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TITLE OF THESIS.....Radiation Induced............
dimerization..of..1,3-cyclohexa-
diene...in..solution..............

UNIVERSITY.....of..Alberta....Edmonton.....

DEGREE......Ph.D...........YEAR GRANTED.....1968....

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THE UNIVERSITY OF ALBERTA

RADIATION INDUCED DIMERIZATION OF 1,3-CYCLOHEXADIENE IN SOLUTION

by

© ROBERT SCHUTTE

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
July, 1968

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

"RADIATION INDUCED DIMERIZATION OF
1,3-CYCLOHEXADIENE IN SOLUTION"

submitted by ROBERT SCHUTTE in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

The formation of dimers of 1,3-cyclohexadiene during γ-radiolysis of solutions of the diene in various solvents has been investigated. Two sets of dimers were formed. The first set consisted of the endo (I) and exo (II) 1,4 adducts. The second set consisted of (II) and the cis-trans-cis (III) and all-cis (IV) 1,2-adducts. The yield of I increased with an increase in diene concentration, until a maximum was reached; a further increase in diene concentration lowered the yield, reaching G(I) = 1.43 in pure 1,3-cyclohexadiene. The maximum yields of I observed were: G(I) = 12 at $\sim$ 0.2 mole % diene in benzene, G(I) = 6.4 at 7 mole % in cyclohexane and hexane, and G(I) = 3.1 at 50 mole % in di-n-propyl ether. Ethanol inhibited the formation of I, a maximum was not observed.

The yield of IV increased with an increase in diene concentration to G(IV) = 0.83 in pure 1,3-cyclohexadiene.

Addition of CCl_4, N_2O, SF_6, and O_2 prior to radiolysis increased the yield of I while the yield of IV was decreased. Addition of ethanol or propyl ether decreased the yield of I in cyclohexane solutions. The yield of I decreased and the yield of IV remained unchanged when ethanol was present in benzene solutions. The yield of IV remained constant in cyclohexane solutions when propyl ether was used as additive. Ethanol completely inhibited the formation of IV in cyclohexane solutions.

Dimer I is formed in a positive ion chain reaction initiated by charge transfer from the solvent in benzene, cyclohexane, and hexane solutions. In ethanol and in dilute solutions of 1,3-cyclohexadiene in propyl ether charge transfer from the solvent does not occur.

To explain the maximum in the G(I) vs diene concentration curves it is suggested that one of the chain carriers can enter into two reactions that differ in order with respect to diene concentration; the lower order reaction propagates the chain and the higher order reaction terminates it.

Electronically excited (triplet) benzene molecules formed directly by the radiation and by ion-neutralization might be precursors to dimer IV in benzene solution. Dimer IV is formed during neutralization or as a result of neutralization in cyclohexane solutions.

Neutralization involving a cyclohexane positive ion does not lead to IV.

ACKNOWLEDGEMENTS

The author would like to express his appreciation to Dr. G. R. Freeman for his encouragement and guidance during this project.

The author is deeply indebted to his wife Margot for her patience and understanding and for typing the initial draft of this thesis.

The author also wishes to thank Mrs. Mary Waters for typing the final draft of this thesis.

The assistance of the members of the radiation chemistry group is gratefully acknowledged.

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A. γ-Radiolysis; General features.

1. Physical stage: energy absorption.

When ^{60}Co γ-rays interact with low atomic weight materials the most important energy transfer process is the Compton process (1a). The primary electrons set in motion by Compton absorption have an average energy (1b) of 0.6 million electron volt (MeV), and a range of approximately 0.3 cm in liquid alkanes (2). Since the irradiation vessels used for liquids are usually 1-2 cm in diameter, these Compton electrons are absorbed in the liquid sample.

A Compton electron may interact with the molecules of a medium by elastic and inelastic collisions and by bremsstrahlung production. Of these three processes inelastic scattering is the most important means of energy loss. Bethe (3) developed an equation for the collisional rate of energy loss of a high energy electron per unit path length in a medium. Bethe (4) also derived the ratio of the bremsstrahlung energy loss $\left(-\frac{dT}{ds}\right)_{rad}$ to that for collisional loss $\left(-\frac{dT}{ds}\right)_{coll}$:

$$\frac{\left(-\frac{dT}{ds}\right)_{rad}}{\left(-\frac{dT}{ds}\right)_{coll}} = \frac{TZ}{1600\ m_oc^2}$$

where T is the relativistic kinetic energy of the electron, Z is the effective atomic number of the medium, m_o is the electron rest mass and c is the velocity of light in vacuum. For a 0.6 MeV Compton electron, moderated by graphite this ratio is about 0.004. Thus, bremsstrahlung as a mode of energy loss may be neglected here, although it is of vital importance in the design of protective shielding of radiation sources.

A primary (Compton) electron interacts with molecules of the medium to produce excitation and ionization. Each ionization produces a secondary electron which in turn, when it possesses sufficient energy, ionizes and excites additional molecules. For simplicity, all liberated electrons other than the primaries may be classified as secondaries.

The above mentioned processes are completed in 10^{-15} sec (5). The vibrations, rotations and translations of the molecules of the medium are slow compared to the speed with which energy absorption by the medium takes place. The medium is effectively static during the absorption process.

2. Physico chemical stage: attainment of thermal equilibrium.

In a period of about 10^{-12} sec following the energy absorption, the excited species reach thermal equilibrium.

Radicals are formed, ion-molecule reactions and energy transfer occur. Within this period the secondary electrons are thermalized.

The fate of the secondary electrons has been the subject of a number of experimental and theoretical studies. Two divergent theories have been proposed for slow electrons in water. Samuel and Magee (6) calculated that a secondary electron would travel, on the average, only about 15 Å from its parent ion and would return to its parent ion in less than 10^{-13} sec. Platzman (7) estimated that the electron would travel at least 50 Å from the parent ion in 10^{-12} sec and would then become solvated. The solvated electron would then have an extended lifetime. The effect of scavengers on the radiolysis of water tends to support Magee's spatial distribution (8) but the spectroscopic observation of large yields of solvated electrons microseconds after their generation (9) supports Platzman's time scale. Solvated electrons have also been produced in other (non-radiolysis) systems (10). Little doubt remains about the existence of solvated electrons in irradiated polar media (11).

3. Chemical Stage: attainment of chemical equilibrium

The chemical stage consists of diffusion and chemical reaction of the reactive species leading to the

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3. Chemical Stage: attainment of chemical equilibrium

The chemical stage consists of diffusion and chemical reaction of the reactive species leading to the establishment of chemical equilibrium. The chemical stage may be divided into two periods. The first period ends at about 10^{-8} sec. By this time the initially produced high local concentrations of reactive species (spurs) have disappeared by reaction and diffusion. The second period from 10^{-8} sec upwards shows chemistry of reactive species homogeneously distributed through the bulk of the medium.

4. Lifetimes of the reactive species.

In this section the discussion will be limited to those reactive species that live longer than about 10^{-12} sec and to the radiolysis of organic liquids.

(a) Ions and electrons.

A fraction of the initially formed ions might undergo geminate recombination (recombination of an electron and its parent ion) within 10^{-12} sec, with formation of an excited molecule. These excited molecules would presumably have similar properties to those formed directly by interaction between the energetic electrons and the medium; they will be discussed later. The net effect of the process might be that G(total ionization) as measured by chemical methods is lower than its real value.

Conductance measurements during γ-radiolysis of hydrocarbons (12,13) and of halogen substituted hydrocarbons and ethers (14) show that a small fraction of the ions does survive a considerable length of time, although no obvious solvation mechanism for electrons exists in non polar media.

The results were accomodated by electron "trapping" in the cavities between the molecules of the medium (14,15). The electron is not viewed as a diffuse cloud of negative charge, extending over several molecular diameters but rather a small entity of molecular dimensions, diffusing through the liquid much like ordinary molecules do, by discrete diffusive jumps.

Electrons and ions are not homogeneously distributed with respect to each other, but they occur in pairs. For instance in cyclohexane about 94% of the electrons have an initial separation distance of less than 100 Å, and 65% are found within 20 Å of the parent positive ion (16).

The non-homogeneous kinetics resulting from this model was applied successfully to quantitatively describe product yields from both positive ion and electron scavenger solutions. Some of the systems to which the kinetics model has been applied are the yield of HD from cyclohexane ethanol-OD solutions (16), the hydrogen yield from methylcyclopentane/SF_6 solutions (17), and (in a slightly modified form) the hydrogen yield from cyclopentane solutions of SF_6 and perfluorocyclobutane (18).

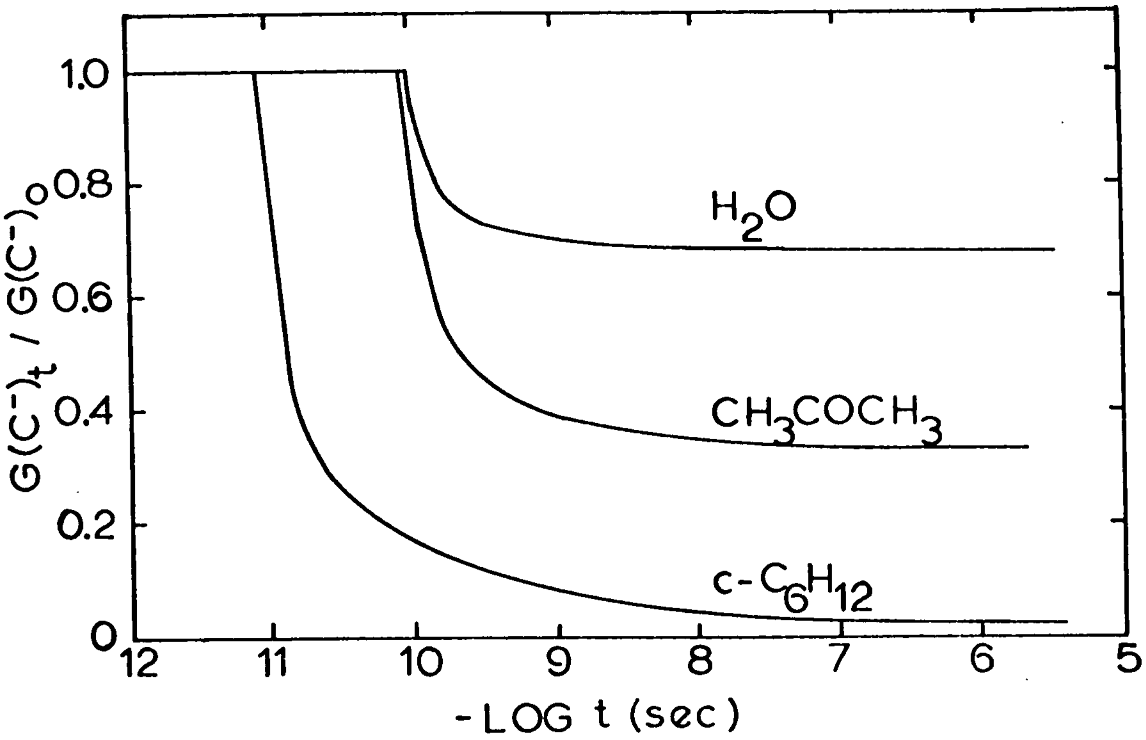


FIGURE I-1 Lifetimes of solvated electrons after an instantaneous pulse of radiation in pure water, acetone and cyclohexane.

The model has also been used to calculate the ion lifetimes in water, acetone, ethanol, and cyclohexane (19). The results, which are in agreement with the limited experimental measurements of ion lifetimes (20,21) are partially reproduced in Fig. I-1. From this figure it can be seen that in cyclohexane about 84% of the ions, that are present at 10^{-12} sec after track formation recombine within 10^{-10} sec.

(b) Excited molecules

There are as many types of excited molecules as there are types of energy levels that can be excited. Each type of excited molecule has its own characteristic behaviour, so they will be treated separately.

Rotational excitation is short-lived, moreover the rotational quanta are so small that product formation from rotationally excited molecules probably does not occur. Vibrationally excited molecules lose their excess energy rapidly by collisions with neighbouring molecules. These collisions have frequencies of about 10^{13} collisions/sec. The spacing between the vibrational energy levels is independent of the energy level, to a first approximation, thus energy transfer to another molecule is a resonance process and consequently very efficient.

The fluorescence spectrum of molecules is independent of the wavelength of the exciting light, thus vibrational excitation of the electronically excited molecule was dissipated within the radiative lifetime of the excited state (22). To sum up, excess vibrational energy is lost within 10^{-12} to 10^{-9} sec. A vibrationally excited molecule may decompose into radicals. The time required for this dissociation is of the same order as the time for one vibration (10^{-13} to 10^{-12} sec).

