in irradiated liquid-phase cyclohexane solutions of ND_3:

$$c\text{-}C_6H_{12}^{+} + ND_3 \longrightarrow c\text{-}C_6H_{11}^{\cdot} + ND_3H^{+} \qquad [IV\text{-}36]$$

$$\Delta H_r^o \approx -22 \text{ kcal mole}^{-1}$$

An analogous reaction with cyclopentane ion and ND_3 has favorable energetics:

$$c\text{-}C_5H_{10}^{+} + ND_3 \longrightarrow c\text{-}C_5H_9^{\cdot} + ND_3H^{+} \qquad [IV\text{-}37]$$

$$\Delta H_r^o \approx -37 \text{ kcal mole}^{-1}$$

The heats of reactions [IV-36] and [IV-37] were estimated from the following data:

a) The proton affinity of ND_3 is assumed to be the same as that of NH_3 which is taken as -202 kcal mole^{-1} (262).

b) The proton affinity (PA) of the cyclohexyl radical is given by the following relation *:

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* PA, BDE, and IP denote proton affinity, bond dissociation energy, and ionization potential, respectively.

$$\mathrm{PA}(c\text{-}C_6H_{11}^{\cdot}) = \mathrm{IP}(c\text{-}C_6H_{12}) - \mathrm{BDE}(c\text{-}C_6H_{11}\text{-}H) + \mathrm{IP}(H\cdot)$$
$$\approx -180 \text{ kcal mole}^{-1} \qquad (\text{IV-81})$$

The following values for the quantities are involved in this calculation:

$\mathrm{IP}(c\text{-}C_6H_{12}) = 9.88$ ev (91) or 288 kcal mole^{-1},

$\mathrm{BDE}(c\text{-}C_6H_{11}\text{-}H) = 94$ kcal mole^{-1} (261),

and $\mathrm{IP}(H\cdot) = 13.6$ ev or 314 kcal mole^{-1}.

c) Using relation (IV-81) the value of the PA $(c\text{-}C_5H_9^{\cdot})$ is -165 kcal mole^{-1} if the $\mathrm{IP}(c\text{-}C_5H_{10}) = 10.5$ ev (91) and the $\mathrm{BDE}(c\text{-}C_5H_9\text{-}H) = 93$ kcal mole^{-1} (261).

A plausible mechanism for HD formation in the $c\text{-}C_5H_{10}$ - ND_3 solutions is a proton transfer from cyclopentane ion to ND_3 followed by the neutralization of the ammonium ion by an electron to give a hydrogen atom (D· or H·). Any resulting D· atoms would preferentially abstract H· atoms from cyclopentane to form HD. The following set of reactions form the basis of the proton transfer mechanism:

$$c\text{-}C_5H_{10} \rightsquigarrow \left[c\text{-}C_5H_{10}^{+},\ e^{-},\ \text{other intermediates}\right] \qquad [\text{IV-38}]$$

$$\left[c\text{-}C_5H_{10}^{+} + e^{-}\right] \longrightarrow \text{products} \qquad [\text{IV-39}]$$

$$\longrightarrow c\text{-}C_5H_{10}^{+} + e^{-}\ (\text{free ions}) \qquad [\text{IV-40}]$$

$$\left[c\text{-}C_5H_{10}^{+} + ND_3\right] \longrightarrow \left[c\text{-}C_5H_9^{\cdot} + ND_3H^{+}\right] \qquad [\text{IV-41}]$$

$$c\text{-}C_5H_{10}^{+} + ND_3 \longrightarrow c\text{-}C_5H_9^{\cdot} + ND_3H^{+} \qquad [\text{IV-42}]$$

$$\left[ND_3H^{+} + e^{-}\right] \longrightarrow \left[ND_2H + D\cdot\right] \qquad [\text{IV-43a}]$$
$$\longrightarrow \left[ND_3 + H\cdot\right] \qquad [\text{IV-43b}]$$

$$ND_3H^+ + e^- \longrightarrow ND_2H + D\cdot \qquad [IV\text{-}44a]$$

$$ND_3H^+ + e^- \longrightarrow ND_3 + H\cdot \qquad [IV\text{-}44b]$$

$$H\cdot + c\text{-}C_5H_{10} \longrightarrow H_2 + c\text{-}C_5H_9^{\cdot} \qquad [IV\text{-}45]$$

$$D\cdot + c\text{-}C_5H_{10} \longrightarrow HD + c\text{-}C_5H_9^{\cdot} \qquad [IV\text{-}46]$$

Species in brackets are assumed to be in spurs.

2. Ammonium Ion Exchange and a Kinetic Isotope Effect in the Decomposition of Ammonium Ions

If the first formed ammonium ions from reactions [IV-41] and [IV-42] encounter other ND_3 molecules before neutralization, ion solvation may occur as well as the following exchange reaction:

$$ND_3H^+ + ND_3 \longrightarrow ND_2H + ND_4^+ \qquad [IV\text{-}47]$$

In the absence of exchange, neutralization of ammonium ions can produce H· atoms and D· atoms, the relative yields of which depend on the statistical factor, 1:3 representing the isotope ratio in the ion, and on any kinetic isotope effect for the nitrogen - hydrogen bond cleavage. The observed values of δ(HD) can only be related to the extent of cyclopentane ion scavenging by ND_3 if information is available on the extent of the exchange reaction [IV-47] and the magnitude of any kinetic isotope effects. A normal isotope effect in the hydrogen ion transfer reaction [IV-47] would reduce the apparent rate of exchange. Only if the exchange reaction [IV-47] is complete for all first formed ammonium ions, will the values of $G(HD)$ equal the yield of scavenged cyclopentane ions.

These problems associated with exchange and isotope effects are not solved at the present time but the few results obtained from the $c\text{-}C_6H_{12}$ - ND_3 and the $c\text{-}C_6D_{12}$ - NH_3 systems give some information about them. In these systems it can be assumed that the G values of the perprotio- and perdeuterio-cyclohexane ions are equal (264, 265). Consequently, for a given concentration of the two kinds of ammonia the yields of the ammonium ions in each system are approximately equal. If the ammonium ion exchange reaction is complete only ND_4^+ ions and NH_4^+ ions are neutralized by electrons in the respective systems. Under these conditions the values of $G(HD)$ with the $c\text{-}C_6H_{12}$ - ND_3 solutions should equal the values of $G(H_2 + HD)$ with the $c\text{-}C_6D_{12}$ - NH_3 solutions. The ratio

$$R = \frac{\left[G(H_2 + HD)\right]_{c\text{-}C_6D_{12} - NH_3}}{\left[G(HD)\right]_{c\text{-}C_6H_{12} - ND_3}}$$

for two concentrations of ammonia ($N_{ND_3} = N_{NH_3}$) are given in Table IV-7 *. The values of R, which differ from unity, indicate that the exchange reaction [IV-47] and its counterpart for the NH_3D^+ ion are not complete at ammonia concentrations between 4×10^{-3} and 1×10^{-2} mole

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* The values of $G(H_2 + HD)$ were obtained from Table III-7 and the values of $G(HD)$ for the $c\text{-}C_6H_{12}$ - ND_3 system were obtained from Fig III-13 by interpolation.

TABLE IV-7

Values of R for Two Ammonia Concentrations

Mole fraction of NH_3 or ND_3	R
4.5×10^{-3}	0.75/0.45 = 1.7
9.9×10^{-3}	0.91/0.66 = 1.4

fraction *. The actual extent of exchange in these systems is not presently known. It is expected, however, that the ammonium ions resulting from the reaction of the hydrocarbon free ions with ammonia are completely exchanged because of their relatively long lifetimes.

Besides revealing an incomplete exchange of the first formed ammonium ions in the two systems, a value of R differing from unity indicates that there is a kinetic isotope effect in the nitrogen - hydrogen bond cleavage upon neutralization of an isotopically mixed ammonium ion. Consider the neutralization of an ND_3H^+ ion by an electron to give an H· atom or a D· atom:

$$ND_3H^+ + e^- \xrightarrow{k_H} ND_3 + H\cdot \qquad \boxed{\text{IV-48a}}$$

$$ND_3H^+ + e^- \xrightarrow[k_D]{} ND_2H + D\cdot \qquad \boxed{\text{IV-48b}}$$

If the relative rate constants for N-H and N-D bond cleavage are k_H and k_D respectively, the ratio of the yields of D·

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* Even if the exchange reaction [IV-47] is negligible the value of R would be unity if there were no isotope effect for the nitrogen - hydrogen bond cleavage.

atoms and H· atoms from an ND_3H^+ ion is

$$\left(\frac{\text{Yield D· atom}}{\text{Yield H· atom}}\right)_{ND_3H^+} = \frac{3\ k_D}{k_H} \qquad \text{(IV-82)}$$

The fraction of neutralizations that give D· atoms is $\frac{3\ k_D}{3\ k_D + k_H}$. Since these D· atoms abstract H· atoms from the perprotio-hydrocarbons the value of δ(HD), in the absence of the exchange reaction [IV-47], is given by

$$\left[\delta(\text{HD})\right]_{\text{no exchange}} = \frac{3\ k_D}{3\ k_D + k_H}(\text{Yield } ND_3H^+) \qquad \text{(IV-83)}$$

However, if the exchange reaction occurs, Eqt (IV-83) is generalized to the following form:

$$\delta(\text{HD}) = \left(\alpha + (1-\alpha)\frac{3\ k_D}{3\ k_D + k_H}\right)(\text{Yield } ND_3H^+) \qquad \text{(IV-84)}$$

where α denotes the fraction of first formed ND_3H^+ ions which are exchanged to ND_4^+ ions. Similarly the value $\delta(H_2 + \text{HD})$ for a $c\text{-}C_6D_{12}$ - NH_3 solution is given by

$$\delta(H_2 + \text{HD}) = \left(\alpha' + (1-\alpha')\ \frac{3\ k_H}{k_D + 3k_H}\right)(\text{Yield } NH_3D^+) \qquad \text{(IV-85)}$$

α and α' are not necessarily the same for equal concentrations of ND_3 and NH_3 in the two systems because there may be an isotope effect in the transfer of a proton or a deuteron from an isotopically mixed ammonium ion to ammonia. Thus the values of R given in Table IV-7 depend upon the degree of exchange, and the kinetic isotope effect ratio $\frac{k_H}{k_D}$:

$$R = \frac{\alpha' + (1-\alpha')\dfrac{3\,k_H}{3\,k_H + k_D}}{\alpha + (1-\alpha)\dfrac{3\,k_D}{k_H + 3\,k_D}} \qquad \text{(IV-86)}$$

If the degree of ammonium ion exchange is assumed to be zero, a lower limit for the kinetic isotope effect $\frac{k_H}{k_D}$ can be calculated from the results in Table IV-7 using Eqt (IV-86). Table IV-8 gives the values of $\frac{k_H}{k_D}$ calculated taking $\alpha = \alpha' = 0$. An isotope effect, $\frac{k_H}{k_D}$, greater than approximately 2 occurs in the decomposition of isotopically mixed ammonium ions.

TABLE IV-8

Limiting Values of $\frac{k_H}{k_D}$ for Two Ammonia Concentrations

Mole fraction of ND_3 or NH_3	Lower limit for $\frac{k_H}{k_D}$
4.5×10^{-3}	2.7
9.9×10^{-3}	1.9

3. The Application of the Ion Scavenging Model

The ion scavenging model is of limited usefulness in interpreting the yields of HD from the c-C_5H_{10} - ND_3 solutions because insufficient information is available on the limiting value of δ(HD) at high concentrations of ND_3. Also the extent of ammonium ion exchange, and the magnitude of the isotope effect in the decomposition of ND_3H^+ ions are not presently known. In the absence of any definite information to the contrary, it is assumed that the G value of acid hydrocarbon ion is 3.4, namely $[\delta(H_2)]_{max}$, the maximum suppression of hydrogen in the c-C_5H_{10} solutions of the fluorinated additives. This one-to-one correspondence between the yield of acid ions and the maximum suppression of H_2 in the c-C_5H_{10} - c-C_4F_8 solutions is chosen since it implies that each acid ion generates one molecule of H_2 (or its equivalent in H_2 precursors) on electron neutralization.

The data on δ(HD) values were treated in two ways: either exchange of first formed ammonium ions was assumed to be complete or it was assumed that no exchange occurs in the solutions and $\frac{k_H}{k_D} = 2$. Table IV-9 gives the values of the fraction of acid ions scavenged under these two conditions for various concentrations of ND_3 assuming G(acid ion)$_{c\text{-}C_5H_{10}}$ = 3.4. Fig IV-5 illustrates the scavenging efficiency under these conditions.