The several modes of deactivation open to electronically excited molecules may be divided into radiative and non-radiative processes. When considering the lifetimes of excited molecules it is more illustrative to make a division between unimolecular and bimolecular processes. For it is in this respect that they differ from ions. When an ion reacts with a neutral molecule the identity of the ion changes but an ionic centre is preserved. The species that will eventually terminate the existence of an ion is also generated by the radiation. Termination occurs in a bimolecular process between reactants that are present in equal amounts. Kinetic complexities occur (see above), but general remarks about ion lifetimes that apply to more than only one system can be made. Electronically excited centres are destroyed by a variety of processes, all of which are dependent on the system under consideration. Consequently each system must be treated on its own and general statements about the lifetime of electronically excited molecules in radiolysis systems are not possible.

The largest single factor determining the lifetime of an electronic excited state is its multiplicity. Transitions between states of the same multiplicity are allowed and take place between 10^{-9} and 10^{-5} sec. Transitions between states of different multiplicity are forbidden. The triplet excited state of a molecule with a singlet ground state has a lifetime that is generally a factor of 10^{3} to 10^{4} longer than the lifetime of the singlet excited state of the same molecule (23).

Among the unimolecular deactivating processes that an excited molecule may undergo are:

- radiationless decay to the ground state (solvent quenching, thermal quenching)
- chemical reaction, e.g. rearrangement, dissociation

Examples of bimolecular processes are:

- concentration quenching
- quenching by a solute or radical
- energy transfer
- chemical reaction with a substrate or solute molecule.

c. Radicals.

Radicals also show a complex decrease in number with time. As with ions and neutral excited molecules, they may be produced in high local concentrations. The distribution of the radicals in space might be more homogeneous than the initial distribution of the ions and excited molecules when an appreciable fraction of the radicals is formed from ion-molecule reactions and from excited molecules, the latter formed directly by the radiation and from neutralization reactions. For in these cases radical formation occurs after expansion of the spurs has already started (24).

A major problem facing the development of a quantitative kinetic treatment of radicals in the early part of the chemical stage is the lack of unambiguous experimental data. An ideal radical scavenger should scavenge only radicals. However many radical scavengers are also good charge scavengers. Nitric oxide, a stable free radical, has been extensively used to suppress radical reactions. Charge transfer from aliphatic hydrocarbon positive ions to nitric oxide can occur since the ionization potential (IP) of NO, 9.25 eV (25), is lower than the IP of saturated aliphatic hydrocarbons, which range approximately from 9.88 eV (cyclohexane) to 12.98 eV (methane) (26). In addition, the electron affinity of nitric oxide, 0.91 eV (27), enables it to be a good electron scavenger. Galvinoxyl[*], a stable free radical, has been shown to quench triplet excited states of benzene in addition to scavenging radicals (28).

After the spurs are dissipated by diffusion in about 10^{-8} sec the kinetic treatment of radicals is straight forward. In order to calculate an average lifetime t_a of radicals during continuous irradiation, the following mechanism is assumed:

$$M \rightarrow 2R\cdot \quad \text{rate: } k'I \qquad (1)$$

$$R\cdot + R\cdot \rightarrow R_2, \text{ rate: } k \qquad (2)$$

in which R• is any radical, I is the irradiation dose rate and reaction (2) is the sum of all radical-radical reactions which terminate their existence. It is assumed that no other reactions remove radical centres from the system. Steady state treatment yields:

$$\frac{d[R]}{dt} = 2k' I - 2k [R\cdot]^2 = 0 \qquad \text{(eq. I-1)}$$

Rearrangement gives $[R\cdot] = (k' I/k)^{\frac{1}{2}}$

The average lifetime t_a of a radical is given by:

$$t_a = (2k[R\cdot])^{-1} \qquad \text{(eq. I-2)}$$

---

[*] 2,6-di-tert-butyl-α-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-p-tolyloxy.

Substitution of the expression for $[\dot{R}]$ obtained from (eq. I-1) into (eq. I-2) gives:

$$t_a = (4k\ k'\ I)^{-\frac{1}{2}} \qquad \text{(eq. I-3)}$$

Eq. I-3 shows that the average lifetime is inversely proportional to the square root of the dose rate. If I is in units of eV/(cm^3 sec) and concentrations are in molar units $2k' = 10\ G(R\cdot)I/N$, where N is the Avogadro number. Substituting in eq. I-3 the number values; $I = 0.8 \times 10^{16}$ eV/(cm^3 sec), which is the dose rate in cyclohexane of the Gammacell 200 used in this work, $G(R\cdot) = 6$, and $k = 3.4 \times 10^9$ 1/(mole sec), which is the rate constant for reaction between two methyl radicals (29), an average lifetime $t_a \approx 10$ msec is obtained. If the radicals can also react with a solute in the medium, with the medium itself, or a radiolysis product, their average lifetimes will be much smaller than this.

B. Reactions of ions, excited molecules and free radicals.

1. Ions.

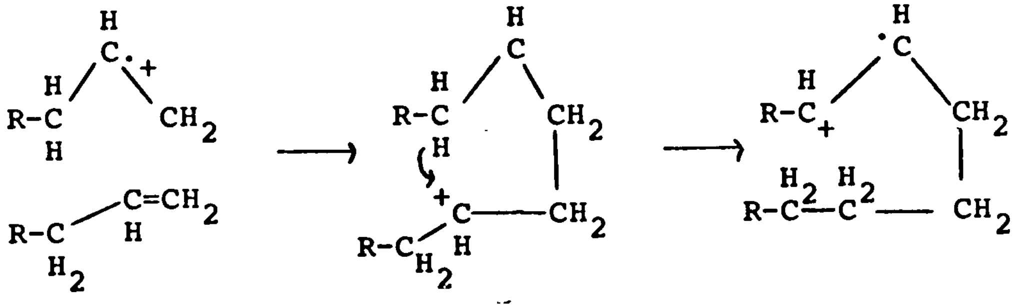
(a) Dissociation.

Some positive ions formed by the radiation contain enough energy to dissociate into smaller ions and molecules or radicals. Evidence for this reaction in the gas phase can be found in the mass spectrum of many compounds.

The occurrence of "metastable" ions in mass spectra indicates that an ion might survive a long period of time (1-10 μsec) before dissociation occurs.

(b) Rearrangement.

Rearrangement of positive ions is a commonly used step in organic reaction mechanisms in solution. Reports of ion rearrangement in radiolysis systems are scarce. Wagner proposes a rearrangement of a radical cation in the radiolysis of 1-pentene, to account for the observed 3-n-decene (30).



Rearrangement of the positive ions of toluene and cycloheptatriene has been advanced as an explanation for the close resemblance between the mass spectra of the two compounds (31). Later studies with deuterated toluenes in a mass spectrometer equipped with a pulsed ion source indicate that rearrangement of the toluene positive ion is accompanied by dissociation (32).

(c) Charge Transfer

Charge transfer from a substrate ion to a solute or radiolysis product molecule can occur when the recombination energy of the ion with an electron is higher than or equal to the ionization potential of the acceptor in the medium.

(d) Ion-molecule reactions.

The occurrence of ion-molecule reactions in the gas phase has been known for a long time. As a matter of fact in the early history of radiation chemistry these reactions were considered exclusively in the rationalization of the observed radiolysis product yields (33).

Most of the information about ion-molecule reactions comes from mass spectrometric studies (34). The role of these reactions in liquid phase radiolysis of hydrocarbons was first recognized by Davison, Pinner and Worrall (35) who held ionic intermediates responsible for the radiation induced polymerization of isobutylene.

Williams (36) observed a change in the isotopic composition of hydrogen evolved from cyclohexane containing small amounts of ND_3:

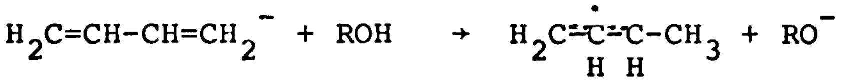
$$AH^+ + ND_3 \rightarrow A + ND_3H^+$$

$$ND_3H^+ + e^- \begin{array}{l} \nearrow ND_3 + H \\ \searrow ND_2H + D \end{array}$$

Irradiation of solid solutions of conjugated dienes in methyltetrahydrofuran at -196°C leads to the formation of solute anions. Ethers provide suitable matrices for solute anions because the positive charge is stabilized by the proton or H-atom transfer reaction (37):

$$ROCH_2R^+ + ROCH_2R \rightarrow (ROCH_2R)H^+ + RO\dot{C}HR$$

Another example of an ion-molecule reaction that occurs in the solid phase at -196°C is the formation of allylic radicals from butadiene negative ions in alcoholic matrices (37):



$$H_2C{=}CH{-}CH{=}CH_2^- + ROH \rightarrow H_2C \doteq \underset{H}{\overset{\bullet}{C}} \doteq \underset{H}{C}{-}CH_3 + RO^-$$

2. Excited molecules.

(a) Photon emission.

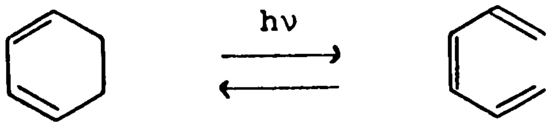
An electronically excited molecule may return to the ground state by emission of a photon: fluorescence and phosphorescence. The ability of a molecule to fluoresce depends in no small measure on its chemical constitution. Aliphatic hydrocarbons do not fluoresce (see below) while many aromatic hydrocarbons including benzene do so (38).

(b) Dissociation and rearrangement.

The energy of the lowest excited singlet state of benzene is 106 kcal/mole, as determined from the short-wavelength onset (2690 Å) of its fluorescence spectrum (39). The heat of dissociation of C_6H_5-H bond is 104 kcal/mole (40a). The energy content of the lowest excited singlet state of benzene is probably not sufficient to cause dissociation of the molecule. In contrast, cyclohexane only absorbs light of wavelength shorter than about 1750 Å (> 163 kcal/mole) (41). The heat of dissociation of aliphatic C-H and C-C bonds is about 98 and 80 kcal/mole respectively. Thus there is sufficient energy available in an excited cyclohexane molecule for dissociation to occur. Dissociation is suspected to cause the failure of aliphatic hydrocarbons to fluoresce (42).

The introduction of olefinic bonds in an aliphatic hydrocarbon increases the wavelength of the absorbed light, but it also reduces the bond dissociation energy of the weakest bond in the molecule. For instance the absorption spectrum of 1,3-cyclohexadiene has a maximum at about 2500 Å; the absorption starts near 2800 Å ($\sim$ 102 kcal/mole) (43). The heat of dissociation of an allylic type hydrogen is about 77 kcal/mole. Again there is sufficient energy available to cause dissociation of singlet excited 1,3-cyclohexadiene into an H atom and a cyclohexadienyl radical.

Rearrangement of the bonds may also occur in the excited state. A facile rearrangement of 1,3-cyclohexadienes is ring opening to 1,3,5-hexatrienes (44,45):



(c) Intersystem crossover.

Intersystem crossover occurs when the total spin quantum number of an excited state changes. Theoretically the process is forbidden in hydrocarbon molecules. To effectuate a change of spin of one electron a magnetic moment must be applied, or a second particle able to preserve the spin must be present. In this respect it is interesting to note that a trapped electron could function as a spin preserving particle, thus increasing the rate of intersystem crossover, both from the singlet excited state to the triplet excited state and from the triplet excited state to the groundstate.

From gas phase studies of the benzene sensitized isomerization of butene-2 (46), a process that involves the triplet state of benzene (47), it was concluded that intersystem crossover was a unimolecular process at pressures below 2 x 10^{-3} mm Hg. At higher pressures it was a bimolecular process.

Intersystem crossover from excited singlet states is not the only source of triplet excited molecules in radiolysis systems. Thomas and coworkers (48), in a pulsed radiolysis study of the system cyclohexane-anthracene, using nanosecond pulses, found a high yield ($G \sim 2$) of anthracene triplets at the end of the pulse. They attributed these to excitation of anthracene directly into the triplet state by interaction with secondary electrons. The latter process is allowed since the exciting electron can conserve the spin.

Another source of triplet state molecules is the ion-neutralization reaction. On statistical grounds it is expected that a neutralization reaction in 75% of the cases will yield a triplet excited molecule. Thomas et al.(48) found that in addition to the triplets present at the end of the pulse, there were triplets formed after the pulse (48). The formation of these latter triplets shows the same kinetics as the disappearance of negative ions.

(d) Energy transfer.

Energy transfer occurs when the energy of the excited state of the acceptor molecule is equal to or lower than the energy of the excited state of the donor. The process is important in sensitized photochemical syntheses and in scintillator solutions, which are widely used in heavy particle and γ-ray spectroscopy and in radioactivity counters.