TABLE IV-9

Estimated Scavenging Efficiencies of ND_3 in Liquid Cyclopentane

Mole fraction ND_3	δ(HD)	Fraction of acid ions scavenged if G(acid ion) = 3.4	
		Complete exchange	No exchange and $\frac{k_H}{k_D} = 2.0$
9.8×10^{-2}	1.52	0.45	0.75
7.2×10^{-2}	1.38	0.41	0.68
6.5×10^{-2}	1.29	0.38	0.63
4.8×10^{-2}	1.14	0.34	0.57
4.7×10^{-2}	1.08	0.32	0.53
4.6×10^{-2}	1.23	0.36	0.60
4.3×10^{-2}	1.02	0.30	0.50
2.8×10^{-2}	0.84	0.25	0.42
2.8×10^{-2}	0.82	0.24	0.40
1.8×10^{-2}	0.66	0.19	0.32
1.4×10^{-2}	0.56	0.16	0.27
1.3×10^{-2}	0.53	0.16	0.27
9.9×10^{-3}	0.47	0.14	0.23
8.8×10^{-3}	0.44	0.13	0.22
5.9×10^{-3}	0.34	0.10	0.17
2.7×10^{-3}	0.26	0.076	0.13
1.2×10^{-3}	0.16	0.047	0.078
8.6×10^{-4}	0.12	0.035	0.058
7.9×10^{-4}	0.11	0.032	0.053
6.4×10^{-4}	0.07	0.02	0.04
5.1×10^{-4}	0.11	0.032	0.053
3.5×10^{-4}	0.10	0.029	0.048
2.4×10^{-4}	0.10	0.029	0.048
1.5×10^{-4}	0.076	0.023	0.038
4.6×10^{-5}	0.060	0.018	0.030
2.6×10^{-5}	0.056	0.017	0.028
2.8×10^{-6}	0.028	0.008	0.013

FIGURE IV-5

Fraction of Acid ions Scavenged at Various Concentrations of ND_3

A. Observed Scavenging Results

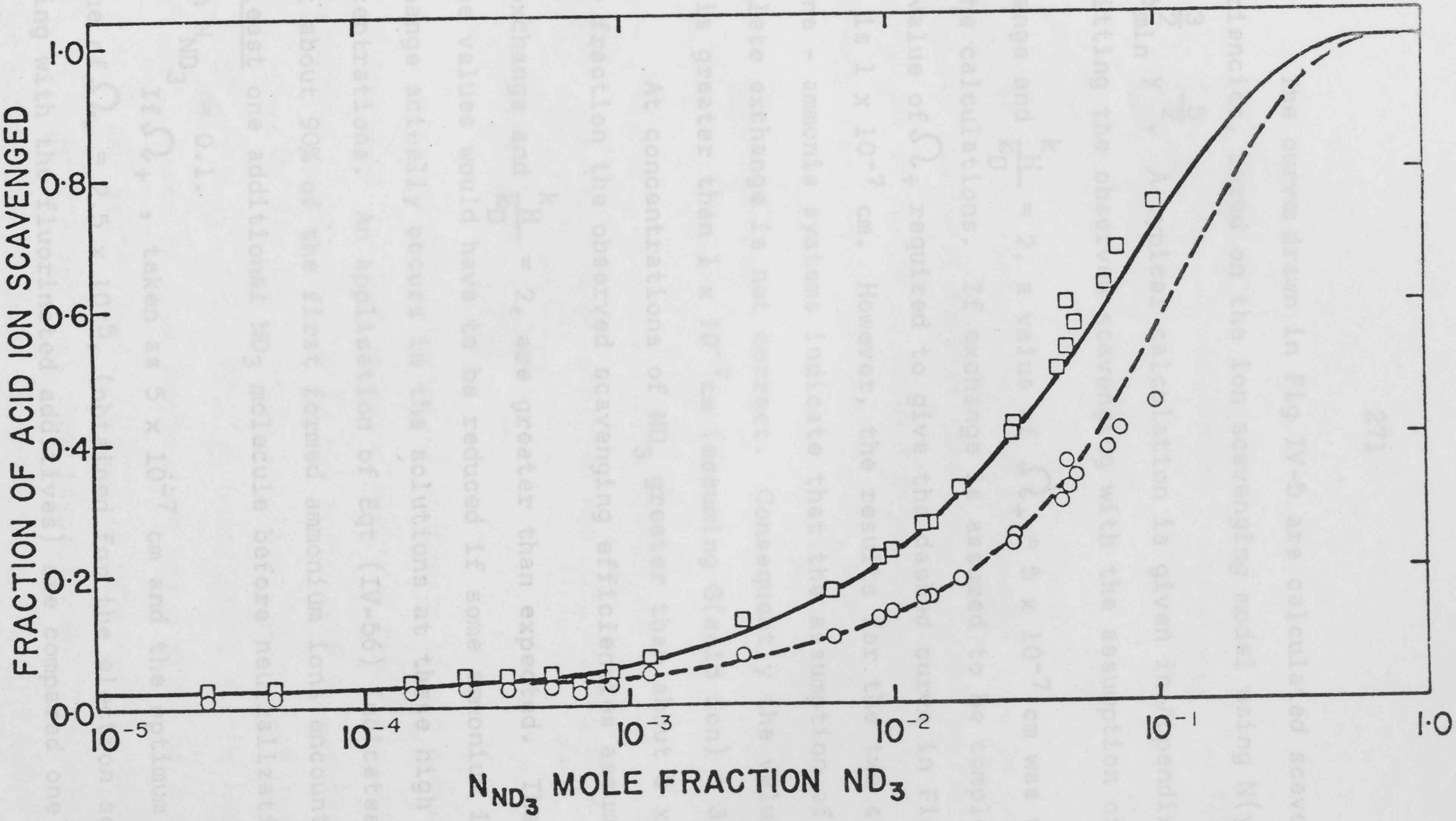
☐ Fraction calculated assuming no exchange, $\frac{k_H}{k_D} = 2.0$, and G(acid ion) = 3.4

○ Fraction calculated assuming complete exchange and G(acid ion) = 3.4

B. Calculated Scavenging Efficiencies Using the Ion Scavenging Model with $N(y,0) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}$, and $y \geqslant y_{min} = 20\ \mathring{A}$

———— $\Omega_+ = 5.0 \times 10^{-7}$ cm

– – – – $\Omega_+ = 1.0 \times 10^{-7}$ cm


FRACTION OF ACID ION SCAVENGED
1·0
0·8
0·6
0·4
0·2
0·0
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1·0
N_{ND_3} MOLE FRACTION ND_3

The curves drawn in Fig IV-5 are calculated scavenging efficiencies, based on the ion scavenging model using $N(y,0) = \frac{3}{2} y_{min}^{\frac{3}{2}} y^{-\frac{5}{2}}$. A typical calculation is given in Appendix D-3. In fitting the observed scavenging with the assumption of no exchange and $\frac{k_H}{k_D} = 2$, a value of $\Omega_+ = 5 \times 10^{-7}$ cm was used in the calculations. If exchange is assumed to be complete the value of Ω_+ required to give the dashed curve in Fig IV-5 is 1×10^{-7} cm. However, the results for the two cyclohexane - ammonia systems indicate that the assumption of complete exchange is not correct. Consequently the value of Ω_+ is greater than 1×10^{-7}cm (assuming G(acid ion) = 3.4).

At concentrations of ND_3 greater than about 5×10^{-2} mole fraction the observed scavenging efficiencies assuming no exchange and $\frac{k_H}{k_D} = 2$, are greater than expected. These large values would have to be reduced if some ammonium ion exchange actually occurs in the solutions at these high ND_3 concentrations. An application of Eqt (IV-56) indicates that about 90% of the first formed ammonium ions encounter <u>at least</u> one additional ND_3 molecule before neutralization when $N_{ND_3} = 0.1$.

If Ω_+ , taken as 5×10^{-7} cm and the optimum value of $\Omega_- = 2.5 \times 10^{-5}$, (obtained for the electron scavenging with the fluorinated additives) are compared one obtains

$$\frac{\left[\left(\frac{\mu_+}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_+^2}\right]_{\text{acid ion scavenging}}}{\left[\left(\frac{\mu_-}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_-^2}\right]_{\text{electron scavenging}}} = \frac{5 \times 10^{-7}}{2.5 \times 10^{-5}} \qquad \text{(IV-87)}$$

$$= 2 \times 10^{-2}$$

If it is assumed that the ratio, $\frac{\mu_-}{\mu_+}$, remains the same for the two scavenger systems, one obtains, from expression (IV-87), the following relation for the primary ions in irradiated cyclopentane:

$$\frac{\mu_-}{\mu_+} \cdot \frac{\overline{\lambda_+^2}}{\overline{\lambda_-^2}} = 50 \qquad \text{(IV-88)}$$

In the discussion of the electron scavenging by the fluorinate additives the value of $\frac{\mu_-}{\mu_+}$ employed was 1.5. Using $\frac{\mu_-}{\mu_+} = 1.5$ in Eqt (IV-88) gives $\left(\frac{\overline{\lambda_+^2}}{\overline{\lambda_-^2}}\right)^{1/2} = 6$.

Ion transport studies of sodium in liquid ammonia at -37° C indicate that the solvated electron has a limiting transference number of 0.86 in the infinitely dilute solution (266). Thus $\frac{\mu_-}{\mu_+}$ for the ions in the liquid ammonia solutions is $\frac{0.86}{1 - 0.86} = 6.1$. The diffusion coefficient of the hydrated electron in water at room temperature has a value of 4.7 ± 0.7×10^{-5} cm^2 sec^{-1} (267). $\mu(e_{aq}^-)$ is consequently about 1.8×10^{-3} cm^2 V^{-1} sec^{-1} at room temperature. The mobility of the sodium ion in water at 25° C is 5.2×10^{-4} cm^2 V^{-1}

sec^{-1} (268). For the hydrated ions

$$\frac{\mu(e^-_{aq})}{\mu(Na^+_{aq})} = 3.5$$

If a value of $\frac{\mu_-}{\mu_+} = 5$ is used for the primary ions in liquid cyclopentane radiolysis then

$\left(\frac{\overline{\lambda^2_+}}{\overline{\lambda^2_-}}\right)^{1/2}$ from relation (IV-88) would be about 3. If in fact, $\frac{\mu_-}{\mu_+} = 5$ is a more realistic value than $\frac{\mu_-}{\mu_+} = 1.5$, the treatment of the decay behavior of the primary ion population, as discussed in section IV-C-3, should be altered; the "non-free ion pairs" would decay faster by a factor of $\frac{6}{2.5}$ or about 2.

E. RADIOLYSIS OF CYCLOPENTANE - BENZENE MIXTURES

The effects of benzene on the radiolysis of cyclopentane are complex; insufficient information is available from the current studies to give a detailed account of the benzene inhibition of cyclopentane product yields.

The value of δ(cyclopentylcyclopentane)$_{max}$ in benzene solutions is 1.3, ie, benzene is able to suppress completely the formation of this product. The following tabulation gives similar data on the other major products.

TABLE IV-10

Values of $\delta(X)_{max}$ for Major Cyclopentane Products

X	$\delta(X)_{max}$	$\frac{\delta(X)_{max}}{G(X)_{c\text{-}C_5H_{10}}}$
Hydrogen	4.9	$>$ 90%
Pentene-1	0.45	~ 60%
Cyclopentene	2.7	$>$ 90%
Cyclopentyl-cyclopentane	1.3	100%

$G(X)_{c\text{-}C_5H_{10}}$ denotes the G value of the product X in pure liquid cyclopentane. Table IV-11 compares the yields of suppressible hydrogen , cyclopentene, and cyclopentylcyclopentane. For solutions containing up to 4 mole % benzene, the values of δ(cyclopentene) + δ(cyclopentylcyclopentane) differ from those of $\delta(H_2)$ by about 0.2, the hydrogen inhibition

TABLE IV-11

Comparison of Suppressible Yields of Hydrogen, Cyclopentene, and Cyclopentylcyclopentane for Various Concentrations of Benzene

Mole fraction benzene	$\delta(H_2)$	$\Sigma = \delta(c\text{-}C_5H_8) + \delta$(cyclopentylcyclopentane)	$\delta(H_2) - \Sigma$	$\frac{\delta(c\text{-}C_5H_8)}{\delta(\text{cyclopentylcyclopentane})}$
0	0	0	0	0
1.0×10^{-2}	0.91	0.64+0.48=1.12	-0.21	1.3
1.7×10^{-2}	1.31	0.96+0.55=1.51	-0.20	1.8
3.7×10^{-2}	1.78	1.22+0.81=2.03	-0.25	1.5
5.8×10^{-2}	2.25	1.44+0.91=2.35	-0.10	1.6
9.6×10^{-2}	2.71	1.62+0.96=2.58	+0.13	1.7
2.1×10^{-1}	3.62	2.18+1.1 =3.3	+0.3	2.0
2.8×10^{-1}	3.92	2.29+1.2 =3.5	+0.4	1.9
4.3×10^{-1}	4.29	2.5 +1.2 =3.7	+0.5	2.1
5.7×10^{-1}	4.5	2.6 +1.3 =3.9	+0.6	2.0
7.8×10^{-1}	4.9	2.6 +1.3 =3.9	+1.0	2.0

being more difficult. At concentrations of benzene greater than about 10 mole %, $\delta(H_2)$ is greater than δ(cyclopentene) + (cyclopentylcyclopentane) by as much as 1.0. The average value of $\frac{\delta(\text{cyclopentene})}{\delta(\text{cyclopentylcyclopentane})}$ is about 1.6 at benzene concentrations below about 10 mole %; at higher concentrations this ratio averages about 2.0. These data suggest that hydrogen, cyclopentene, and cyclopentylcyclopentane result from at least two activated cyclopentane species with distinct susceptibilities to "protection" by benzene.

The rates of reaction of hydrogen atoms and hydrocarbon radicals with benzene in the liquid phase are not presently known. Panfilov and Voedvodskii (269) measured the Arrhenius parameters for the reaction of hydrogen atoms with benzene in the gas phase at about 600° C. by an ESR technique; they suggest that the A factor and E_a for the reaction are 8×10^{10} l mole^{-1} sec^{-1} and 6.4 kcal mole^{-1}, respectively. Consequently at 25° C the rate constant for the reaction of the H· atom with benzene is about 2×10^{6} l mole^{-1} sec^{-1}. This rate constant is not more than an order of magnitude larger than the rate constant of reaction [III-2] at 25° C.

$$H\cdot + c\text{-}C_5H_{10} \longrightarrow H_2 + c\text{-}C_5H_9\cdot \qquad [\text{III-2}]$$

No results were obtained for the consumption of benzene in the current study. However, the results of Burr and Goodspeed (270) and Stone, Dyne, and Bailey (271) indicate that G(-benzene) in cyclohexane solutions containing about 10 mole % of benzene is as large as 1.0. G(-cyclohexane) which is incorporated into products larger than dimers is as large as 2. Thus the relatively small yields of cyclopentylbenzene and cyclopentylcyclohexadienes are not a good measure of the extent of cyclopentyl radical and hydrogen atom scavenging that may occur in these solutions. Short radical or ionic chain polymerization of benzene may occur. For cyclohexane solutions containing between 1% and 10% benzene Burr and Goodspeed (270) noted that the consumption of benzene depends approximately on the square root of the benzene concentration, indicating that ion scavenging may be an important process in the radiolysis of these benzene solutions.

The current radiolysis work suggests that benzene is relatively unreactive towards the cyclopentyl radical. For example, a 4 x 10^{-3} molar cyclopentane solution of iodine gave a limiting value of G(cyclopentylcyclopentane) = 0.17 (93); the same yield of cyclopentylcyclopentane occurs with a 1.3 molar cyclopentane solution of benzene. The concentration of iodine employed to suppress the dimer is not sufficient to interfere appreciably with ionic precursors for the cyclopentyl radical. For example, if iodine is assumed to have the same efficiency for electron scavenging as SF_6, the fraction of electrons scavenged in a 4 x 10^{-3} molar iodine solution (mole fraction $I_2 \approx 4 \times 10^{-4}$) is, from Fig IV-3, about 15%. On the other hand, at the concentrations of benzene used to give G(cyclopentylcyclopentane) = 0.2, benzene probably interferes with the ionic precursors of the cyclopentyl radicals that generate the dimer.

Some possible reactions of benzene with the ionic intermediates will be briefly discussed. Benzene probably does not attach electrons; the gas phase electron affinity of benzene is reported to be negative by about one ev (272). If the proton affinity of benzene is 150 kcal $mole^{-1}$(273), proton transfer from cyclopentane ion to benzene is endothermic *; this reaction is then unlikely to be the cause of the observed reactivity transfer from cyclopentane to benzene. Benzene may react with cyclopentane ion by charge transfer since the ionization potential of cyclopentane is approximately 1.3 ev higher than that of benzene. (IP = 9.24 ev $molecule^{-1}$ (91)).

The G value of hydrogen having cyclopentane ions as precursors is 3.4, as determined from the value of $\delta(H_2)_{max}$ in the $c\text{-}C_5H_{10}$ - $c\text{-}C_4F_8$ solutions. An equal value for the maximum suppression of the hydrogen yield is expected for the complete scavenging of cyclopentane ions by benzene. Fig IV-6 shows the expected hydrogen scavenging efficiency in this case using $\delta(H_2)_{max\ ionic} = 3.4$ and $\Omega_+ = 1 \times 10^{-6}$ cm. The calculations are given in Table IV-12. Clearly, cyclo-

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* The proton affinity of the cyclopentyl radical is about 165 kcal $mole^{-1}$ (p 271).

FIGURE IV-6

Contributions of $\delta(H_2)_{ionic}$ and $\delta(H_2)_{\substack{non\\ionic}}$ to the Total Suppression of Hydrogen by Benzene

○ Observed $\delta(H_2)_{total}$

– – – – – – Calculated $\delta(H_2)_{ionic}$ assuming $\delta(H_2)_{\substack{max\\ionic}} = 3.4$ and $\Omega_+ = 1.0 \times 10^{-6}$ cm

● $\delta(H_2)_{\substack{non\\ionic}} = \delta(H_2)_{total} - \delta(H_2)_{ionic}$

—— – —— – —— – Calculated $\delta(H_2)_{\substack{non\\ionic}}$ assuming activation mechanism with $G(c\text{-}C_5H_{10}^*)_{c\text{-}C_5H_{10}} = 2.0$ and $\frac{k_2}{k_1} = 0.18$

. . . . Calculated $\delta(H_2)_{\substack{non\\ionic}}$ assuming H· atom scavenging mechanism with $G(H\cdot)_{c\text{-}C_5H_{10}} = 2.0$ and $\frac{k'_2}{k'_1} = 1.25$

———————— Calculated total scavenging efficiency, $\delta(H_2)_{total}$, assuming the activation transfer mechanism

—·—·—·—·— Calculated total scavenging efficiency, $\delta(H_2)_{total}$ assuming the H· atom scavenging mechanism

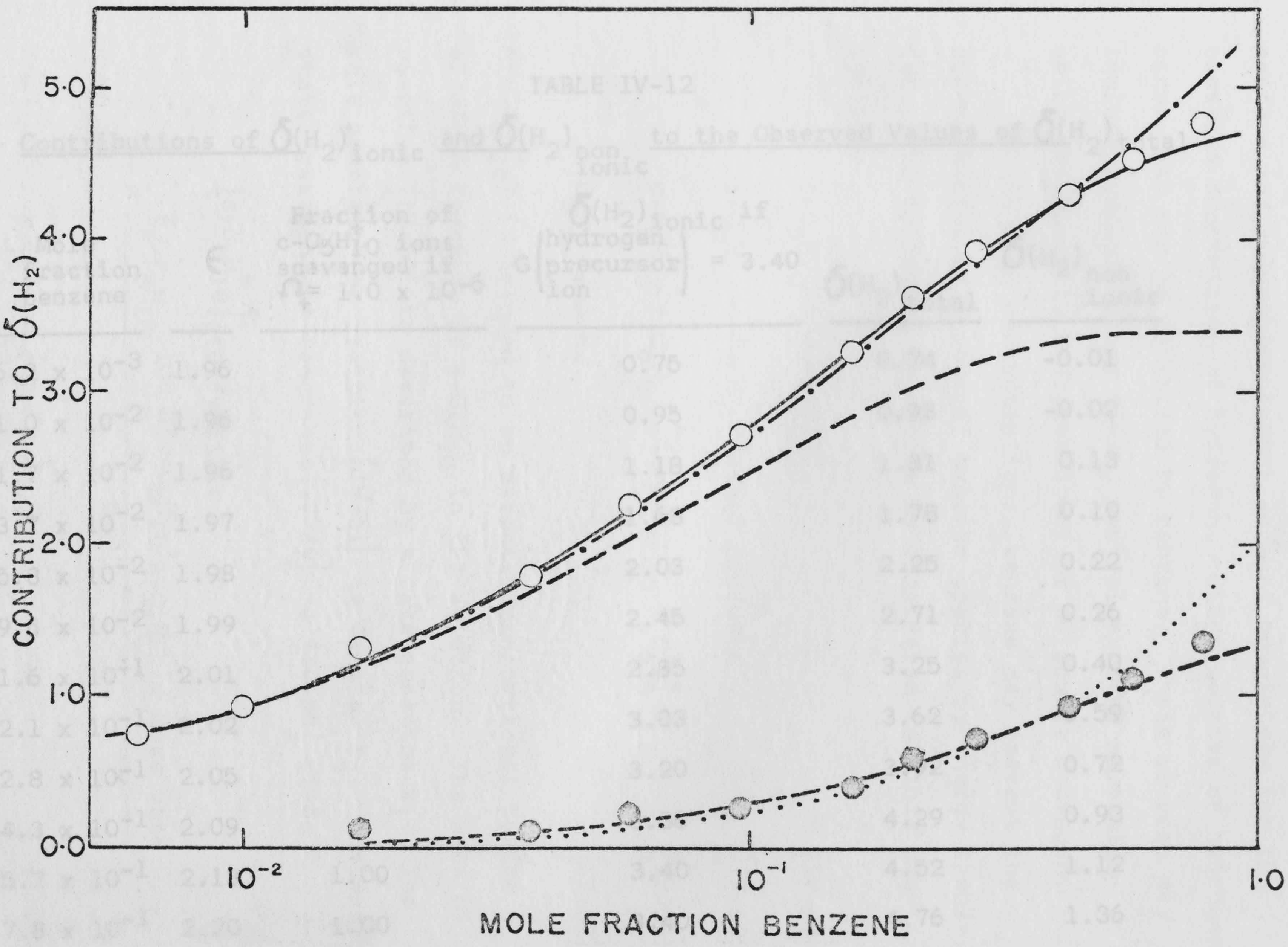
CONTRIBUTION TO G(H₂)
5·0
4·0
3·0
2·0
1·0
0·0
10⁻²
10⁻¹
1·0
MOLE FRACTION BENZENE

TABLE IV-12

Contributions of $\delta(H_2)_{ionic}$ and $\delta(H_2)_{non\ ionic}$ to the Observed Values of $\delta(H_2)_{total}$

Mole fraction benzene	ϵ	Fraction of $c\text{-}C_5H_{10}^+$ ions scavenged if $\Omega_+ = 1.0 \times 10^{-6}$	$\delta(H_2)_{ionic}$ if $G\begin{pmatrix}\text{hydrogen}\\\text{precursor}\\\text{ion}\end{pmatrix} = 3.40$	$\delta(H_2)_{total}$	$\delta(H_2)_{non\ ionic}$
6.2×10^{-3}	1.96		0.75	0.74	-0.01
1.0×10^{-2}	1.96		0.95	0.93	-0.02
1.7×10^{-2}	1.96		1.18	1.31	0.13
3.7×10^{-2}	1.97		1.68	1.78	0.10
5.8×10^{-2}	1.98		2.03	2.25	0.22
9.6×10^{-2}	1.99		2.45	2.71	0.26
1.6×10^{-1}	2.01		2.85	3.25	0.40
2.1×10^{-1}	2.02		3.03	3.62	0.59
2.8×10^{-1}	2.05		3.20	3.92	0.72
4.3×10^{-1}	2.09		3.36	4.29	0.93
5.7×10^{-1}	2.13	1.00	3.40	4.52	1.12
7.8×10^{-1}	2.20	1.00	3.40	4.76	1.36

pentane ion scavenging cannot account completely for the observed suppression of hydrogen. Other sources of hydrogen occur that can be inhibited by benzene. These sources may include hydrogen atoms and/or neutral excited molecules which decompose to hydrogen atoms or molecular hydrogen.

At high concentrations, benzene may prevent the decomposition of a neutral excited species by energy transfer. The following mechanism is considered for this protection:

$$c\text{-}C_5H_{10} \rightsquigarrow c\text{-}C_5H_{10}^* \qquad [IV\text{-}49]$$

$$c\text{-}C_5H_{10}^* \xrightarrow{k_1} H_2 + \text{other products} \qquad [IV\text{-}50]$$

$$c\text{-}C_5H_{10}^* + C_6H_6 \xrightarrow{k_2} c\text{-}C_5H_{10} + C_6H_6^* \qquad [IV\text{-}51]$$

$$C_6H_6^* \not\rightarrow H_2 \qquad [IV\text{-}52]$$

$G(c\text{-}C_5H_{10}^*)$ is assumed to be directly proportional to the electron fraction of $c\text{-}C_5H_{10}$ in the solution. The rate of reaction [IV-50] is described by a rate constant k_1. The rate constant for reaction [IV-51] is denoted k_2. A steady-state treatment of reactions [IV-49] to [IV-52] gives

$$\left[c\text{-}C_5H_{10}^*\right]_{\text{steady-state}} = \frac{\epsilon_{c\text{-}C_5H_{10}}\ 100\ G(c\text{-}C_5H_{10}^*)_{c\text{-}C_5H_{10}} \times \text{dose rate}}{N_o} \times \left(\frac{1}{k_1 + k_2[C_6H_6]}\right) \qquad (IV\text{-}89)$$

$$\frac{d(H_2)_{c\text{-}C_5H_{10}^*}}{dt} = \frac{100\left[G(H_2)_{obs}\right]_{c\text{-}C_5H_{10}^*} \times \text{dose rate}}{N_o} \qquad \text{(IV-90)}$$

But
$$\frac{d(H_2)_{c\text{-}C_5H_{10}^*}}{dt} = k_1\left[c\text{-}C_5H_{10}^*\right]_{\text{steady state}} \qquad \text{(IV-91)}$$

Thus
$$\left[G(H_2)_{obs}\right]_{c\text{-}C_5H_{10}^*} = \frac{k_1\,\epsilon_{c\text{-}C_5H_{10}}\,G(c\text{-}C_5H_{10}^*)_{c\text{-}C_5H_{10}}}{k_1 + k_2[C_6H_6]} \qquad \text{(IV-92)}$$