Triplet-triplet energy transfer appears to proceed at diffusion controlled rates when the process is about 3 to 5 kcal/mole exothermic (49). Cundall and Griffiths (50, 51a) used the sensitized cis-trans isomerization of 2-butene in benzene solution to determine the yield of triplet state benzene molecules in the γ-radiolysis of benzene. The sum of G(cis→trans) and G(trans→cis) gave G(triplet benzene) = 4.23 which was later revised to 4.67 (51b). Golub and coworkers (52) using the same technique with homologs of 2-butene estimated G(triplet benzene) = 5.0.

Several groups attempted to measure G(triplets) in benzene by isomerization of cis and trans stilbene (1,2 diphenylethene). G(triplet benzene) was variously estimated as: 0.4 (53); ∿ 1 (54); 5.0 (55); and 9.9 (56). The situation seems to have been clarified a great deal by Hentz and coworkers (57,58) who showed that isomerization of cis to trans stilbene in benzene might proceed via an ionic chain mechanism:

$$\mathrm{B} \rightarrow \mathrm{B}^{+} + e^{-}$$

$$e^{-} + \text{c-St} \rightarrow \text{t-St}^{-}$$

$$\text{t-St}^{-} + \text{c-St} \rightarrow \text{t-St} + \text{tSt}^{-}$$

where B is benzene and St is stilbene. G(c→t) as high as 210 was measured after thorough purification of cis-Stilbene. The mechanism is supported by the spectroscopic observation of the negative ion absorption spectrum of cis and trans stilbene during pulsed radiolysis. The two spectra are identical, indicating that cis stilbene upon capturing of an electron immediately acquires the trans negative ion configuration (59). From G(t→c) = 3.0 and the known ratio of quantum yields for the photolytic isomerization of the stilbenes (sensitizer benzophenone) (60) they (57) arrive at G(triplets) = 5.4. The occurrence of trans to cis isomerization in cyclohexane (2-butene does not isomerize in cyclohexane) and the marked effect of CCl_4 on G(t→c) in benzene and cyclohexane solutions (57) make the interpretation of the observed isomerization in terms of G(triplet benzene) a hazardous operation. It was assumed that a fraction of the stilbene triplets involved were formed upon neutralization of a stilbene negative ion. If a yield G(ion pairs) of $\sim$ 3 is assumed it follows from G(triplets) = 5.4 that the yield for production of benzene triplets via excitation alone must be $\sim$ 2.4 (57).

The complex isomerization of the stilbenes and the spectroscopic observation of anthracene and naphthalene triplets in cyclohexane (48), as was already mentioned in the previous section, indicate that caution with respect to energy transfer as source of triplet state solute molecules in radiolysis systems is warranted.

(e) Quenching.

Quenching is the interaction between an electronic excited molecule and a second molecule which leads to the transformation of electronic excitation into an other form of energy, such as vibrational or chemical energy. The term quenching is often used to indicate energy transfer although the two processes are basically different.

Molecules such as naphthalene, which are diamagnetic, quench triplet states because of the favorable position of their lowest triplet state. In the process a naphthalene triplet is produced which in turn might transfer its energy to a third compound. Thus it is possible that naphthalene is a quencher, inert, or even a sensitizer, depending on the energies of the triplet states of the other components of the system.

Paramagnetic molecules are postulated to quench triplet states through the perturbation caused by the uncoupled spins. Quenching of triplet states by oxygen and the reverse process: enhancement of singlet triplet absorption under high pressures of oxygen have been the subject of many theoretical and experimental studies. Charge transfer states appear to be involved in both processes (61,62). The energy of the triplet excited state of many compounds has been measured by the absorption spectrum produced under high pressures of oxygen (64).

Quenching of triplet excited states may be accomplished by triplet excited molecules:

$$^3B + {}^3B \rightarrow {}^1B + B$$

where B is benzene and the superscript 3 and 1 refer to triplet and singlet excited states respectively. This process is thought to cause the shorter lifetime of benzene triplets in radiolysis systems as compared to the lifetime in systems where radiation is absent (48). However Cundall et al (65) considered radical quenching as being responsible for the short lifetimes. A third reason might be quenching by trapped electrons, as was mentioned in section B-2-c.

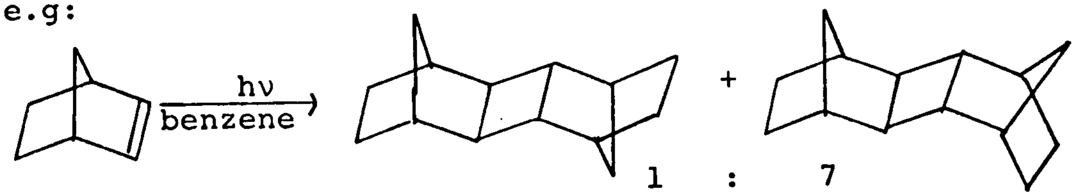
(f) Chemical reaction.

A classic example of deactivation of an excited molecule through chemical reaction is the dimerization of anthracene during photolysis in benzene solution (66). The fluorescence yield decreases and the dimer yield increases with an increase in anthracene concentration:

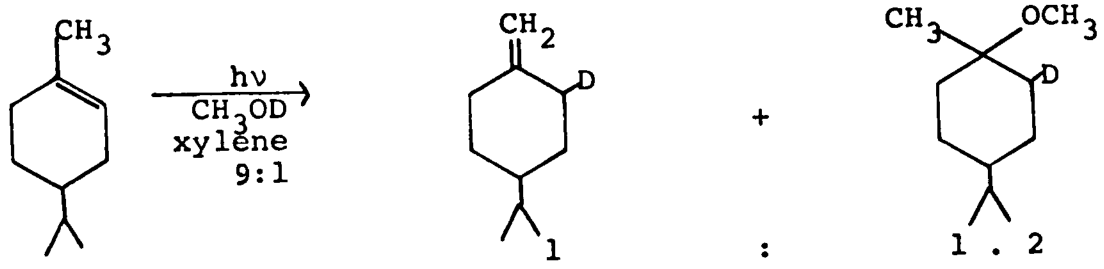
$$\begin{aligned} A &\xrightarrow{h\nu} A^* \\ A^* &\rightarrow A + h\nu' \\ A^* + A &\rightarrow AA. \end{aligned}$$

This process is a rather general phenomenon (67). It is known as self-quenching or concentration quenching. In some instances the dimers formed are themselves electronically excited, thus giving rise to a change in the fluorescence spectrum of the solution (68).

Acyclic or macrocyclic olefins in the triplet excited state undergo cis-trans isomerization of the double bond, undoubtedly as a consequence of the preferred orthogonal conformation of triplet olefins (69). Dimers from noncyclic olefins could not be obtained (70). Olefins in which the trans isomer would be highly strained, for instance small ring olefins, are reported to dimerize (71) e.g:



and to undergo addition reactions with alcohols (72,73).

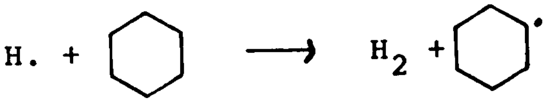


Conjugated dienes in the triplet excited state show similar reactions. Cis-trans isomerization has been reported for 1,3-pentadiene (74). Dimerization occurs with 1,3-butadiene (75,76) and 1,3-cyclohexadiene (77).

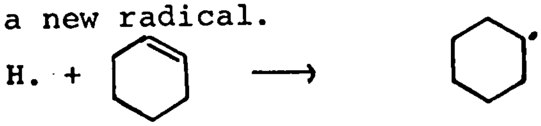
3. Radicals

The reactions of radicals are most conveniently studied in systems where excited molecules and ions are absent, such as the mercury photosensitized decomposition of saturated hydrocarbons (78,79), where only C-H bond rupture results from the reaction between an excited mercury atom and a substrate molecule. At room temperature in the liquid phase radicals may undergo the following reactions:

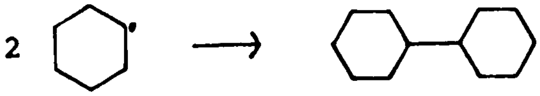
(a) abstraction



(b) addition to a double bond resulting in the formation of a new radical.



(c) combination:



(d) disproportionation:

When radicals finally disappear they do so by reaction c or d.

C. Some physical and chemical properties of 1,3-cyclohexadiene.

Since the principal compound in the present study was 1,3-cyclohexadiene (CHD) it was thought useful to describe this compound and some of its reactions in detail.

1. Molecular structure.

From an investigation of the microwave spectrum of CHD, Butcher (80) was able to deduce the dipole moment ($\mu = 0.437 \pm 0.014$ D), and the degree of nonplanarity of the molecule. It was assumed that the ethylene groups were planar. The angle over which one ethylene group was rotated relative to the other ethylene group about the C_2-C_3 bond was found to be $17.5 \pm 2°$, relative to 0° for the planar ring. It appears that the effects of resonance, which would favor conjugate double bonds to be coplanar, are outweighed by the steric effects between protons and the bond angle strain which would exist in the planar ring.

2. Resonance energy.

In accordance with this nonplanar picture of the molecule is the low resonance energy, viz. 1.8 kcal/mole, as compared to the resonance energies of 1,3-butadiene and 1,3-pentadiene which are 3.5 and 4.2 kcal/mole respectively (40b).

3. Energy levels of the first excited singlet and triplet states.

The absorption spectrum of CHD consists of a broad band with a maximum in the vicinity of 2500 Å. The absorption starts near 2800 Å (41). If this latter wavelength is taken as corresponding to the 0 → 0 band, the energy of the lowest excited singlet state of CHD is about 102 kcal/mole.

Singlet-triplet absorption under high pressure of oxygen exhibits a maximum at approximately 4350 Å. Evans (64) placed the 0 → 0 band at 5350 Å, corresponding to an energy of 53.5 kcal/mole for the lowest excited triplet state of CHD.

4. Ionization potential.

The appearance potentials of the parent ions of several compounds have been measured by Wakeford (81). The values found were: cyclohexene and 1,4-cyclohexadiene 9.2 ± 0.2 eV, CHD 8.7 ± 0.3 eV. Thus the appearance potential of CHD is about 0.5 eV lower than the appearance potential of the parent ion of cyclohexene. The ionization potential of cyclohexene, measured by the photoionization method is given by Watanabe et al. (25) as 8.945 ± 0.01 eV. The value of the ionization potential of CHD would then be about 8.45 eV. Kiser in his compilation of ionization potentials (26) lists cyclohexadiene, but unfortunately no specification of 1,3 or 1,4 is given. The listed value is 8.40 eV. It may be assumed that 1,3-cyclohexadiene was intended by Kiser, since the ionization potential of 1,4-cyclohexadiene would be closer to the value for cyclohexene, if the appearance potentials are taken as an indication.

As Kiser's value agrees so well with the value obtained from the appearance potentials it seems reasonable to take 8.40 eV (193 kcal/mole) as the ionization potential of 1,3-cyclohexadiene.

5. Photolysis.

The photochemistry of CHD has recently been reviewed by Srinivasan (82).

The products that are attributed to the singlet excited state are 1,3,5-hexatriene and 1,2,4-hexatriene. Other products including benzene, hydrogen, acetylene, and ethylene are thought to be formed from the vibrationally excited ground state. In line with this interpretation is the formation of the latter products during pyrolysis.

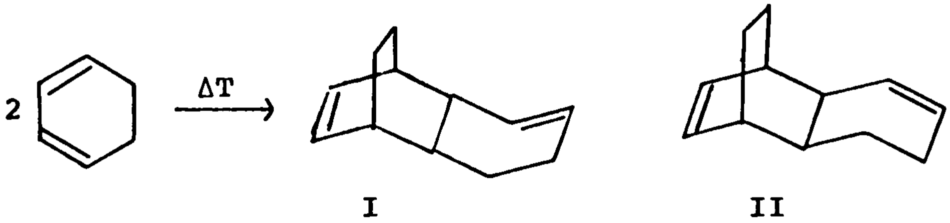
Experimentally, the crossover of the singlet excited state to the triplet excited state has not been observed.

6. Thermal and photosensitized dimerizations.

Two papers dealing with the thermal and photosensitized dimerizations of CHD have been published since the work presented in this report was started. Although the theoretical interpretations of the results differ widely in these papers, the basic results are identical, thus reinforcing each other.

(a) Thermal dimerization.