But
$$\left[G(H_2)_{obs}\right]_{c\text{-}C_5H_{10}^*}$$
$$= \epsilon_{c\text{-}C_5H_{10}}\,G(c\text{-}C_5H_{10}^*)_{c\text{-}C_5H_{10}} - \epsilon_{c\text{-}C_5H_{10}}\,\delta(H_2)_{\substack{\text{non}\\\text{ionic}}} \qquad \text{(IV-93)}$$

where
$$\delta(H_2)_{\substack{\text{non}\\\text{ionic}}} = \delta(H_2)_{\text{total}} - \delta(H_2)_{\text{ionic}} \qquad \text{(IV-94)}$$

Therefore
$$G(c\text{-}C_5H_{10}^*)_{c\text{-}C_5H_{10}} - \delta(H_2)_{\substack{\text{non}\\\text{ionic}}}$$
$$= G(c\text{-}C_5H_{10}^*)_{c\text{-}C_5H_{10}} \times \left(\frac{k_1}{k_1 + k_2[C_6H_6]}\right) \qquad \text{(IV-95)}$$

or
$$\delta(H_2)_{\substack{\text{non}\\\text{ionic}}} = G(c\text{-}C_5H_{10}^*)_{c\text{-}C_5H_{10}}\left(1 - \frac{k_1}{k_1 + k_2\,[C_6H_6]}\right) \qquad \text{(IV-96)}$$

Table IV-13 gives calculated values of $\delta(H_2)_{\substack{\text{non}\\\text{ionic}}}$ for several benzene concentrations using an optimum value of $\frac{k_2}{k_1} = 0.18$ and $G(c\text{-}C_5H_{10}^*)_{c\text{-}C_5H_{10}} = 2.0$. These values of $\delta(H_2)_{\substack{\text{non}\\\text{ionic}}}$ are

TABLE IV-13

Energy Transfer Mechanism

Mole fraction benzene	Molarity benzene	$\frac{k_2}{k_1}[\text{benzene}]$	$\delta(H_2)$ c-$C_5H_{10}^*$
1.7×10^{-2}	0.181	3.26×10^{-2}	0.06
3.7×10^{-2}	0.394	7.10×10^{-2}	0.13
5.8×10^{-2}	0.618	1.11×10^{-1}	0.20
9.6×10^{-2}	1.02	1.84×10^{-1}	0.30
1.6×10^{-1}	1.71	3.07×10^{-1}	0.48
2.1×10^{-1}	2.26	4.07×10^{-1}	0.58
2.8×10^{-1}	3.02	5.45×10^{-1}	0.70
4.3×10^{-1}	4.70	8.46×10^{-1}	0.92
5.7×10^{-1}	6.25	1.12	1.06
7.8×10^{-1}	8.7	1.57	1.22

$\frac{k_2}{k_1} = 0.18$; $G(\text{c-}C_5H_{10}^*) = 2.00$

also shown in Fig IV-6 where a comparison is made with the values of $\delta(H_2)_{total} - \delta(H_2)_{ionic}$.

Hydrogen atom scavenging by benzene at high concentrations will now be considered. The following mechanism is developed to test this possibility:

$$c\text{-}C_5H_{10} \rightsquigarrow H\cdot + \text{other products} \qquad [IV\text{-}53]$$

$$H\cdot + c\text{-}C_5H_{10} \xrightarrow{k_1'} H_2 + c\text{-}C_5H_9^{\cdot} \qquad [IV\text{-}54]$$

$$H\cdot + C_6H_6 \xrightarrow{k_2'} \text{no hydrogen} \qquad [IV\text{-}55]$$

The rate of reaction [IV-54] is described by the rate constant k_1'. The rate constant for the H· atom scavenging reaction [IV-55] involving benzene is denoted by k_2'. A steady-state treatment of reactions [IV-53] to [IV-55] gives:

$$\delta(H_2)_{\substack{non\\ionic}} = G(H\cdot)_{\substack{non\\ionic}} \left(1 - \frac{1}{1 + \frac{k_2'[C_6H_6]}{k_1'[c\text{-}C_5H_{10}]}}\right) \qquad (IV\text{-}97)$$

Table IV-14 gives the calculated values of $\delta(H_2)_{\substack{non\\ionic}}$ calculated by assuming that all the non-ionic hydrogen suppression is due to hydrogen atom scavenging. $G(H\cdot)_{\substack{non\\ionic}}$ is taken as 2.0 and $\frac{k_2'}{k_1'} = 1.25$ gives an optimum fit with the values of $\delta(H_2)_{total} - \delta(H_2)_{ionic}$. These results are also shown in Fig IV-6. The value of $\frac{k_2'}{k_1'} = 1.2$ is unreasonably small for the reactions of thermal hydrogen atoms. This result indicates that epithermal hydrogen atoms may be

TABLE IV-14

H· Atom Scavenging Mechanism

$$\frac{k_2'}{k_1'} = 1.25; \; G(H\cdot)_{c\text{-}C_5H_{10}} = 2.00$$

Mole fraction benzene	Molarity benzene	Molarity $c\text{-}C_5H_{10}$	$\frac{k_2'[C_6H_6]}{k_1'[RH]}$	$1-\frac{1}{1+\frac{k_2'[C_6H_6]}{k_1'[RH]}}$	$\delta(H_2)_{H\cdot}$
1.7×10^{-2}	0.181	10.5	0.0216	0.02	0.04
3.7×10^{-2}	0.394	10.3	0.0479	0.046	0.09
5.8×10^{-2}	0.618	10.1	0.0764	0.067	0.13
9.6×10^{-2}	1.02	9.66	0.131	0.11	0.23
1.6×10^{-1}	1.71	9.02	0.236	0.19	0.38
2.1×10^{-1}	2.26	8.50	0.333	0.25	0.50
2.8×10^{-1}	3.02	7.80	0.482	0.33	0.65
4.3×10^{-1}	4.70	6.22	0.945	0.49	0.98
5.7×10^{-1}	6.25	4.72	1.65	0.62	1.24
7.8×10^{-1}	8.7	2.45	4.44	0.82	1.64

involved in the formation of H_2 that has non-ionic precursors.

Further data are required to interpret the effects of benzene on the liquid product yields. In particular, study is needed of the limiting suppressions of cyclopentene and cyclopentylcyclopentane with ion scavengers that do not result in radical formation from the ions scavenged and that do not interfere with radicals produced in non-ionic processes. If the disproportionation to combination ratio for cyclopentyl radicals is taken as unity (68) then the value of $\delta(c\text{-}C_5H_8)_{\text{max non-radical}}$ is about 1.3 which is approximately the value observed for $\delta(H_2)_{\text{max non-ionic}}$ (ie $\sim$1.5). This result suggests that $c\text{-}C_5H_{10}^*$ may decompose mainly to give molecular hydrogen and cyclopentene. Pentene-1 inhibition shows similar characteristics to the non-ionic hydrogen suppression. Pentene-1 may be formed from a neutral excited species but only about 60% of these may be "protected" by activation transfer to benzene.

F. SUMMARY

The major products and several minor ones in the gamma radiolysis of liquid cyclopentane were determined over a wide dose range at room temperature. The yields of the major products extrapolated to zero dose are $G(H_2)_o = 5.35$, $G(\text{pentene-1})_o = 0.74$, $G(\text{cyclopentene})_o = 2.97$, and $G(\text{cyclopentylcyclopentane})_o = 1.29$. A satisfactory material balance for fragmentation products was observed. The G value for cyclopentane incorporated into a polymeric product is about 0.7 at sample doses above 1×10^{20} ev gm^{-1}, a result which greatly improves the hydrogen material balance. However, further work is required to determine its yield at lower doses as well as a characterization of its chemical structure.

Cyclopentane solutions of additives with three distinctly different effects on the hydrogen yield were studied. For each additive the following processes were considered for their mode of action:

(a) hydrogen atom scavenging,

(b) hydrocarbon positive ion scavenging, in some cases, by H_2 transfer, $H\cdot$ atom transfer, proton transfer, and positive charge transfer,

and (c) electron scavenging.

The effect of each additive was interpreted in terms of a specific interaction with the ionic precursors to the hydrogen yield. A kinetic model for the scavenging of ion pairs produced in saturated hydrocarbons by radiation of low LET was presented. The efficiency of ion scavenging by the additives when examined on the basis of the ion scavenging model gives some information of the type of ions scavenged (positive ion or electron), the distribution of separation distances for ion pairs, and the ionic mobility parameters.

The suppression of the hydrogen yield from cyclopentane by sulfur hexafluoride and octafluorocyclobutane probably results from the scavenging of electrons by these fluorinated additives. The limiting suppression of hydrogen from cyclopentane solutions of octafluorocyclobutane indicates that the G value for hydrogen having ionic precursors is 3.4. The electron scavenging efficiencies of the fluorinated compounds when interpreted on the basis of the ion scavenging model suggest that the ion pair population has a distribution of initial separation distances, N(y,0) which is well approximated by the truncated power function

$$\begin{aligned} N(y,0) &= \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}, \quad y \geqslant y_{min} = 20\ \text{Å} \\ &= 0, \quad y < y_{min} \end{aligned}$$

Addition of ND_3 to cyclopentane produced no change in the total hydrogen yield. The appreciable yields of HD observed were rationalized by a proton transfer mechanism in which a hydrocarbon ion acts as a Brønsted acid toward ammonia. The Brønsted acid ion is probably the cyclopentane ion. The neutralization of the resulting isotopically mixed ammonium ions by electrons to give H· atoms or D· atoms has an isotope effect with a lower limit of about two favoring N—H over N—D bond cleavage. Further work on the extent of the exchange of first formed ammonium ions with ND_3 is required to determine the actual value of the isotope effect and the yield of the hydrocarbon acid ion.

Benzene may suppress the hydrogen yield from cyclopentane by scavenging positive ions through charge transfer and at high benzene concentrations by either the quenching of neutral electronically excited cyclopentane or possibly by hydrogen atom scavenging.

APPENDIX A

Mass Spectral "Cracking Patterns" of Trapped-Off Radiolysis Products *

A. "Condensable Gases" from Pure Cyclopentane

1. Nominal Ethane from Silica Gel Column

m/e	Radiolysis product	API #111 for ethane
12	0.17	0.47
13	0.38	1.06
14	1.46	3.14
15	2.68	4.60
24	0.50	0.51
25	3.16	3.63
26	21.0	23.5
27	30.6	33.6
28	100	100
29	21.0	21.2
30 (p)**	19.7	24.1
31 (i)**	0.42	0.54

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* 70 v scans except where noted.

** (p) and (i) designate parent ion and isotopic ion peaks, respectively

2. Nominal Ethylene from Silica Gel Column

m/e	Radiolysis product	API #23 for ethylene
12	1.21	2.14
13	2.12	3.52
14	4.20	6.31
24	3.64	3.71
25	12.4	11.7
26	61.8	62.3
27	61.8	64.8
28 (p)	100	100
29 (i)	3.03	2.22

3. Nominal Propane from Silica Gel Column

m/e	Radiolysis product	API #3 for Propane
12	0.12	0.37
13	0.30	0.71
14	1.35	2.08
15	2.61	6.19
26	7.21	8.59
27	37.1	39.4
28	63.3(inc N_2)	59.1
29	100	100
30	2.15	2.2
36	0.48	0.52
37	3.29	3.38

3. Nominal Propane from Silica Gel Column (continued)

m/e	Radiolysis product	API #3 for propane
38	5.27	5.29
39	18.0	17.0
40	2.82	2.52
41	15.3	12.7
42	5.61	5.82
43	24.3	22.8
44 (p)	64.8(inc CO_2)	29.0

4. Nominal Acetylene from Silica Gel Column

m/e	Radiolysis product	API #72 for acetylene
12	1.17	2.5
13	3.36	5.6
14	0.22	0.2
24	6.13	5.6
25	21.6	20.1
26 (p)	100	100
27 (i)	2.31	2.8

5. Nominal Cyclopropane

m/e	Product from o-TCP column	Product from Silica gel col.	Authentic sample	API #172 for cyclopropane
26	8	9	7.7	14.8
27	34	28	40.4	38.4

5. Nominal Cyclopropane (continued)

m/e	Product from o-TCP column	Product from silica gel col.	Authentic sample	API #172 for cyclopropane
28	--	air present	--	3.0
36	--	3	2.3	2.1
37	10	14	13.5	11.5
38	15	18	18.3	15.5
39	71	82	82.7	71.3
40	39	30	33.6	32.9
41	100	100	100	91.2
42 (p)	96.6	86	97.3	100
43 (i)	--	--	3.2	3.3

6. Nominal Propylene from Silica Gel Column

m/e	Radiolysis product	API #24 for Propylene
12	1.59	1.26
13	0.64	1.80
14	1.49	3.61
15	2.69	5.40
19	1.96	3.32
19.5 (doubly charged)	1.18	1.96
20	1.33	2.35
25	1.20	2.16
26	6.99	10.5
27	29.6	38.3

6. Nominal Propylene from Silica Gel Column (continued)

m/e	Radiolysis product	API #24 for Propylene
36	2.08	2.42
37	12.1	13.6
38	17.8	19.3
39	78.2	71.1
40	26.0	28.9
41	100	100
42 (p)	67.3	67.7
43 (i)	2.44	2.24

7. Nominal Allene from Silica Gel Column (contains propylene)

m/e	Radiolysis product	Intensity corrected for propylene	API #1134 for Propadiene
12	6.7	7.2	4.09
13	1.8	2.1	3.39
14	6.0	6.5	3.96
15	3.0	2.7	0.28
19	3.0	2.9	3.14
19.5	2.4	2.4	3.89
20	3.0	3.1	3.76
24	1.8	2.1	2.73
25	4.2	4.5	4.60
26	11.5	11.2	4.79
36	8.79	9.48	9.44
37	32.1	33.2	32.56
38	40.3	41.0	40.45
39	100	92.4	96.18
40 (p)	93.9	100	100
41 (i)	25.4	1.38	3.32
42	16.4	0	0.04
43	4.5	0	0

8. Nominal Cyclopentane from Silica Gel Column

m/e	"Radiolysis product"	Research Grade cyclopentane	API #182 for cyclopentane
15	1.0	1.24	3.44
26	1.2	1.91	3.35
27	6.8	10.1	14.7
28	--	--	3.73
29	3.2	4.25	4.56
37	0.8	1.04	1.42
38	1.9	2.43	3.16
39	17.2	18.3	20.9
40	5.5	6.44	7.33
41	28.3	28.4	28.9
42 (p)	100	100	100
43	3.72	3.66	3.35
51	0.87	0.95	0.98
53	1.9	1.93	1.86
54	1.5	1.04	0.91
55	38.7	31.7	29.0
56	1.8	1.50	1.25
67	1.6	1.73	1.51
69	1.2	1.19	1.07
70 (p)	15.7	21.9	29.3
71 (i)	0.86	1.32	1.60

B. "Congruent Liquid Products" from Pure Cyclopentane

1. Nominal n-Pentane from Squalane Column; rerun on o-TCP Column

m/e	Radiolysis product	API #6 for n-pentane
27	28.2	34.6
29	22.0	24.2
39	15.6	14.2
41	37.4	40.5
42	61.2	57.9
43	100	100
57	14.4	12.6
72 (p)	5.8	8.79

2. Nominal Pentene-1 from Squalane Column

m/e	Radiolysis product	API #152 for pentene-1
29	26.9	27.1
39	33.0	34.6
40	7.5	8.55
41	52.4	44.3
42	100	100
43	10.9	4.09
53	5.8	4.93
55	63.8	60.1
56	3.1	2.65
69	1.8	1.68
70 (p)	35.8	30.9
71 (i)	2.2	1.70

3. Nominal Ethylcyclopropane from Squalane Column; rerun on o-TCP Column

m/e	Radiolysis product	Authentic sample	API #1652 for ethylcyclopropane	API #30 for cis-pentene-2
15	6.21	2.78	--	6.03
26	6.38	3.77	7.81	4.73
27	34.3	24.3	34.1	28.7
28	--	5.56	6.56	4.81
29	27.4	20.9	21.8	29.3
37	2.6	2.00	3.00	2.08
38	6.0	3.11	6.17	4.37
39	46.8	29.2	38.0	33.1
40	13.7	9.46	9.10	5.82
41	53.8	40.0	42.3	29.0
42	100	100	100	45.9
43	3.3	4.28	3.76	2.06
50	2.4	1.91	2.88	2.20
51	4.7	2.42	3.30	2.88
53	12.8	5.12	6.29	7.65
55	64.5	48.4	50.2	100
56	5.1	2.21	2.26	4.28
69	4.9	1.14	1.04	2.23
70 (p)	31	21.6	28.1	33.6
71 (i)	3.3	1.3	1.53	1.77

4. Nominal Cyclopentene from Squalane Column

m/e	Radiolysis product	API #208 for cyclopentene
15	1.0	3.21
26	2.3	4.39
27	10.8	14.8
31	2.4	2.43
37	3.1	4.10
38	6.6	8.50
39	31.6	36.4
40	15.3	15.9
41	18.1	19.0
42	8.8	8.38
50	2.2	2.18
51	2.9	2.93
53	23.5	23.4
62	2.2	2.04
63	2.9	2.84
65	7.4	5.12
66	6.0	9.50
67	100	100
68 (p)	40.4	41.6
69 (i)	2.3	2.13

C. "Liquid Products" Having Molecular Weights Greater than 70 from Pure Cyclopentane

1. Nominal Ethylcyclopentane from "Tris" Column

m/e	Radiolysis product (45 v scan)	Authentic sample (45 v scan)	API #184 (50 v scan)
27	18	12.7	37.4
29	17.9	15.0	26.1
39	30.6	27.8	38.0
40	6.1	5.9	7.29
41	105	109	95.5
42	53.2	59.6	52.1
43	10.9	9.64	9.92
53	9.6	6.45	8.07
54	8.0	5.87	7.81
55	70.6	53.5	55.9
56	25.0	39.5	54.1
57	9.3	6.6	7.80
67	19.1	16.0	10.7
68	60.2	57.6	72.6

1. Nominal Ethylcyclopentane from "Tris" Column (continued)

m/e	Radiolysis product (45 v scan)	Authentic sample (45 v scan)	API #184 (50 v scan)
69	100	100	100
70	55.0	55.0	53.9
71	3.4	2.8	2.73
83	7.5	7.3	7.70
98 (p)	4.1	2.6	16.5

2. Nominal Allylcyclopentane from "Tris" Column

m/e	Radiolysis product	Authentic sample	API #1490
26	1.4	1.4	--
27	12.5	11.2	31.2
29	6.1	4.8	7.86
39	27.3	23.2	47.8
40	6.1	4.5	8.71
41	100	100	100
42	12.1	5.5	8.45
43	7.8	2.2	2.09
51	3.5	2.3	5.25
52	4.2	1.4	2.75
53	11.4	7.4	12.4
54	12.9	9.4	11.0
55	9.2	4.7	6.55
65	4.2	3.5	3.93
66	10.3	9.2	14.4
67	67.4	58.8	51.9
68	84.9	83.3	88.8
69	98.0	98.6	96.1
70	7.0	5.3	5.38
79	3.6	2.7	2.88
81	9.0	7.1	7.14
82	7.9	7.0	8.51
95	3.0	2.1	1.97
110 (p)	1.6	0.6	2.95

3. Nominal n-Pentylcyclopentane from "Tris" Column

m/e	Radiolysis product	Authentic sample
39	13.8	13.9
40	3.45	2.75
41	68.6	66.8
42	20.8	21.9
43	27.3	30.8
53	5.30	4.96
54	6.83	6.60
55	72.6	75.0
56	44.7	48.2
57	15.0	16.3
65	1.78	1.34
66	3.08	1.35
67	33.9	19.8
68	73.4	68.8
69	100	100
70	54.5	52.8
71	7.65	8.25
79	1.92	1.15
81	5.34	2.36
82	19.6	19.0
83	43.6	48.2
84	21.8	28.7
85	3.57	4.89
95	4.47	0.67
96	3.77	4.10
97	21.0	25.0
98	8.71	12.0
109	2.16	0.0
110	3.37	1.50
111	12.0	14.3
112	8.25	10.7
140 (p)	5.08	7.08
141 (i)	0.55	0.77

4. Nominal Cyclopentylcyclopentane from "Tris" Column

m/e	Radiolysis product	Authentic sample
27	7.52	9.35
39	13.4	15.3
41	52.8	60.9
53	7.07	7.43
54	8.49	9.35

4. Nominal Cyclopentylcyclopentane from "Tris" Column (continued)

m/e	Radiolysis product	Authentic sample
55	19.8	18.5
66	9.22	9.13
67	93.6	95.7
68	100	100
69	51.7	50.9
70	6.46	4.08
79	7.29	6.09
81	44.2	40.0
82	62.5	54.3
83	14.3	10.7
95	57.3	51.3
96	51.8	40.4
97	7.86	5.50
109	14.8	12.0
110	6.49	4.83
138 (p)	4.88	3.14

5. Nominal 3-Cyclopentylcyclopentene from "Tris" Column

m/e	Radiolysis product (45 v scan)	Authentic sample (70 v scan)
39	19.6	17.1
40	5.0	3.7
41	33.0	35.1
51	1.9	3.1
53	4.8	5.1
55	2.4	2.4
65	10.0	8.1
66	33.8	34.7
67	100	100
68	34.1	38.4
69	11.6	12.6
77	7.4	6.5
79	10.8	9.2
91	6.6	4.2
93	5.2	4.8
94	4.7	4.1
95	16.2	17.7
107	2.3	2.2
121	3.2	2.0
136 (p)	11.8	12.0

D. Product from Benzene - Cyclopentane Solutions

Nominal phenylcyclopentane from Ucon 550LB50 Column

m/e	Radiolysis product	Authentic sample
27	4.37	6.18
29	1.07	1.40
39	11.6	14.4
40	1.41	1.84
41	7.43	8.83
50	2.88	4.02
51	9.22	11.2
52	2.62	3.49
53	1.85	2.32
55	2.01	2.68
58	1.15	1.16
62	1.09	1.55
63	4.51	5.86
65	8.19	8.36
66	1.09	1.22
67	4.76	5.04
68	8.84	9.53
75	1.18	1.57
76	1.66	2.00
77	10.9	11.6
78	14.2	13.8
79	4.24	3.28
89	3.24	3.50
91	42.9	44.1
92	13.8	13.7
102	2.52	3.10
103	10.6	11.2
104	77.9	79.2
105	19.7	19.5
106	1.32	1.04
115	20.5	18.8
116	5.98	6.60
117	100	100
118	22.2	24.4
119	1.74	1.91
128	3.05	2.94
129	1.90	1.71
131	10.7	10.2
145	3.65	3.84
146 (p)	50.0	51.8
147 (i)	5.98	6.28

APPENDIX B

Hydrogen Gas Yields in the Radiolysis of Some Alkanes and Cycloalkanes

When this project on cyclopentane radiolysis was initiated the radiolytic yield of hydrogen obtained did not agree with published values (148, 177). It was uncertain at the time whether the discrepancy resulted, on this worker's part, from insufficiently pure cyclopentane, improper dosimetry, faulty calibration of gas measuring equipment, etc., or from erroneous results in the literature. To check all these factors several highly purified hydrocarbons were irradiated. Where possible, the hydrogen yields obtained were compared with all literature values reported. It was concluded that the $G(H_2)$ originally obtained for cyclopentane in this work was satisfactory. This $G(H_2)$ has since been abundantly corroborated by the subsequent results of many workers (93, 103, 182, 183). Table B-1 lists the $G(H_2)$ for several gas chromatographically purified hydrocarbons at a dose of 2.0 x 10^{19} ev gm^{-1} (except where noted otherwise).

TABLE B-1

Hydrogen Yields in Cycloalkanes

Compound	$G(H_2)$	Dose rate (ev ϵ-mole^{-1} hr^{-1})
spiropentane	0.34	1.02×10^{19}
n-pentane	5.06	7.65×10^{19}
cyclopentane	5.24	7.6×10^{19} to 9.0×10^{19}
cyclohexane	5.72	1.16×10^{19}
cycloheptane	5.89	1.18×10^{19}
cyclooctane	6.30	1.16×10^{19}
cyclodecane	6.34	8.58×10^{19}
n-decane	5.30 (dose of 1.30 $\times 10^{19}$ ev gm^{-1})	1.14×10^{19}

APPENDIX C

Carbene Intermediates in the Gamma Radiolysis of Liquid Cycloalkanes

From their study of liquid cyclohexane containing up to 6% c-C_6D_{12} Dyne and Denhartog (172) suggest that about 6% of the hydrogen yield arises by molecular detachment.(Any isotope effect was not considered.) It is not known if this hydrogen is removed from a single carbon atom of the cyclohexane molecule. The possibility exists that carbenoid intermediates are produced during the radiolysis of alkanes. Vacuum ultraviolet photolysis of suitably labeled cyclohexane has demonstrated that some of the hydrogen is detached molecularly from a single carbon atom to give a carbene (174).

Friedman and Shechter (228)have shown that the aprotic decomposition of cycloalkanone p-tosylhydrazones gives products which arise from the presence of a short-lived cycloalkane carbenoid intermediate. Products from the cyclopentanone and cyclohexanone p-tosylhydrazones gave exclusively (as well as could be measured) the corresponding ring olefins. However, as the cycloalkane ring size increased, products having bridged rings were found. The decomposition of cyclodecanone p-tosylhydrazone gave predominantly bridged bicyclic compounds with a minor yield of the congruent olefins. Product yields for the C_{10}

ring compound were said to be:

cis-decalin, 18%
cis-decahydroazulene, 62%
cis-cyclodecene, 14%
and trans-cyclodecene, 6%

A search for bridged bicyclic compounds was made in the cases of irradiated liquid cyclopentane, cyclohexane, and cyclodecane. This search was undertaken primarily for two reasons:

a) the bridged-ring compounds are hydrogen deficient relative to the parent cycloalkane. The presence of this class of compounds as radiolysis products would improve the product material balance.

b) the presence of bridged-ring compounds would indicate the occurrence of carbenoid intermediates similar to those present in the aprotic decompostion of the p-tosylhydrazones.