Heating of CHD in a closed tube at 200°C for 24 hr gives a mixture of two dimers, I and II, in a ratio of approximately 3:1 (77,83)



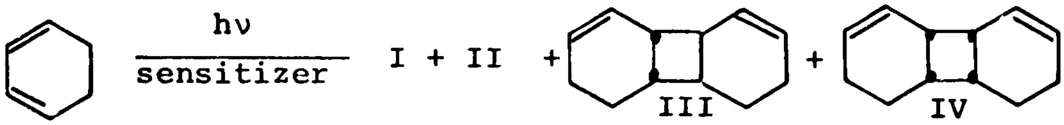
I = endo-tricyclo[$6.2.2.0^{2,7}$]dodeca-3,9-diene

II = exo-tricyclo[$6.2.2.0^{2,7}$]dodeca-3,9-diene

These dimers will be referred to as thermal dimers.

(b) Photosensitized dimerization.

Photolysis of solutions of CHD in isopentane in the presence of the sensitizer β-acetonaphthone leads to the formation of four dimers in 90% yield (77). Two dimers were the same as the thermal dimers (77) described above.



relative yields (trace) 1 : 3 : 1

III: trans-cis-trans-tricyclo[$6.4.0.0^{2,7}$]dodeca-3,11-diene

IV: cis-cis-cis -tricyclo[$6.4.0.0^{2,7}$]dodeca-3,11-diene

Photolysis of the neat liquid with light of wavelength > 3300 Å in the presence or absence of a sensitizer (benzophenone) also produces these dimers (83).

The dimers III and IV will be referred to as photodimers.

Upon heating in a closed tube the dimers III and IV rearrange into I and II respectively (77, 83). The entropy and enthalpy of activation of these rearrangements have been measured (77):

$$\text{III} \rightarrow \text{I} \quad \Delta H^{*} = 36.8 \text{ kcal/mole} \quad \Delta S^{*} = -3.2 \text{ e.u.}$$

$$\text{IV} \rightarrow \text{II} \quad \Delta H^{*} = 33.0 \text{ kcal/mole} \quad \Delta S^{*} = +4.6 \text{ e.u.}$$

Thus IV is less stable than III at elevated temperatures. Above 160°C the isomerizations occur at measurable rate (77,83).

D. Dimerization during γ-radiolysis.

In the course of a study of the γ-radiolysis of cyclohexene Wakeford (81) found that addition of small amounts of CHD to the cyclohexene prior to radiolysis led to the formation of a new product that was tentatively identified as the Diels Alder dimer (I) of CHD. The same product was formed during the radiolysis of cyclohexane solutions of CHD. The yield of the dimer was a sensitive function of the amount of diene present. The yield increased rapidly with an increase in concentration. G(dimer) reached a maximum of about 6.5 between 2 and 9 mole % CHD, then decreased to a value < 4.0 by the time 70 mole % CHD had been added to cyclohexene.

The structure of the dimer ruled out a radical mechanism for its formation. Charge scavenging alone could not account for the observed dimer yield, since G(total ionization) is about 4.5 for hydrocarbons in the gas phase and probably the same value applies to the liquid phase. Charge scavenging in combination with energy transfer from excited molecules or energy transfer alone were proposed as being instrumental in the diene formation.

E. Extent of present study.

The present investigation of the dimerization of 1,3-cyclohexadiene was undertaken to elucidate the mechanism of dimer formation during γ-radiolysis and then to use the dimer formation as an indicator for primary processes in radiolysis systems.

To determine the role of the solvent in the dimerization, solutions of 1,3-cyclohexadiene in benzene, cyclohexane, n-hexane, di-n-propylether, and ethanol were irradiated. The dimer formation was studied as a function of total dose and dose rate in cyclohexane and benzene solutions. Ternary solutions of 1,3-cyclohexadiene, cyclohexane, and a number of scavengers were studied. The scavengers include ethanol, di-n-propylether, nitrous oxide, sulfur hexafluoride, carbon tetrachloride, and oxygen. To facilitate a comparison of the solvents, carbon tetrachloride was used as additive in dilute and concentrated solutions of 1,3-cyclohexadiene in cyclohexane, benzene, and di-n-propylether.

EXPERIMENTAL

A. Materials

1. Materials for irradiation

(a) 1,3-Cyclohexadiene

Aldrich Chemical Co. 1,3-cyclohexadiene contained various amounts of benzene, cyclohexene, 1,4-cyclohexadiene, and polymer as impurities. Distillation in a nitrogen atmosphere removed the polymer. The distillation must not be carried too far, because the 1,3-cyclohexadiene peroxides that are present whenever the diene has been in contact with air decompose readily at higher temperature, thus initiating a rapid polymerization that might lead to an explosion. Washing the diene with 0.3% $FeSO_4$ solution prior to distillation greatly reduced the danger of explosion. The ready formation of peroxides had another consequence: whenever the diene was handled, polymerization occurred to some extent, thus increasing the level of the impurities. This was the limiting factor in the purification procedure. After distillation the material was further purified by gas chromatography on a β,β'-oxydipropionitrile column. The diene was separated from the carrier gas immediately after it emerged from the column. It did not pass through the thermal conductivity detector. If necessary the procedure was repeated until the impurities were below the following levels:

benzene < 2%, cyclohexene < 5%, 1,4-cyclohexadiene < 0.3%. The material was then dried with $MgSO_4$ and distilled into a storage bulb that could be disconnected from the vacuum system for cold storage.

Later batches of 1,3-cyclohexadiene from Aldrich Chemical Co. were 99.4% pure, however they contained hydroquinone. The latter compound virtually eliminated the formation of polymer. It was removed by repeated vacuum distillation. The diene was dried with $LiAlH_4$ and distilled into the storage bulb. Impurity levels of this diene were: benzene 0.4%, cyclohexene 0.13%, and 1,4-cyclohexadiene 0.07%.

(b) Benzene

Phillips Petroleum Co. Research grade benzene was treated with concentrated sulfuric acid until no colouring of the sulfuric acid occurred, usually two treatments were sufficient. The benzene was then washed 3 times with doubly distilled water, once with 0.5% sodium bicarbonate solution and again 3 times with doubly distilled water and left to dry over anhydrous $MgSO_4$. It was then decanted and stored at 5°C. After two thirds of the benzene was crystallized the liquid phase was decanted, and the crystallisation procedure was repeated once more. Finally the benzene was distilled from sodium metal into a storage bulb on the vacuum system. The benzene so treated contained about 0.02% toluene.

(c) Cyclohexane

Phillips Petroleum Co. Research grade or Eastman Organic Chemicals spectro grade cyclohexane was shaken for 12 hour period until no further colouration of the sulfuric acid occurred. It was washed with doubly distilled water, then with 0.5% sodium bicarbonate solution and again with doubly distilled water and left to dry over $MgSO_4$ overnight. It was then distilled through a 30 cm Vigreux column; the middle half was retained. Finally, it was dried over sodium and distilled into a storage bulb on the vacuum system.

(d) Propyl ether

Eastman Organic Chemicals di-n-propyl ether (100 g) was shaken 3 times with 100 ml of 0.3% $FeSO_4$ in doubly distilled water to remove peroxides, followed by three more washings with 100 ml aliquots of water. After drying with $MgSO_4$ it was decanted into a 250 ml flask; chips of sodium were added, the mixture was degassed and left overnight. The first 80% was then distilled on top of fresh sodium metal and after one more day of drying it was distilled into the storage bulb on the vacuum system. Later, it was dried again, now with a sodium mirror, and stored in contact with a sodium mirror. The purified ether was 99.7% pure; none of the 5 impurities was an alcohol.

(e) Ethyl alcohol

Benzene-free absolute ethanol from Reliance Chemical Co. was used as received.

(f) Hexane

Phillips Petroleum Co. pure grade hexane was shaken with H_2SO_4. No colouring of the sulfuric acid occurred. The hexane was washed with doubly distilled water 3 times, then with a sodium bicarbonate solution and again with doubly distilled water 3 times. It was dried with anhydrous $MgSO_4$ and slowly distilled under vacuum through a 5 cm thick layer of P_2O_5 into a storage bulb.

(g) Additives for irradiation

SF_6 and N_2O (Matheson of Canada Ltd.) were purified by E. D. Stover by trap to trap distillation, the first portion being pumped away. The minimum purities were 98.0% and 99.6%, respectively.

Carbon tetrachloride (McArthur Chemical Co.) was used as received.

Oxygen from Liquid Carbonic Canadian Corp. Ltd. (Industrial grade) was passed over KOH pellets and through P_2O_5 into a 2 l storage bulb. It was condensed into a trap that was cooled in liquid nitrogen, then allowed to evaporate into a storage bulb after removal of the liquid nitrogen. The last 10% was discarded. This procedure was repeated once more.

2. Materials for calibration and identification

The materials used for purposes of calibration and identification are given in Table II-1. They were used without further purification.

3. Materials for gas chromatography

A number of ready to use column packings were supplied by F & M Scientific: di(2-ethylhexyl) sebacate, di-ethylene glycol succinate (LAC-728), polyphenylether, Silicone Rubber SE-30. In all cases the solid support was Diatoport W. A. W. 60-80 mesh and the liquid loading was 10% by weight.

Other materials used for gas chromatography are listed in Table II-2.

4. Water

Doubly distilled water was used for rinsing glassware, for preparing the Fricke dosimeter, and for the washing of compounds that were to be irradiated. It was prepared by distillation from a solution containing 0.1 g $KMnO_4$ and 0.2 g KOH per liter of water, followed by a second distillation.

TABLE II-1

Materials used for calibration and identification

Name	Source	Remarks
n-dodecane	Phillips Petroleum Co.	Pure grade
bicyclohexyl	Aldrich Chemical Co.	-
cyclohexene	Eastman Organic Chemicals	-
cyclohexylcyclohexene	Frinton Laboratories	-
2,2'-bicyclohexenyl	prepared as described	i
1,1'-bicyclohexenyl	Frinton Laboratories	-
thermal dimers	prepared as described	ii
photo dimers	prepared as described	iii
n-propanol	Fisher Scientific Co.	Reagent grade
isopropyl alcohol	Nichols Chemical Co.	Reagent grade
n-butanol	British Drug Houses,Ltd.	Reagent grade
sec-butanol	Eastman Organic Chemicals	-

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i 2,2'-bicyclohexenyl was prepared by B. Wakeford from cyclohexene, using the method described by Farmer and Moore (84).

ii Thermal dimers were prepared by heating 2.8 g of

cont'd.........

TABLE II-1 (continued)

freshly distilled and degassed 1,3-cyclohexadiene for 15 hours in a sealed tube at 195°C. The reaction mixture was then distilled and the dimers were redistilled, bp 80 - 86°C/7 mm; yield 1.5 g (55%).

iii Photodimers were prepared using the method of Valentine (77). 60 g of 1,3-cyclohexadiene and 5.5 g of 2-acetonaphthone were dissolved in enough 2-methylbutane to give a total volume of 300 ml. Nitrogen was bubbled through the solution to remove oxygen. The solution was photolysed for 22 hours by a Hanovia medium pressure mercury lamp, surrounded by a water jacket, immersed in the solution. The reaction mixture was distilled and the dimer fraction was redistilled; bp 63 - 66°C/2 mm, yield 24 g (40%).

TABLE II-2

Materials for gas chromatography

Name	Source
Apiezon Greases	Metropolitan-Vickers
L,T	Electrical Co., Ltd.
J	Varian Associates
Chromosorb W HMDS treated	Chromatographic Specialties
Chromosorb W. A. W.	F & M Scientific
Firebrick (Kromat FB)	Burrell Corporation
Helium	Canadian Helium Ltd.
Hydrogen	Canadian Liquid Air Ltd.
Molecular Sieve (Type 4A)	Linde
Nickel Catalyst Ni-0101	Harshaw Chemical
β,β'-oxydipropionitrile	F & M Scientific
Silicone oil - 710	Dow Corning
Silicone Rubber SE-30	F & M Scientific

B. Apparatus

1 High Vacuum System

A high vacuum system was used for (i) the handling and accurate measurement of gaseous additives, (ii) the preparation of samples, and (iii) for the purification and storage of solvents. The glassware required for these purposes is described below. Each system was connected with a high- and an auxiliary-vacuum manifold. The auxiliary vacuum manifold was used whenever a part of the system at atmospheric pressure was to be evacuated. In this way the high vacuum manifold was never exposed to large volumes of gases or vapours; this reduced the time required to attain high vacuum (< 10^{-5} mm Hg) and it prevented oxydation of the mercury in the diffusion pump.

(a) Main manifold

An outline of the main manifold system is given in Fig. II-1. The pressure in the main manifold was measured with a Pirani vacuum gauge (Consolidated Electrodynamics Type GP-110). Pressures less than 5 microns were measured by a McLeod gauge. The bulk volume of the McLeod gauge was 526 ml; the diameter of the measuring capillary was 0.205 mm^2.