The isotopic composition of radiolytic hydrogen is not easily interpreted in condensed phase systems because of possible cage effects influencing the reactions of atomic hydrogen. For example,

$$RH \rightsquigarrow \left[R\cdot + H\cdot\right] \longrightarrow R(-H) + H_2 \qquad [C\text{-}1]$$

$$\longrightarrow R\cdot + H\cdot \qquad [C\text{-}2]$$

or

$$RH \rightsquigarrow \left[R^1(-H) + 2H\cdot\right] \longrightarrow R^1(-H) + H_2 \qquad [C\text{-}3]$$

where species in brackets occur in the same cage, and R(-H) and R^1(-H) are olefins or olefin precursors (eg. carbenes). If the tendency for bridged-ring formation is characteristic of the large ring carbenes then the presence of the bicyclic compounds in, for example, irradiated cyclodecane would give a measure of the yield of such intermediates.

Bicyclo[2·1·0]pentane was undetectable gas chromatographically (on the squalane column) in a cyclopentane sample irradiated to a dose of 3.5×10^{20} ev gm^{-1}. Thus, at this dose, G(bicyclo[2·1·0]pentane) is less than 0.01.

In cyclohexane irradiated to 4×10^{20} ev gm^{-1} bicyclo[3·1·0]hexane was detectable on the "Tris" column with a 100 ev yield of about 0.01. The identity of the bicyclic compound was confirmed by a comparison of retention times of the nominal compound and the authentic hydrocarbon on the "Tris" column and on the silver nitrate - propylene glycol column. The mass spectrum of the collected peaks of the radiolysis product from the two gas chromatograph columns is shown in Table C-1 where a comparison is made with the cracking patterns of authentic bicyclo[3·1·0]hexane, cyclohexene, and cyclohexane. A search for other bridged-ring hydrocarbons related to cyclohexane, for example, bicyclo[2·2·0]hexane and bicyclo[2·1·1]hexane was not pursued.

The yields of cis-decalin and cis-decahydroazulene in irradiated cyclodecane were too low to detect gas chromatographically in a sample receiving 2.2×10^{20} ev

TABLE C-1

Mass Spectrum of Nominal Bicyclo [3·1·0]hexane from Irradiated Cyclohexane

Material m/e	Trapped peak	Authentic bicyclo [3·1·0] hexane	Cyclohexene (API#209)	Cyclohexane (API#118)
26	2.64	3.82	5.68	4.64
27	15.8	15.4	28.7	30.4
28	6.26	6.90	8.06	14.1
29	3.79	3.70	3.32	12.0
38	2.58	3.57	4.81	2.41
39	36.8	40.3	41.3	28.8
40	4.25	5.59	5.64	6.45
41	42.4	46.8	40.4	65.1
42	4.60	4.82	2.96	30.1
50	3.66	5.73	6.36	2.12
51	5.95	6.95	9.49	3.33
52	2.95	4.22	4.82	1.39
53	11.1	11.3	13.2	5.04
54	63.1	71.3	80.0	7.07
56	1.03	1.59	0.45	100
65	5.60	5.86	3.43	0.75
66	2.32	3.32	2.52	0.37
67	100	100	100	3.26
68	6.05	7.45	5.38	1.84
77	4.47	5.36	4.92	0.79
79	7.22	6.18	6.13	0.53
81	9.60	13.7	10.8	0.47
82	17.8 (p)	18.0 (p)	38.0 (p)	0.22
83	1.18(i)	2.04(i)	2.45(i)	4.61
84	--	--	--	74.9 (p)

gm^{-1}. One microlitre aliquots of the irradiated cyclodecane were analysed on a "Tris" column using a hydrogen flame detector *. The 100 ev yields of the bridged bicyclic hydrocarbons appeared to be less than 0.05. G(total olefin) was determined by the bromine titration technique to be 4.2.

Although a fraction of the radiolytic hydrogen yield appears to arise by molecular detachment from a single carbon atom of a cycloalkane, the fate of any resulting carbene is not certain. For gas phase reactions of carbenes the source of the intermediate and the gas pressure have an effect on the distribution of products. Yields of carbene insertion products increase (here congruent olefins are not considered as insertion products)as the excess energy in the carbene diminishes and also when collisional deactivation is enhanced (274). The photolysis of isobutane at 1470 Å produces only small amounts of methylcyclopropane that probably result from intramolecular insertion of the butylidene intermediates. For example, the ratio of isomerization of isobutylidene into isobutene to intramolecular cyclization was found under optimum conditions ** to be 19:1 (275). On the other hand,

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* I am indebted to Wm. Holtslander for assistance with these analyses.

** The excitation energy of the methylcyclopropane may be as high as 157 kcal in these experiments. High pressures of substrate or dilution with large amounts of nitrogen were conducive to higher yields of methylcyclopropane.

isobutylidene generated by the liquid phase decomposition of the p-tosylhydrazone of isobutanal gave 62% isobutene and 38% methylcyclopropane (276). It is believed that a more valid interpretation can be made by comparing liquid phase radiolysis yields with carbene reaction product yields generated in solution rather than in the gas phase. The yields of bridge-ring compounds is so small in the case of cycloalkane radiolysis that they have no bearing on the material balance. The low yields of such compounds in irradiated cyclodecane indicates a very minor role for carbenoid intermediates in liquid cycloalkane radiolysis. The 100 ev yield of carbene intermediates in irradiated cycloalkanes appears to be less than 0.1.

APPENDIX D

Evaluation of Some Integrals Associated with Ion Scavenging Kinetics *

1. Evaluation of $I_1 + \int_{y_{min}}^{\infty} \left[\frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}\right]\left[1-N_s\right]^b dy$

This integral occurs in Eqt (IV-33) if the distribution of ion pair separation distances is taken as

$$N(y) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}} \qquad \text{(D-1)}$$

Since $(1-N_s)^b = \exp\left[b \ln(1-N_s)\right]$ (D-2)

where $b = (m_1 + 1)\nu$ (D-3)

and $m_1 = \frac{2\epsilon kT}{e^2}\, \frac{1}{\lambda_1^2} \left(\frac{\mu_1}{\mu_1 + \mu_2}\right)\left(y^3 - y_{min}^3\right)$ (D-4)

then $(1-N_s)^b$ can be replaced by

$$(1-N_s)^b = P \exp(-Qy^3) \qquad \text{(D-5)}$$

where $P = \exp\left(\left[1 - \frac{2\epsilon kT}{e^2}\, \frac{1}{\lambda_1^2}\, \frac{\mu_1}{\mu_1 + \mu_2}\, y_{min}^3\right]\nu \ln(1-N_s)\right)$ (D-6)

and $Q = -\frac{2\epsilon kT}{e^2}\, \frac{1}{\lambda_1^2} \left(\frac{\mu_1}{\mu_1 + \mu_2}\right)\nu \ln(1-N_s)$ (D-7)

Now $I_1 = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, P \int_{y_{min}}^{\infty} y^{-\frac{5}{2}} \exp(-Qy^3)\, dy$ (D-8)

Let $Qy^3 = u^2$. Then $y^{-\frac{5}{2}} = \left(\frac{u^2}{Q}\right)^{-\frac{5}{6}}$ and $dy = \frac{2}{3}\,(Q)^{-\frac{1}{2}} \left(\frac{u^2}{Q}\right)^{-\frac{1}{6}}$

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* The symbols used here are defined in Section IV-B-1.

and Eqt (D-8) becomes

$$I_1 = y_{min}^{\frac{3}{2}} P(Q)^{-\frac{1}{2}} \int_{u_{min}}^{\infty} \left(\frac{u^2}{Q}\right)^{-\frac{5}{6}} \exp\left[-u^2\right] \cdot \left(\frac{u^2}{Q}\right)^{-\frac{1}{6}} du \qquad \text{(D-9)}$$

$$= P \left(Qy_{min}^3\right)^{\frac{1}{2}} \int_{u_{min}}^{\infty} u^{-2} \exp(-u^2)\, du \qquad \text{(D-10)}$$

Now

$$\int_{u_{min}}^{\infty} u^{-2} \exp(-u^2)\, du$$

$$= \int_{u_{min}}^{\infty} u^{-2} \left[\exp(-u^2) - 1\right] du + \int_{u_{min}}^{\infty} u^{-2}\, du \qquad \text{(D-11)}$$

$$= \int_{0}^{\infty} u^{-2} \left[\exp(-u^2) - 1\right] du - \int_{0}^{u_{min}} u^{-2} \left[\exp(-u^2) - 1\right] du + \frac{1}{u_{min}} \qquad \text{(D-12)}$$

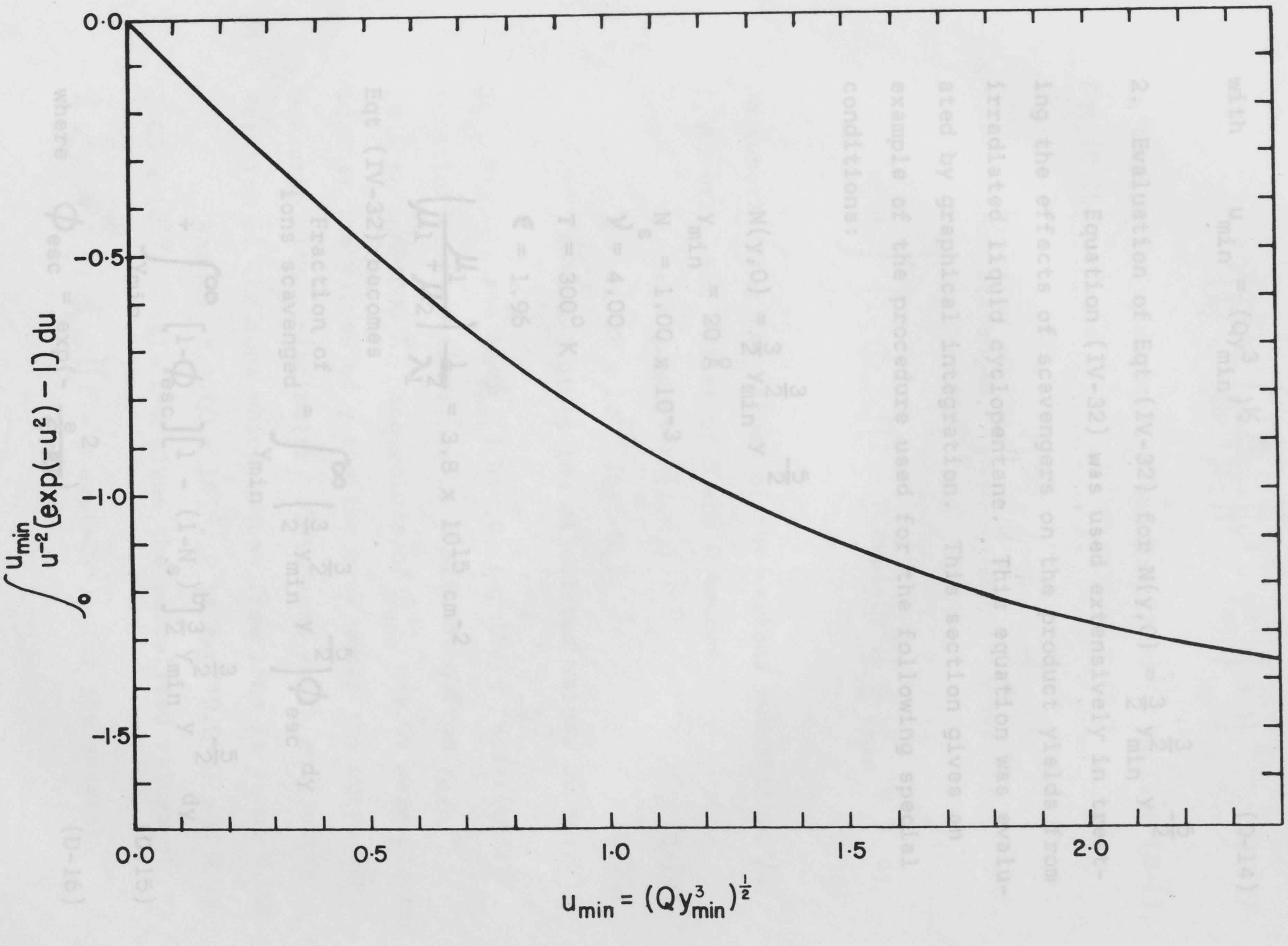
The first integral of the right hand side of Eqt (D-12) is $-\sqrt{\pi}$; $\frac{1}{u_{min}}$ is $(Qy_{min}^3)^{-\frac{1}{2}}$. The remaining integral, $\int_0^{u_{min}} u^{-2}\left[\exp(-u^2) - 1\right] du$, was evaluated graphically for various values of u_{min} between 0.00 and 2.40. The results for this integral are plotted in Fig (D-1). Thus

$$I_1 = P\left[1 - (Qy_{min}^3)^{\frac{1}{2}} \left(\sqrt{\pi} + \int_0^{u_{min}} u^{-2} \left[\exp(-u^2) - 1\right] du\right)\right] \qquad \text{(D-13)}$$

FIGURE D-1

Values of $\int_{0}^{u_{min}} u^{-2} \left[\exp(-u^2) - 1 \right] du$ for Various Values of

$$u_{min} = (Qy^3_{min})^{1/2}$$


$\int_0^{u_{min}} u^{-2}(\exp(-u^2) - 1)\,du$
0·0
-0·5
-1·0
-1·5
0·0
0·5
1·0
1·5
2·0
$u_{min} = (Qy_{min}^3)^{\frac{1}{2}}$

with $$u_{min} = (Qy^3_{min})^{\frac{1}{2}} \qquad \text{(D-14)}$$

2. Evaluation of Eqt (IV-32) for $N(y,0) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}$

Equation (IV-32) was used extensively in treating the effects of scavengers on the product yields from irradiated liquid cyclopentane. This equation was evaluated by graphical integration. This section gives an example of the procedure used for the following special conditions:

$$N(y,0) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}$$

$$y_{min} = 20 \text{ Å}$$

$$N_s = 1.00 \times 10^{-3}$$

$$\nu = 4.00$$

$$T = 300^{\circ}\text{ K}$$

$$\epsilon = 1.96$$

$$\left(\frac{\mu_1}{\mu_1 + \mu_2}\right)\frac{1}{\lambda_1^2} = 3.8 \times 10^{15}\ \text{cm}^{-2}$$

Eqt (IV-32) becomes

$$\begin{aligned}\text{Fraction of ions scavenged} &= \int_{y_{min}}^{\infty}\left(\frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}\right)\phi_{esc}\, dy \\ &+ \int_{y_{min}}^{\infty}\left[1-\phi_{esc}\right]\left[1-(1-N_s)^b\right]\frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}\, dy\end{aligned} \qquad \text{(D-15)}$$

where $$\phi_{esc} = \exp\left(-\frac{e^2}{\epsilon y k T}\right) \qquad \text{(D-16)}$$

and $$b = \nu\left[\frac{2\epsilon kT}{\lambda_1^2\, e^2}\left(\frac{\mu_1}{\mu_1+\mu_2}\right)\left(y^3 - y_{min}^3\right) + 1\right] \qquad \text{(D-17)}$$

In terms of the quantities P and Q defined in section (D-1), Eqt (D-15) becomes

$$\text{Fraction of ions scavenged} = \int_{y_{min}}^{\infty} \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}\, \phi_{esc}\, dy$$

$$+ \int_{y_{min}}^{\infty} \left[1 - \phi_{esc}\right]\left[1 - P\exp(-Qy^3)\right] \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}\, dy \qquad \text{(D-18)}$$

On substituting the values of the various quantities, ν, T, ϵ, etc., the values of P and Q become

$$P = \exp(-78.6)\ \ln(1-N_s) \qquad \text{(D-19)}$$

$$Q = -1.03 \times 10^{22}\ \ln(1-N_s) \qquad \text{(D-20)}$$

Table D-1 gives the calculated values of N(y,0), ϕ_{esc} N(y,0), and $(1-\phi_{esc})$ N(y,0) for the $y^{-\frac{5}{2}}$ distribution function at several values of y extending from y_{min} = 20 Å to y = 1000 Å. The values of ϕ_{esc} N(y,0) were plotted against the values of y and the area under the curve was measured with a planimeter. This area which equals the fraction of the ions which become free ions is about 0.022.

When $N_s = 1.00 \times 10^{-3}$, P is exp(+0.079) and Q is 1.03×10^{19}. Table D-2 gives the calculated values of $\frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}\left[1-\phi_{esc}\right]\left[1 - P\exp(-Qy^3)\right]$ for the several

TABLE D-1

$N(y,0) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}}$; $y_{min} = 20.0$ Å

y(Å)	N(y,0)	$(1-\phi_{esc})$ N(y,0)	ϕ_{esc} N(y,0)
20	7.50×10^{-2}	7.50×10^{-2}	-
21	6.64×10^{-2}	6.64×10^{-2}	-
22	5.91×10^{-2}	5.91×10^{-2}	-
23	5.29×10^{-2}	5.29×10^{-2}	-
24	4.75×10^{-2}	4.75×10^{-2}	-
25	4.29×10^{-2}	4.29×10^{-2}	-
26	3.89×10^{-2}	3.89×10^{-2}	-
27	3.54×10^{-2}	3.54×10^{-2}	-
28	3.23×10^{-2}	3.23×10^{-2}	-
29	2.96×10^{-2}	2.96×10^{-2}	-
30	2.72×10^{-2}	2.72×10^{-2}	1.63×10^{-6}
35	1.85×10^{-2}	1.85×10^{-2}	3.70×10^{-6}
40	1.33×10^{-2}	1.33×10^{-2}	9.28×10^{-6}
45	9.88×10^{-3}	9.86×10^{-3}	1.58×10^{-5}
50	7.59×10^{-3}	7.57×10^{-3}	2.28×10^{-5}
60	4.81×10^{-3}	4.77×10^{-3}	3.80×10^{-5}
70	3.22×10^{-3}	3.17×10^{-3}	5.09×10^{-5}
80	2.34×10^{-3}	2.28×10^{-3}	6.21×10^{-5}
90	1.75×10^{-3}	1.68×10^{-3}	6.91×10^{-5}
100	1.34×10^{-3}	1.27×10^{-3}	7.35×10^{-5}
110	1.06×10^{-3}	9.82×10^{-4}	7.55×10^{-5}
120	8.50×10^{-4}	7.75×10^{-4}	7.56×10^{-5}
150	4.87×10^{-4}	4.17×10^{-4}	7.02×10^{-5}
180	3.09×10^{-4}	2.47×10^{-4}	6.14×10^{-5}
220	1.87×10^{-4}	1.37×10^{-4}	4.99×10^{-5}
280	1.02×10^{-4}	6.60×10^{-5}	3.62×10^{-5}
350	5.99×10^{-5}	3.38×10^{-5}	2.61×10^{-5}
450	3.11×10^{-5}	1.48×10^{-5}	1.63×10^{-5}
550	1.87×10^{-5}	7.67×10^{-6}	1.10×10^{-5}
700	1.02×10^{-5}	4.23×10^{-6}	6.00×10^{-6}
1000	4.23×10^{-6}	1.23×10^{-6}	3.00×10^{-6}

TABLE D-2

Sample Calculation of Scavenging Efficiency

$N_s = 1.00 \times 10^{-3}$, $\ln(1-N_s) = -1.00 \times 10^{-3}$, $y_{min} = 20.0$ Å, $P = \exp(+0.079)$, $Q = 1.03 \times 10^{19}$

y(Å)	Qy^3	$P \exp(-Qy^3)$	$1 - P \exp(-Qy^3)$	$(1 - \phi_{esc}) \times \left\|1 - P \exp(-Qy^3)\right\| \times N(y,0)$
20	0.083	0.996	0.004	3.07×10^{-4}
21	0.096	0.983	0.017	1.13×10^{-3}
22	0.110	0.969	0.031	1.83×10^{-3}
23	0.126	0.954	0.046	2.44×10^{-3}
24	0.143	0.938	0.062	2.96×10^{-3}
25	0.161	0.920	0.080	3.42×10^{-3}
26	0.182	0.902	0.098	3.81×10^{-3}
27	0.204	0.883	0.117	4.16×10^{-3}
28	0.227	0.862	0.138	4.70×10^{-3}
29	0.252	0.841	0.159	5.02×10^{-3}
30	0.279	0.818	0.182	4.95×10^{-3}
35	0.443	0.694	0.306	5.66×10^{-3}
40	0.662	0.558	0.442	5.86×10^{-3}
45	0.941	0.422	0.578	5.70×10^{-3}
50	1.29	0.297	0.703	5.32×10^{-3}
60	2.23	0.116	0.884	4.22×10^{-3}
70	3.55	0.031	0.969	3.07×10^{-3}
80	5.29	0.000	1.000	2.28×10^{-3}
90		0.000	1.000	1.68×10^{-3}
100		0.000	1.000	1.27×10^{-3}
110		0.000	1.000	9.82×10^{-4}
120		0.000	1.000	7.75×10^{-4}
150		0.000	1.000	4.17×10^{-4}
180		0.000	1.000	2.47×10^{-4}
220		0.000	1.000	1.37×10^{-4}
280		0.000	1.000	6.60×10^{-5}
350		0.000	1.000	3.38×10^{-5}
450		0.000	1.000	1.48×10^{-5}
550		0.000	1.000	7.67×10^{-6}
700		0.000	1.000	4.23×10^{-6}

values of y between y_{min} and 1000 Å for $N_s = 1.00 \times 10^{-3}$. This quantity was plotted for each value of y and the area under the curve measured with a planimeter. This area which corresponds to the fraction of "non-free ions" that are scavenged is 0.358. Consequently the fraction of all ions scavenged with $N_s = 1.00 \times 10^{-3}$ is (0.358 + 0.022) or 0.380.

3. Typical Calculations of Ion Scavenging Efficiencies

The following calculations of the fraction of acid ions scavenged by ND_3 are used as examples of one method of estimating scavenging efficiencies. The method is based on Eqt (IV-33) and on the evaluation of I_1 as presented in Appendix D-1.

Part A. Evaluation of Scavenging Efficiency Parameters

Example: $N_{ND_3} = 0.100$

$$\ln(1-N_{ND_3}) = -0.1054$$

$$\epsilon = 1.96\ N_{c\text{-}C_5H_{10}} + 16.9\ N_{ND_3} = 3.45$$

$$N(y,0) = \frac{3}{2}\, y_{min}^{\frac{3}{2}}\, y^{-\frac{5}{2}},\quad y \geq y_{min} = 20\ \text{Å}$$

$$\nu = 4.00$$

Let $$\Omega_+ = \left(\frac{\mu_+}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_+^2}\, y_{min}^3 = 5.00 \times 10^{-7}\ \text{cm}$$

Then $$\frac{2\epsilon kT}{e^2}\left(\frac{\mu_+}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_+^2}\, y_{min}^3 = \frac{2 \times 3.45 \times 1.38 \times 10^{-16}}{(4.80 \times 10^{-10})^2}$$

$$\times\ 300 \times 5.00 \times 10^{-7}$$

$= 0.620$

$$\frac{2\epsilon kT}{e^2}\left(\frac{\mu_+}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_+^2} = 7.75 \times 10^{19}\ \text{cm}^{-3}$$

and
$$\nu\left[1 - \frac{2\epsilon kT}{e^2}\left(\frac{\mu_+}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_+^2}\, y_{\text{min}}^3\right] = 4(1.000 - 0.620)$$
$$= 1.52$$

$$P = \exp\left(\nu\left[1 - \frac{2\epsilon kT}{e^2}\left(\frac{\mu_+}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_+^2}\, y_{\text{min}}^3\right] \ln(1-N_{ND_3})\right)$$
$$= \exp 1.52 \times (-0.105)$$
$$= \exp(-0.160)$$

$$Q = -\frac{2\nu\epsilon kT}{e^2}\left(\frac{\mu_+}{\mu_+ + \mu_-}\right)\frac{1}{\lambda_+^2} \ln(1-N_{ND_3})$$
$$= 4.00 \times (-7.75 \times 10^{19})(-0.105)$$
$$= 3.23 \times 10^{19}\ \text{cm}^{-3}$$

Part B. Evaluation of Scavenging Efficiencies at Various Concentrations of ND_3

N_{ND_3}	$\ln(1-N_{ND_3})$	ϵ	ln P	P	$Q \times 10^{-20}$	Qy^3_{min}
3.00×10^{-1}	-0.357	6.44	0.228	1.25_6	2.07	1.66_5
2.50×10^{-1}	-0.288	5.69	0.023	1.023	1.47	1.175
2.00×10^{-1}	-0.223	4.95	-0.098	0.907	0.992	0.791
1.00×10^{-1}	-0.105	3.45	-0.160	0.853	0.323	0.261

N_{ND_3}	u_{min}	$P\,u_{\text{min}}$	$\int_0^{u_{\text{min}}} u^{-2}\left[\exp(-u^2) - 1\right] du$ [a]
3.00×10^{-1}	1.29	1.62	-1.02
2.50×10^{-1}	1.08	1.10	-0.920
2.00×10^{-1}	0.891	0.808	-0.785
1.00×10^{-1}	0.516	0.440	-0.501

[a] See Fig D-1 for the value of this integral.

N_{ND_3}	I_1 ⓐ	Fraction of acid ions scavenged = (A + B) ⓑ
3.00×10^{-1}	0.05	0.95
2.50×10^{-1}	0.08	0.92
2.00×10^{-1}	0.11	0.89
1.00×10^{-1}	0.29	0.72

ⓐ $I_1 = \int_{y_{min}}^{\infty} N(y,0)\, P \exp(-Qy^3)\, dy$. This integral is evaluated in appendix D-1 for the $y^{-\frac{5}{2}}$ distribution function where it is shown that

$$I_1 = P - P\, u_{min} \left(\sqrt{\pi} + \int_0^{u_{min}} u^{-2} \left[\exp(-u^2) - 1 \right] du \right)$$

ⓑ $A = 1 - I_1$

and $B = \int_{y_{min}}^{\infty} N(y,0)\, \phi_{esc}\, P \exp(-Qy^3)\, dy$

$$\approx 0.025 \int_{y_{min}}^{\infty} N(y,0)\, P \exp(-Qy^3)\, dy$$

$$= 0.025\, I_1$$

Thus $A + B \approx 1 - 0.975\, I_1$

I am indebted to Prof. Pounder of the Mathematics Department for useful discussions about the integrals involved in this work.