(b) Gas handling system

Figure II-2 shows the lay-out of the gas handling

FIGURE II-1

High Vacuum and Auxiliary Vacuum Manifold

MDP	Mercury diffusion pump
OP-1	Rotary oil pump, Welch Duo-Seal Model 1405
OP-2	Rotary oil pump, Welch Duo-Seal Model 1400
T1, T2	Cold traps. 4.5 x 30 cm with 𝕊 45/50 joints
	Inner tube 2.5 x 26 cm.
S	Stopcocks, high vacuum,
	1,7 2-mm bore to atmosphere
	2 10-mm bore "L" shaped
	3 10-mm bore cranked
	4 8-mm bore
	5 4-mm bore
	6 4-mm bore "L" shaped
	Manifold tubing-Pyrex, 25 mm.

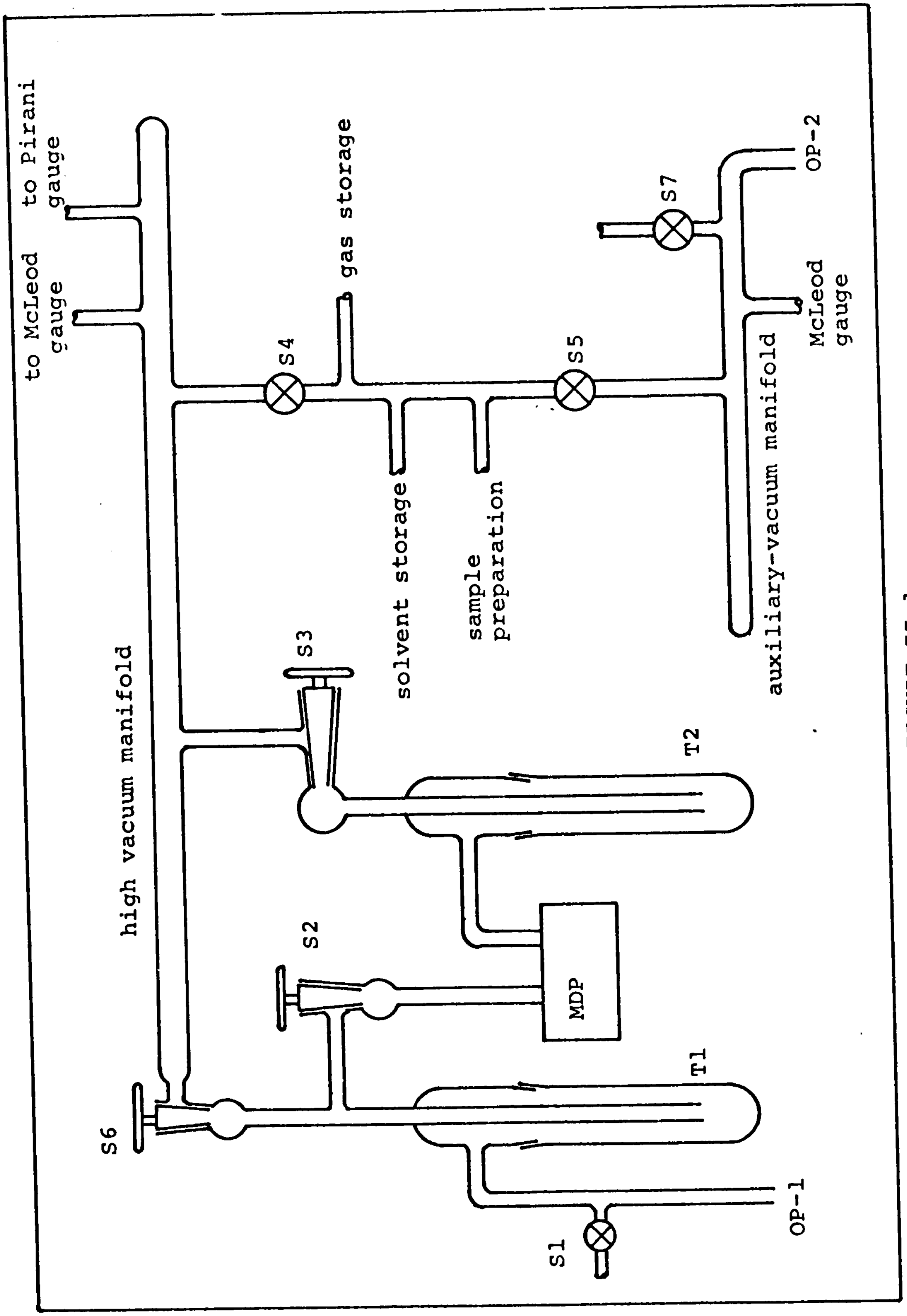
to Pirani gauge
to McLeod gauge
gas storage
S4
S5
S7
OP-2
McLeod gauge
solvent storage
sample preparation
auxiliary-vacuum manifold
high vacuum manifold
S3
T2
S2
MDP
T1
S6
S1
OP-1

FIGURE II-1

FIGURE II-2

Gas Handling System

ML	Mercury Lock for introduction of gases.
P	P_2O_5 drying tube
F1,2	sintered glass disk, 25-50 micron
T3	Trap
S8,9	Stopcocks high vacuum 2-mm
S10	Stopcock high vacuum 2-mm L shaped
	All other stopcocks are 4-mm high vacuum
SB1	Storage bulb 2 l.
SB2	Storage bulb 1 l., equipped with "cold finger"
M	Mercury manometer
C1	calibrated volume 12.15 ml to dotted line
C2	calibrated volume 1.646 ml to dotted line

The volume enclosed by the dotted lines is 121 ml.

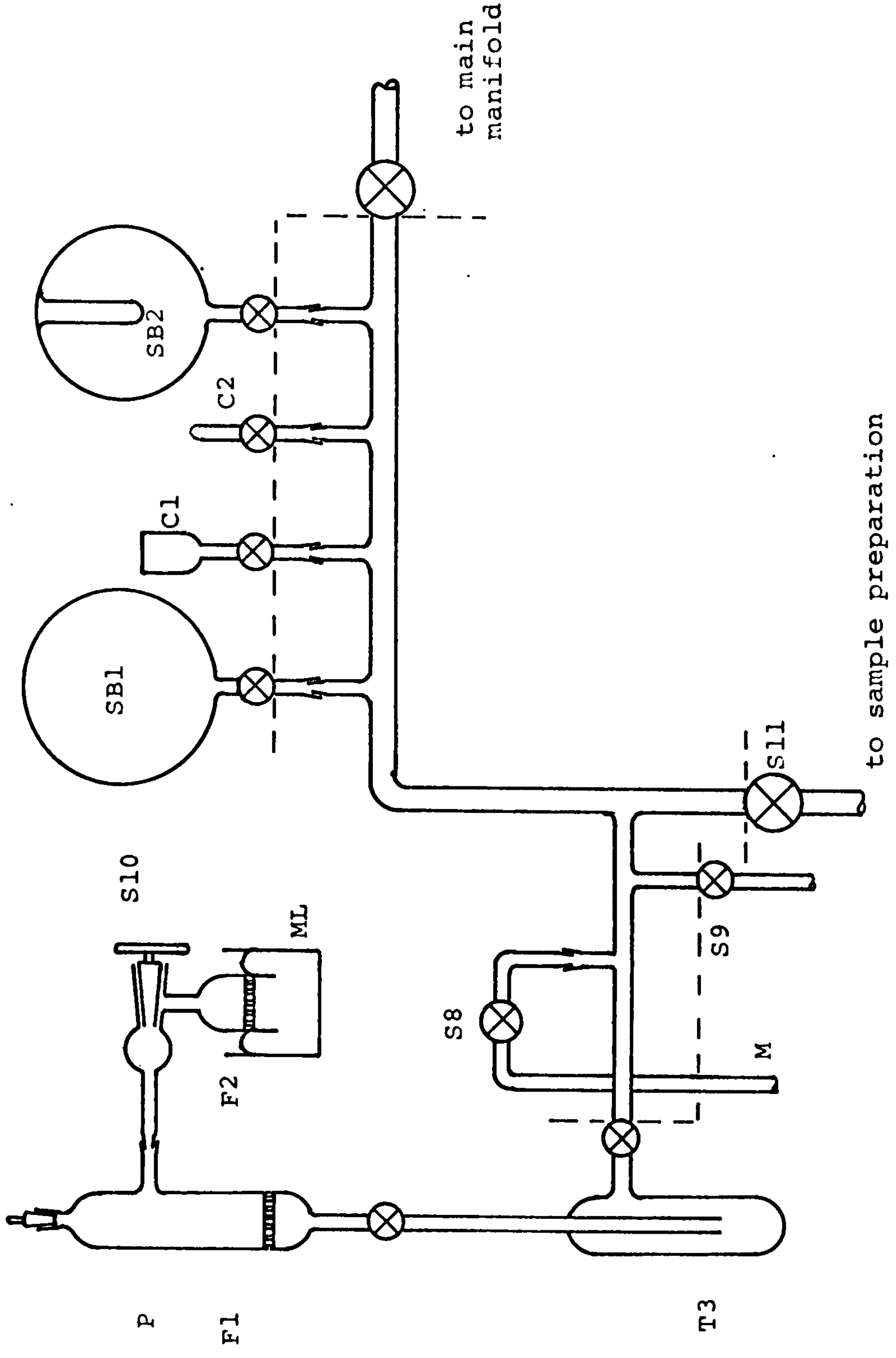
P
F1
T3
F2
S10
ML
S8
M
S9
SB1
C1
C2
SB2
S11
to main manifold
to sample preparation

FIGURE II-2

system, together with a listing of some calibrated volumes.

(c) Liquid Storage System

The liquid storage system consisted of one 16 mm o.d. tube to which several storage bulbs, sidearms equipped with 12/30 joints, and "seal off" sidearms were attached. The storage vessels for benzene, cyclohexane, and 1,3-cyclohexadiene were equipped with Republic metal bellows valves. The n-hexane storage bulb was closed with a greaseless Springham valve with Viton-A diaphragm. The bulb containing propyl ether was closed with a Delmar greaseless valve. The liquid storage system was connected with the main manifold by means of a 4 mm Springham valve with Viton-A diaphragm.

(d) Sample Preparation System.

The sample preparation system is illustrated in Figure II-3. Trap T4 has a 24/40 ground joint to permit easy cleaning. Five samples could be degassed simultaneously with this system.*

2. Gas Chromatographic Instruments

A gas chromatograph (g.c.) was used for (i) the

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* I am indebted to J. W. Fletcher of the Radiation Chemistry group for the design of the degassing equipment.

FIGURE II-3

Sample Preparation System

GJ	Ground joint 10/30 \$ for glass blowing purposes.
T4	Trap
SC	Sample cells.
A,B	Position of stopcock during degassing and distillation into trap T4 respectively (see text for details of the degassing procedure).
S12, S13	Stopcock high vacuum 4 mm bore.

The volume of the sample filling line including sample bulbs and stopcocks S13 closed was 228 ml.