APPENDIX E

Electron Tunnelling Model for Electrons Trapped in a Coulomb Field

The probability, $\overline{P}$, that an electron does not tunnel within a time t when separated by a distance y from a counter ion is given by the expression

$$\overline{P} = \exp(-\lambda t) \tag{E-1}$$

where λ is the decay constant for electron tunnelling. To determine the dependence of λ on y an argument similar to that of Dexter (277, 278) is followed. The thermalized electron is assumed to be trapped in the liquid medium in sites of uniform depth E_o, with steep potential barriers. The distance between the trapped electron and its counter ion is assumed to represent a single barrier. The potential field of the counter ion is taken as coulombic and the gradient of this field over the site of the trapped electron is assumed to be negligible. The decay constant, λ, is given by

$$\lambda = \frac{E}{h} \cdot g \cdot K \tag{E-2}$$

where E is the energy of the electron in a trap of intrinsic depth E_o (a negative quantity) at a point where the coulomb potential is $-\frac{e^2}{\epsilon(y - r_o)}$, ie

$$E = E_o - \frac{e^2}{\epsilon(y - r_o)} \tag{E-3}$$

r_o, the radius of an ion, is assumed to be the same for the trapped electron and its counter ion. It is taken as 3.0×10^{-8} cm. g is a geometrical factor taken as the fractional solid angle subtended by the counter ion at the trapped electron site. The value of g is given by

$$g = \frac{r_o^2}{4(y - r_o)^2} \qquad \text{(E-4)}$$

κ is the transmission coefficient which is given approximately by (279)

$$\kappa \approx \exp\left(-2\int_0^{\sigma}\left|\frac{2m}{h^2}\left[\frac{e^2}{\epsilon(y - r_o - r)} + E\right]\right|^{1/2} dr\right) \qquad \text{(E-5)}$$

where r is the penetration into the barrier confining the electron at y. σ is that value of r required to enable the electron to resume a positive kinetic energy after penetrating the barrier. The value of σ is determined by

$$E = -\frac{e^2}{\epsilon(y - r_o - \sigma)} \qquad \text{(E-6)}$$

or

$$\sigma = (y - r_o)\left(\frac{E_o}{E_o - \dfrac{e^2}{\epsilon(y - r_o)}}\right) \qquad \text{(E-7)}$$

The integral in Eqt (E-5) can be evaluated * in closed form giving

$$\lambda \approx \frac{|E|}{h} \cdot \frac{r_o^2}{4(y - r_o)^2} \cdot \exp(-2W) \qquad \text{(E-8)}$$

---

* Integrals #64 and #61 of the Handbook of Chemistry and Physics, 46th Ed. (1965), PA-139 were used.

where
$$W = \left(\frac{y - r_o}{a_o}\right)\left(\frac{-2\ a_o}{\epsilon\,(y - r_o)} - \frac{2a_oE}{e}\right)^{1/2} - \frac{\sqrt{2}\,e}{\epsilon(-Ea_o)^{1/2}}\tanh^{-1}\left[1 + \frac{e^2}{\epsilon E(y - r_o)}\right]^{1/2} \qquad \text{(E-9)}$$

with a_o the Bohr radius of the ground state hydrogen atom, 5.29×10^{-9} cm. Eqt (E-8) was evaluated for cyclopentane with the results shown in Fig E-1. In the numerical calculations E_o was taken as either $-\frac{1}{8}$ ev, the value of the activation energy for the mobility of the negative ion in irradiated n-hexane (240), or $-\frac{1}{2}$ ev. The static dielectric constant of cyclopentane at 20° C, 1.96, and r_o, 3.0×10^{-8} cm, were used. Fig E-1 indicates that $\log_{10}\lambda$ is close to a linear function of $(y - r_o)$. The relations obtained from this figure for the two trap depths may be expressed as

$$\log_{10}\lambda = 13.4 - 0.11(y - r_o) \qquad \text{(E-10)}$$

when $E_o = -\frac{1}{8}$ ev, and

$$\log_{10}\lambda = 14.9 - 0.28(y - r_o) \qquad \text{(E-11)}$$

when $E_o = -\frac{1}{2}$ ev. These expressions, (E-10) and (E-11) may be used with Eqt (E-1) to give the probability of ions remaining at a given separation distance for various times after electron "solvation". Fig E-2 shows some results of such calculations.

FIGURE E-1

Decay Constant for Tunnelling of Electrons for Various Separation Distances

———————— Intrinsic trap depth of $\frac{1}{8}$ ev

– – – – – – – – Intrinsic trap depth of $\frac{1}{2}$ ev

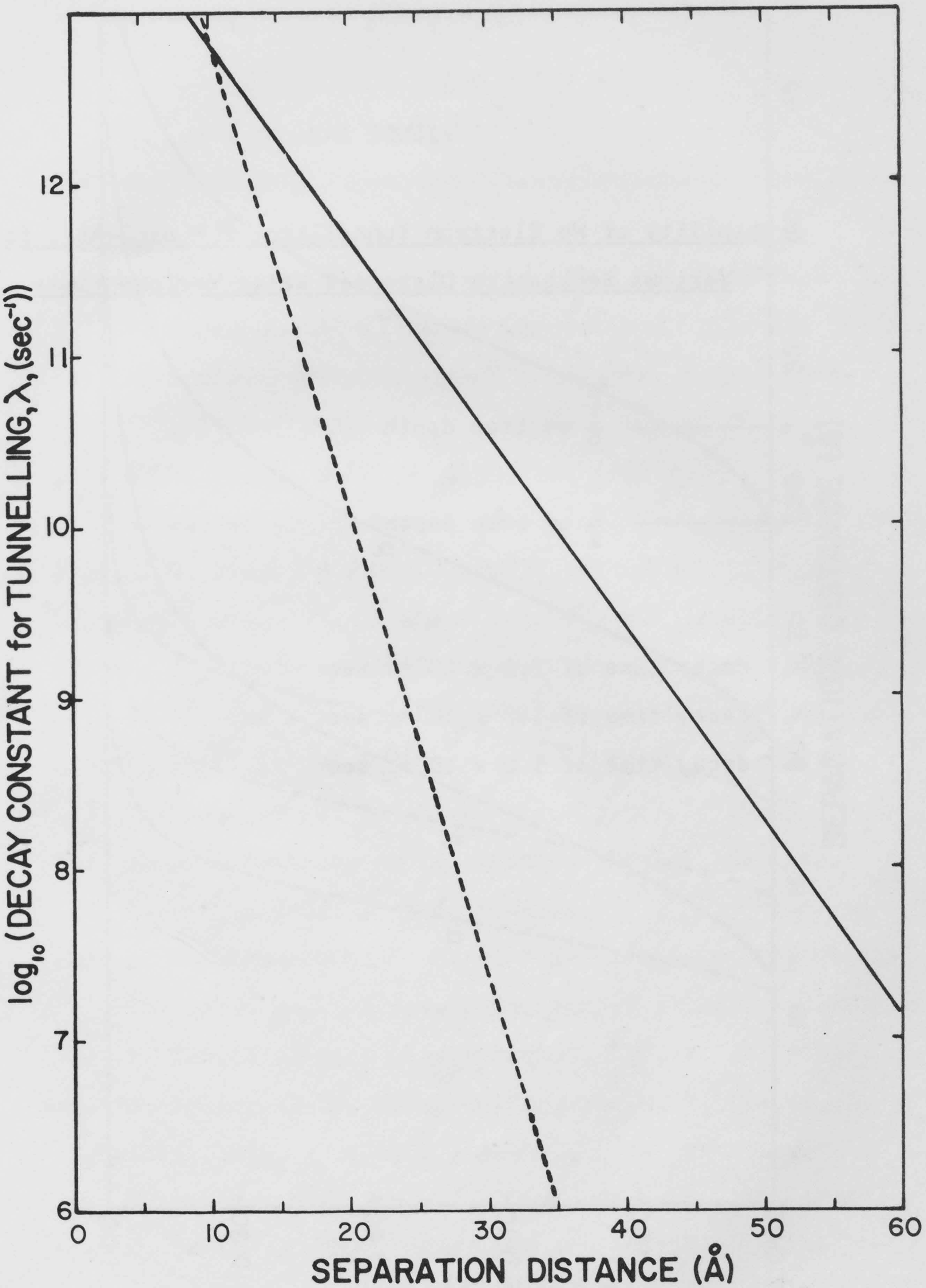

log₁₀ (DECAY CONSTANT for TUNNELLING, λ, (sec⁻¹))
12
11
10
9
8
7
6
0
10
20
30
40
50
60
SEPARATION DISTANCE (Å)

FIGURE E-2

Probability of No Electron Tunnelling, $\overline{P} = \exp(-\lambda t)$, for Various Separation Distances after Various Times

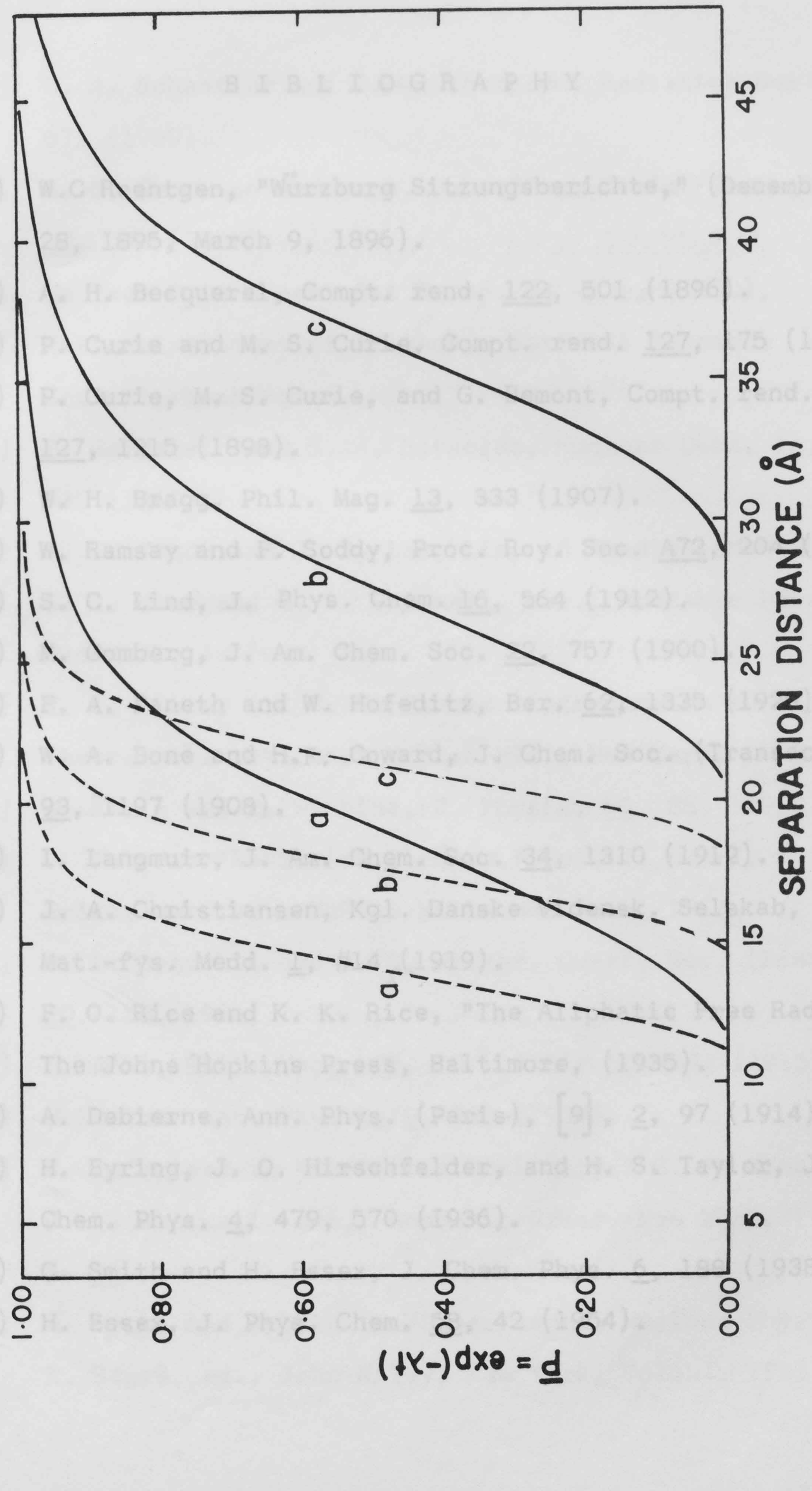
———————— $\frac{1}{8}$ ev trap depth

— — — — — — — $\frac{1}{2}$ ev trap depth

a. decay time of 1.0×10^{-12} sec

b. decay time of 1.0×10^{-11} sec

c. decay time of 1.0×10^{-10} sec


$P = \exp(-\lambda t)$
1.00
0.80
0.60
0.40
0.20
0.00
SEPARATION DISTANCE (Å)
5
10
15
20
25
30
35
40
45
a
b
c
a
b
c

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