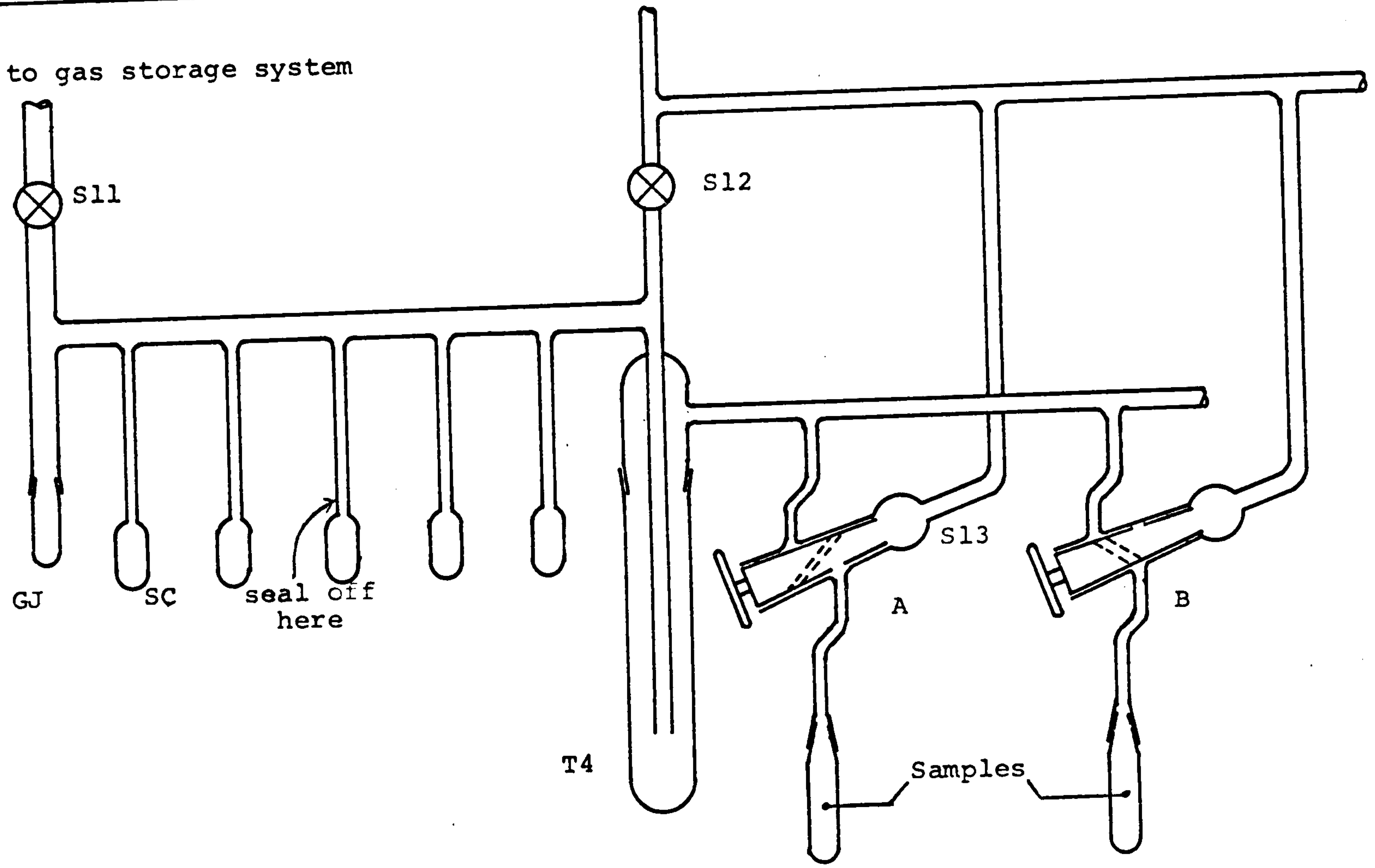
to gas storage system
S11
S12
GJ
SC
seal off here
T4
S13
A
B
Samples

FIGURE II-3

purification of 1,3-cyclohexadiene, (ii) the identification and quantitative measurement of impurities in the materials used for irradiations, (iii) the identification of radiolysis products and (iv) the analysis of irradiated samples. Of the several different instruments used during the course of this work only the instrument used for the analysis of most of the benzene samples (g.c. with converter) and the final modification of the instrument used for all other samples (g.c. with flame detector) will be described here in detail.

(a) Gas chromatograph with converter.

A Gow-Mac Instruments thermal conductivity detector equipped with Tungsten Type W_2 filaments was employed as detector in the instrument used for most of the benzene samples. To prevent condensation of high boiling materials in the detector, the detector must be heated to a temperature close to the boiling point of the material, in this case about 230°C. However, the maximum allowable current through the filaments at this temperature (with He as carrier gas) is 225 mA; this compares to 340 mA at 100°C. Since the response of the detector is proportional to the third power of the current,the drop in maximum current corresponds to a 3.5

fold loss in sensitivity. In order to fully utilize the potential of the W_2 filaments a converter (85,86) was inserted between the column and the detector.* The function of the converter was to quantitatively reduce the organic compounds in the column effluent to methane with the aid of hydrogen that was used as carrier gas. The converter consisted of 30-60 mesh Harshaw Ni-0101 Nickel catalyst (86) contained in a U shaped Pyrex tube 16.5 cm long with 0.45 cm i.d. The temperature of the catalyst was not critical as long as it was held between 300 and 450°C.

The advantages of the converter system were:

- detector temperature lowered to 100°C.
- sensitivity for methane was higher than for C_{12} compounds. This, combined with the lower detector temperature increased the sensitivity by a factor of 15.
- calibration for methane only. This was very important in the early stages when measurements were done on essentially unknown products, for which no standards could be used. The only

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*I am indebted to L. G. Walker of the Radiation Chemistry group for pointing out his procedure and for the supply of a catalyst that was used in an earlier instrument.

assumption that had to be made was that the measured peaks were those of C_{12} compounds.

Disadvantages of the converter system were:

-minimum carrier gas flow rate of 70 ml/min.

-hydrogen carrier gas, which is always somewhat dangerous.

-long conditioning periods after shut-down

-broadening of the peaks by 10-20%.

The most serious shortcoming of the g.c. with converter was insufficient sensitivity. With the radiolytic system under study it was not possible to irradiate for longer periods to increase the amount of product that was to be measured. At the sample sizes necessary to obtain measurable peaks (∿ 100 μl) the amounts of polymer present in the irradiated samples impaired the efficiency of the column after a few injections: an increase in sample size would thus decrease the number of analyses that could be done in a certain period. The solution to these problems was found in the hydrogen flame detector.

(b) Gas chromatograph with hydrogen flame detector.

Important features of the hydrogen flame detector are the high sensitivity towards organic compounds and the absence of baseline drift due to changes in the carrier gas flow rate. Basically the gas chromatograph was an Aerograph Autoprep 705 (Varian Associates) equipped with variable effluent splitter and hydrogen flame detector. Some modifications were carried out; they will be described below together with the detector characteristics (specificity, sensitivity and linearity).

(b1) Column connections

The Aerograph Autoprep has a large-volume injector to facilitate the injection of milliliter quantities of material. In analytical work a small volume injector is desirable to minimize peak broadening. Although a small volume is a less stringent requirement in programmed temperature gas chromatography (87) an injection insert was constructed of 1/8" copper tubing (Fig. II-4) in order to reduce to a minimum the residence time of the sample in the relatively hot injector.

The variable effluent splitter was closed off by a silicone seal (Fig. II-5) to permit passage of the whole sample through the detector for analytical work.

(b2) Carrier gas regulation

The carrier gas flow rate was regulated with a needle valve (Edwards High Vacuum Ltd) in line with a Moore constant-differential type flow controller, Model

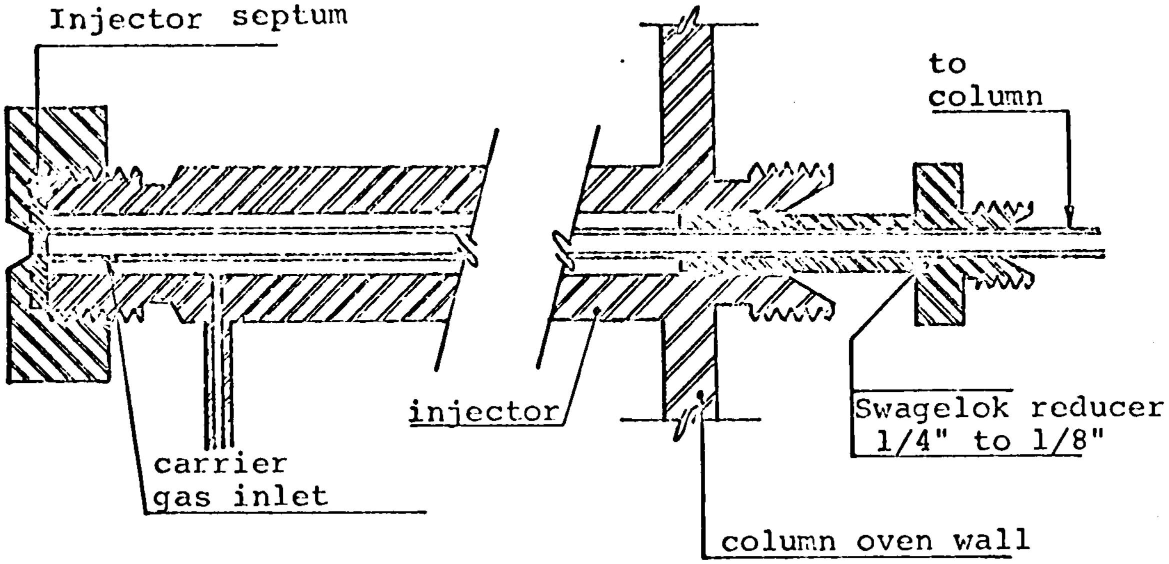


FIGURE II-4. Injector insert. The Swagelok nuts and ferrules on the outlet side have been omitted from the drawing for reasons of clarity.

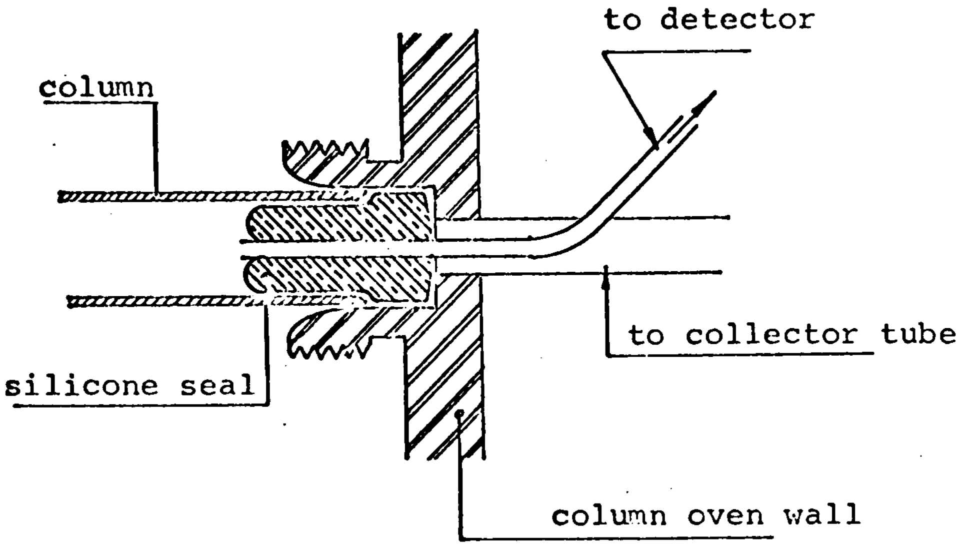


FIGURE II-5. Column outlet assembly, showing the position of the silicone seal during analytical work. The Swagelok nut and ferrules on the outlet end of the column are not drawn for reasons of clarity.

63 BU-L. The pressure drop over the flow controller was about 15 p.s.i.

(b3) Column oven temperature control.

A linear temperature programmer (West Instruments) was installed to improve the reproducibility of the temperature of the column oven at the time of injection, and to extend the linear portion of the temperature-time profile, that otherwise would have been of the ballistic type.

(b4) Specific response of the detector.

The response of hydrogen flame detectors to organic compounds is roughly proportional to the amount of carbon they contain (88a). Thus when two C_{12} compounds give identical peak areas the number of moles of each of the compounds are identical. This proportionality of the signal to the number of carbon atoms present was tested in the following way. Standard solutions of cyclohexane containing n-dodecane ($C_{12}H_{26}$) and thermal dimers ($C_{12}H_{16}$) in ratios varying between 1:3 and 3:1 were injected on the g.c. The area under the n-dodecane peak served as a "standard", i.e. this area was a measure of the amount of standard solution injected. From the ratio of the peak areas the amount of thermal dimers in the standard solution was calculated, assuming that the peak areas were proportional to the number of moles present in each peak. A second calculation assumed the peak areas to be proportional to the weight of the compounds in the standard solutions. Since the amount of thermal dimers in each standard solution was accurately known, a plot of the measured amount vs the amount weighed-in would reveal which one of the two assumptions was the more accurate. The result is depicted in Fig. II-6. The slope of the line through the points is 0.975. With the second assumption the slope is 1.03. It was expected that the slope would be < 1.0, since there were some impurities (∿ 1%) in the thermal dimers. The signal from the flame ionisation detector was thus taken as being proportional to the number of carbon atoms present.

(b5) Sensitivity and linearity of the response of the detector.

The linearity of the response of the detector was established by injecting various amounts of a standard solution. For instance, the graph obtained in the experiments to establish the specificity of the detector also shows that the response is linear over at least a three fold range. When analytical measurements were performed, n-dodecane was always added to the samples as internal standard (see procedure for details of this technique), in amounts roughly equal to the expected amounts of

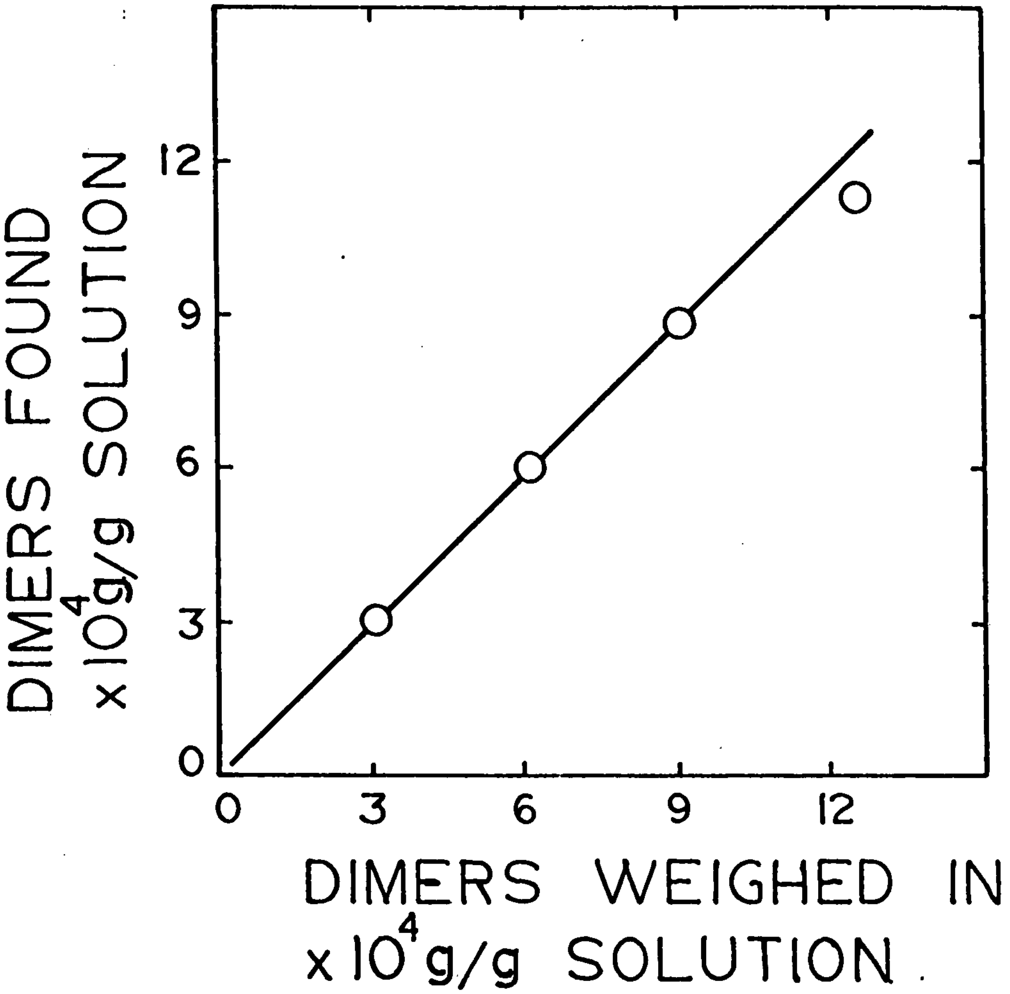


FIGURE II-6. Specific response of hydrogen flame detector. The calibration points are calculated on the assumption that the flame detector response is proportional to the number of moles rather than to the mass of the organic compound.

ducts to be measured. It was thus sufficient to establish the linearity of the detector (and recorder) response over a three fold range.

The sensitivity of the g.c. is the slope s of the line with the equation: $A/c = s V + b$, where A is the peak area in cm^2, c is the concentration of the compound for which the sensitivity is being measured in moles/μl, V is the volume injected in μl and b is a correction that arises from the evaporation of sample from the needle of the syringe. Figure II-7 depicts the results obtained for a series of irradiated samples to which n-dodecane was added in known amounts. The good straight line obtained indicates that the g.c.-recorder pair gave a linear response over the region of interest. The slope of the line corresponds to a sensitivity of 0.85 cm^2 peak area for 10^{-10} moles n-dodecane (attenuation x 16, chartspeed 1"/min), and the intercept with the volume axis clearly demonstrates that about 0.35 μl of sample evaporates from the needle into the injector.

3. Radiation sources

Two radiation sources were used in this work. For the dose rate studies a ^{60}Co radiation cave was used. All other irradiations were done in a Gammacell-220 (Atomic Energy of Canada Ltd.) with a strength of about

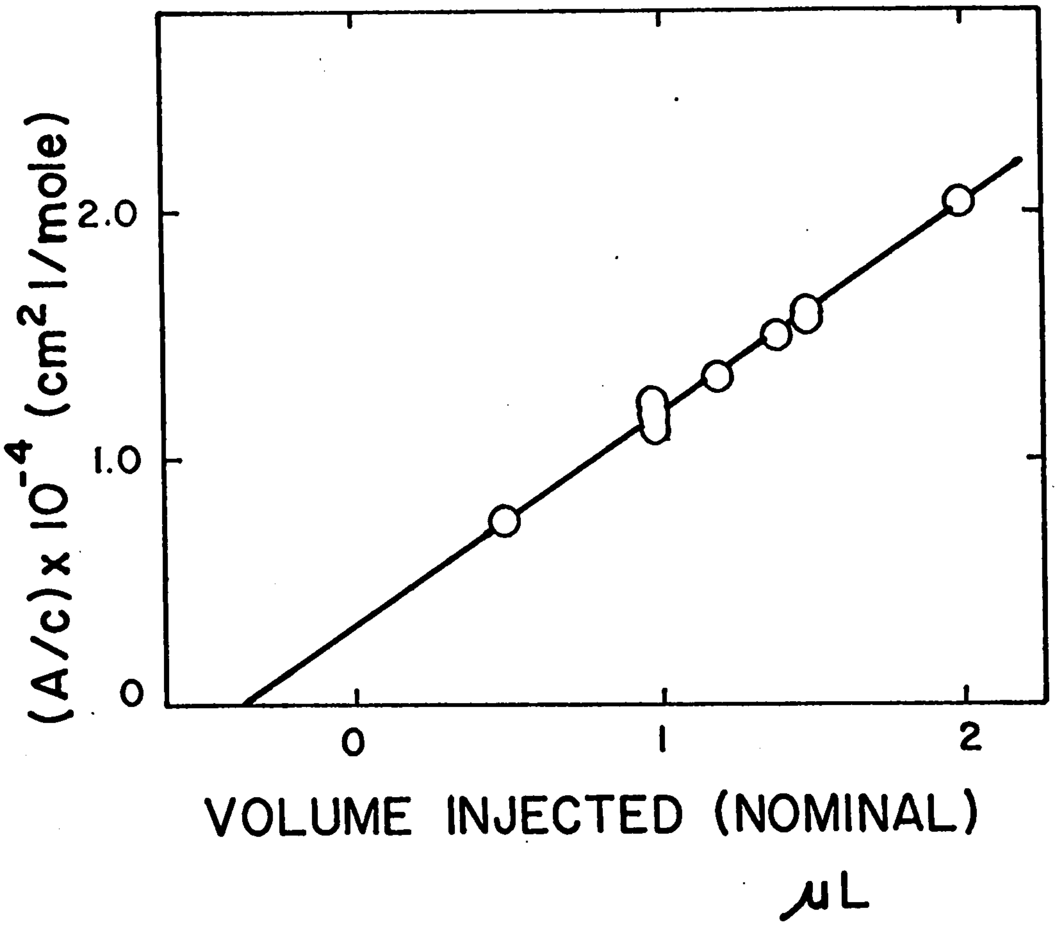


FIGURE II-7 Sensitivity and linearity of hydrogen flame detector.

8000 curies ^{60}Co. The samples were contained in an aluminum sample holder in which the dose rate was 7.47×10^{19} eV (electron-mole)$^{-1}$ hr^{-1} for a 2.0 ml sample in position #1 on January 1, 1966. The temperature of the samples during radiolysis was 23 ± 2°C.

C. Procedure.

1. Dosimetry

Dosimetry of the radiation intensity in the Gammacell was done with Fricke dosimeter solution (89). 2.0 ml samples were irradiated for time intervals ranging from 0.5 to 3.0 minutes. 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 ferric-ion concentration is given by:

$$[\mathrm{Fe}^{+++}] = \frac{\mathrm{OD}}{2201[1 + 0.007(t-25)]}$$

where OD is the optical density of the solution at 304 nm, t is the temperature of the aliquot analysed in the spectrophotometer in degrees centigrade, and $\varepsilon\mathrm{Fe}^{+++}$ = 2201 at 25°C and 304 nm. Figure II-8 shows an irradiation time vs Ferric-ion concentration plot obtained for Fricke solution irradiated in the Gammacell (position #11 in aluminum holder). The intercept with the time axis occurs because the timer is actuated when the sample

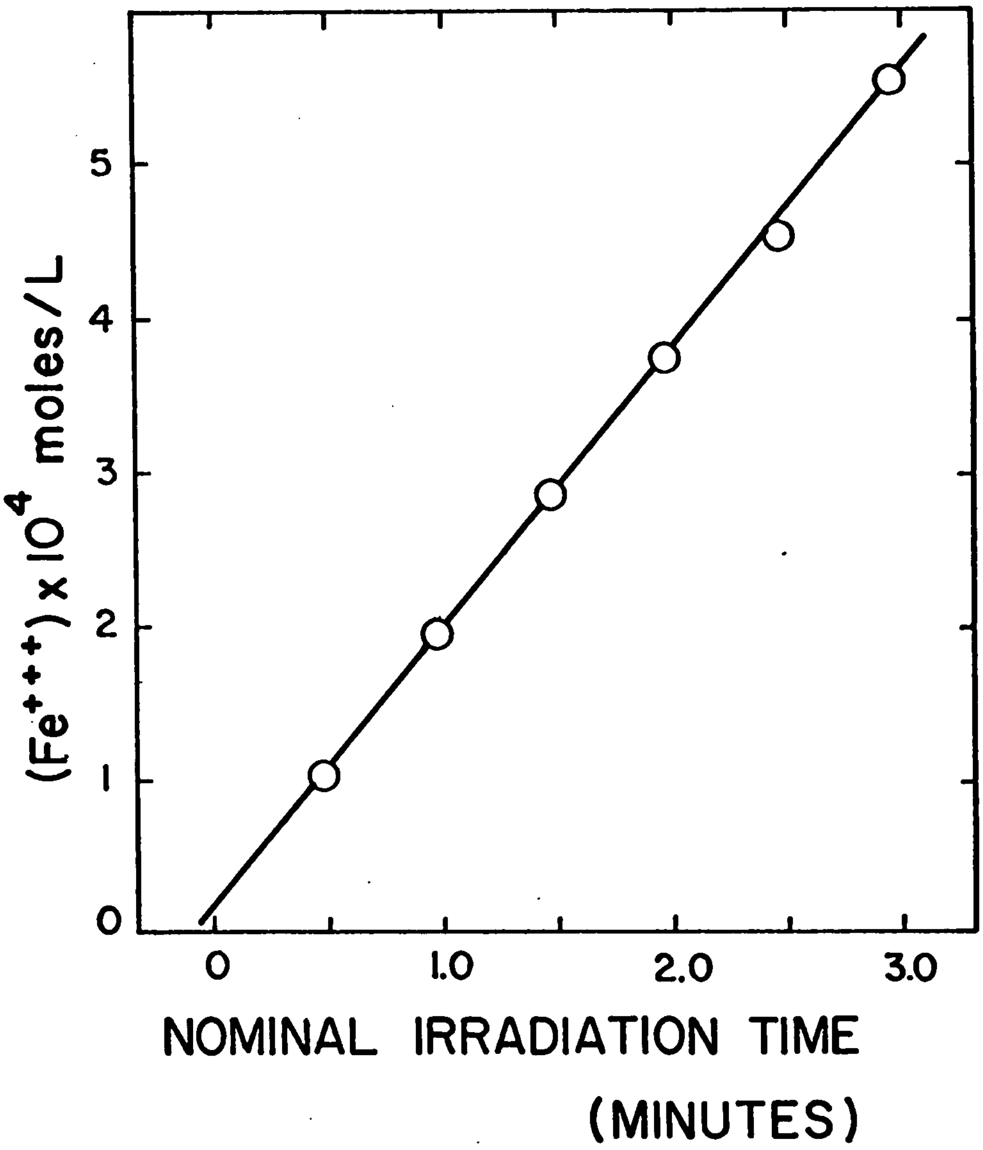


FIGURE II-8 Irradiation time-Ferric-ion concentration plot for Gammacell Dosimetry with the Fricke dosimeter solution.

drawer is in its final lowered position. The dose rate to which the sample was subjected is given by:

$$D = \frac{F \times 10^{-3} \times 60 \times N_o}{15.6} \times 100$$

where D is the dose rate in eV ml^{-1} hr^{-1}, N_o is Avogadro's number, F is the slope of the Ferric-ion concentration vs irradiation time plot in moles l^{-1} min^{-1} and 15.6 = $G(Fe^{+++})$.

In calculating the dose rate for liquids other than the Fricke solution it was assumed that the dose rate is proportional to the electron density of the liquid. The electron density of Fricke solution was taken as 0.566 electron moles/ml at 25°.

The dose rate at a time t months after doing dosimetry was calculated from the decay law:

$$D = D_o \exp(-\lambda t)$$

where λ was taken as 1.096×10^{-2} $month^{-1}$ (90).

2. Sample preparation.

(a) Sample cells

Sample cells (Fig. II-3) were made from 15 mm o.d. Pyrex glass. They were cleaned with boiling sulfo-nitric acid (3:1), then rinsed many times with doubly distilled water. After drying in a clean oven the cells were attached to the sample preparation manifold. Prior to filling, the cells were evacuated, heated with an open flame and pumped on for one hour more.

(b) 1,3-Cyclohexadiene solutions.

The filling procedure for 1,3-cyclohexadiene solutions consisted of the following steps.

- The desired concentration of diene in solvent was made up by weighing the components into a small covered vial.
- The vial was attached to the filling line via a 12/30 ground joint at stopcock S13 (Fig.II-3)
- Degassing the mixture by three freeze-pump-thaw cycles. The construction of the filling line was such that during the pumping stage of the degassing cycle, the vacuum in the remainder of the line was not disturbed (S12 closed, S13 in position A of Fig. II-3).
- Distillation of the degassed sample into the cold trap, while pumping on the trap (S12 open, S13 in position B).
- Distillation from the trap to the cell and sealing off by collapsing the filling tube with a flame.

(c) Samples with gaseous additives.

The procedure followed for the preparation of samples with gaseous additives (N_2O, SF_6) was the same as the one described for the solutions. However before the cell was sealed off, a known amount of the additive was frozen on top of the sample.

The concentration of the additive in the liquid phase of the sample was calculated from the Ostwald absorption coefficient α.

$$\alpha = \frac{[\text{gas in liquid}]}{[\text{gas in vapour}]} = \frac{\frac{x}{V_l}}{\frac{n-x}{V_g}} \qquad \text{(eq. II-1)}$$

where x is number of moles of additive in the liquid, n is total number of moles of additive, V_l is volume of the liquid phase and V_g is volume of the gas phase. Rearrangement of eq. II-1 gives:

$$\frac{x}{n} = \frac{\alpha V_l}{V_g + \alpha V_l}$$

In all samples V_l was 2.0 ml, V_g was measured after sealing off, by holding the sample vertical and placing a mark at the middle of the meniscus. The sample was then turned upside down and again the meniscus was marked. From the distance between the two marks and the known inner diameter of the sample tube (12.4 mm) the volume of the vapour phase was calculated.

The Ostwald absorption coefficient of N_2O in cyclohexane was taken as 2.62 (91) and that of SF_6 as 1.30 (92).

(d) Samples containing oxygen.

Oxygen has an appreciable vapour pressure at liquid nitrogen temperature (∿ 15 cm). It is thus not possible to completely condense a known amount on top of the frozen sample. The amount of oxygen sealed into the sample was determined as follows.

Oxygen was let into the part of the gas handling system that is enclosed by the dotted line in Fig. II-2 and the pressure was measured. Stopcock S11 (Fig.II-3) was opened and the system was allowed to reach equilibrium with the sample immersed in liquid nitrogen. The sample was sealed off and the pressure in the filling and gas handling line was measured. From initial and final pressure and volume the amount of oxygen in the sample was calculated.

This technique is not recommended when it is desirable to accurately know the amount of oxygen in the samples. The oxygen added is calculated as the small difference between two large quantities and is thus subject to considerable error.

The solubility of oxygen in cyclohexane was interpolated from the solubilities of oxygen and nitrogen in various solvents (93)(Fig. II-9). The solubility of

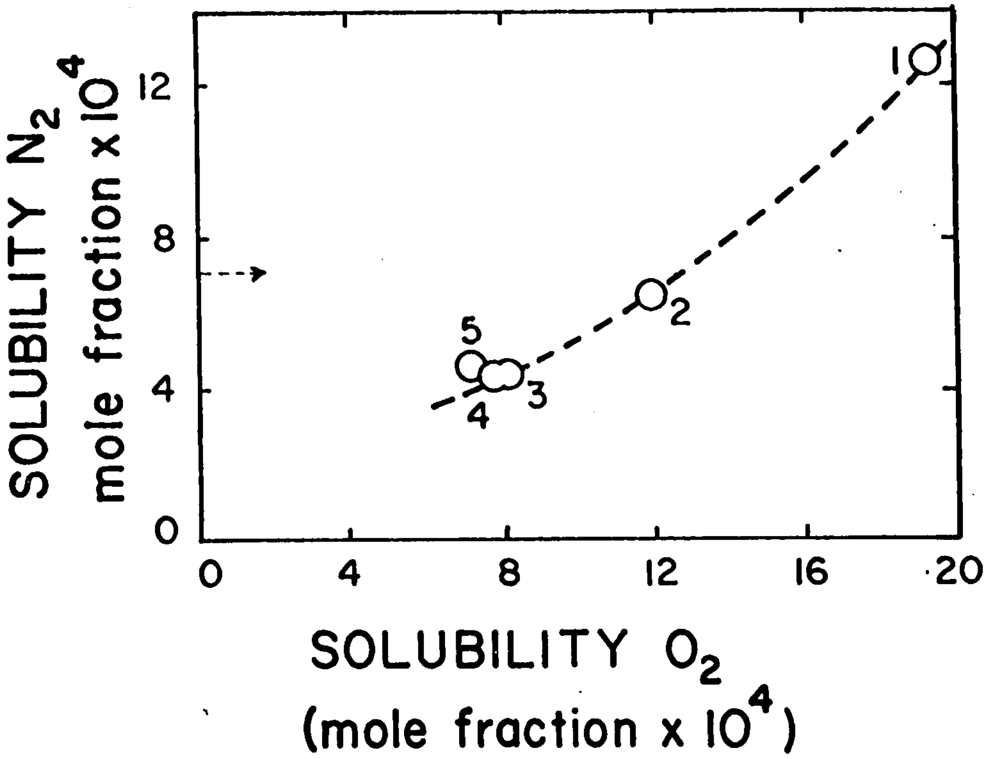


FIGURE II-9. Solubility of oxygen and nitrogen for various solvents at 25°C and 1 atm. 1. n-hexane; 2. Carbon tetrachloride; 3. Benzene; 4. chlorobenzene; 5. chloroform. The arrow indicates the solubility of nitrogen in cyclohexane (7.22). All data taken from ref. 93, p.243.

nitrogen in cyclohexane is 7.22×10^{-4} mole fraction at 25°C and 1 atm; this gives a value of 13×10^{-4} mole fraction for the solubility of oxygen in cyclohexane. The corresponding Ostwald absorption coefficient is 0.29 at 25°C.

(e) Samples with extra drying

In some cases it was suspected that moisture from the air was absorbed during the preparation of the solutions. The samples were then placed over 0.2 g $LiAlH_4$ in special vials (Fig. II-10). The fritted-glass disc in these vials prevented the $LiAlH_4$ from entering the sample filling line. The samples were considered to be dry when no more gas evolved from the hydride. Usually a four hour drying period was sufficient.

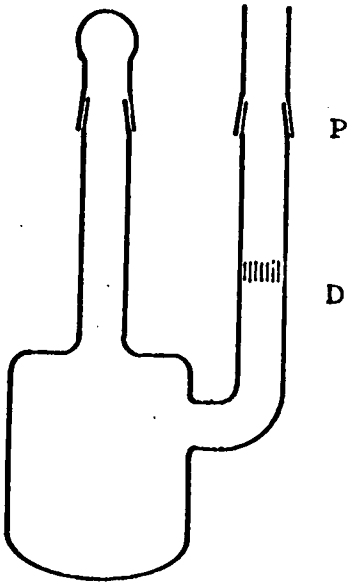


FIGURE II-10

Vial for additional drying of sample.

D. Fritted-glass disc 70 - 100 μ.

P. To sample preparation line.

3. Sample analysis.

The analysis of irradiated samples naturally divides into two parts: (i) qualitative analysis and (ii) quantitative analysis. The techniques used in the qualitative analysis will be briefly described here, followed by a more detailed description of the quantitative analysis.

(a) Qualitative analysis.

The chief method of identification was comparison of retention times of product peaks on the g.c. with the retention times of authentic samples of the products. At least two different columns were used with this method.

In some cases the product peaks were trapped after elution from a preparative Apiezon L column and analysed by mass spectrometry, nmr, or ir spectroscopy. The products found are given in the results section.

(b) Quantitative analysis.

The quantitative analysis was done exclusively by gas chromatography. A list of the gas chromatographic columns that were used for the analysis of the materials to be irradiated is given in Table II-3. The columns that were tried to obtain optimum resolution of the C_{12} products are given in Table II-4. For a number of columns the separation obtained between the two thermal

TABLE II-3

Gas Chromatographic Columns for Substrate Analysis

Columns	Conditions	Compounds separated	Retention time in minutes.
2.5 m x 3/16" β,β'-oxydipropionitrile 10% on Diatoport WAW 60-80 mesh.	isothermal 40°C. He carrier 35 ml/min	cyclohexane	1.2
		cyclohexene	3.5
		1,3-cyclohexadiene	6.1
		cis and *trans* 1,3,5 hexatriene	6.7 and 7.7
		1,4-cyclohexadiene	9.1
		ethanol	11.9
		benzene	13.7
		toluene	18.0
2.5 m x 3/16" Di-2-ethylhexylsebacate 10% on Diatoport WAW 60-80 mesh	isothermal 76°C He carrier 35 ml/min.	ethanol	3.5
		2-propanol	4.5
		n-propanol	7.5
		di-n-propylether	9.0
		2-butanol	10.0
		n-butanol	17.5

TABLE II-4

Columns for Gas Chromatography

Helium was used as carrier gas in all cases. Carrier gas flow rate was between 35 and 45 ml/min.

Length m	o.d. inches	Liquid phase	Support	Mesh size	Temp* °C.	Ret. time* min.	$R_{1,2}$*	Remarks
4	1/8	3% Silicone DC 550	Chromosorb W	60-80	120	11	0.8	
6	1/8	2% Apiezon L	Chromosorb W HMDS treated	80-100	130	28	1.2	tailing
4.5	3/16	2% Apiezon oil C	Chromosorb WAW	60-80	130		1.2	high background.
3	3/16	2% Apiezon L	Chromosorb WAW	60-80	135	18	1.2	tailing
2.5	3/16	3% Apiezon T	Firebrick	40-60	140	18	1.1	leading
3	3/16	10% Ucon 75H-1400	Firebrick	40-60	115	20	0	
3.6	3/16	10% LAC-728	Diatoport WAW	60-80	160	60	1.05	
4.5	3/16	10% polyphenylether	Chromosorb W	60-80	180	50	1.05	
5	3/16	2% Apiezon J	Chromosorb WAW	60-80	140	15	1.2	
3	3/16	2% OS-124	Chromosorb WAW	60-80	115	14	0	

cont'd.......

TABLE II-4 continued

Length m	o.d. inches	Liquid phase	Support	Mesh size	Temp* °C	Ret. time*	$R_{1,2}$	Remarks
4.5	3/16	10% Silicone Gum Rubber SE-30	Diatoport WAW	60-80	155	45	1.2	
2.5	1/4	15% Silicone Rubber GE-XE 60	Chromosorb W HMDS treated	80-100	155	18	1.2	
2.5	1/4	25% Silicone Oil 710	Chromosorb W HMDS treated	80-100	180	16	-	i
2.5	3/16	10% Carbowax 20M	Chromosorb WAW	60-80	120	20	0	
2	3/16	15% 1,3-cyclohexadiene polymer	Chromosorb W HMDS treated	80-100	120	--	-	high background
2.5	1/4	2% Apiezon L	Silicagel Medium Activity	60-80	200	35	-	isomerisation of dimers
4	3/16	2% Silicone Gum Rubber SE-30	Diatoport WAW	60-80	120	18	1.2	
60	1/8	Apiezon J	--	--	122	12.5	2.1	ii

Remarks from Table II-4

i. Carrier gas Hydrogen at 70 ml/min.

cont'd ....

TABLE II-4 continued

Remarks from Table II-4 continued.

ii. Open tubular column from Perkin Elmer. Helium carrier gas flow rate 20 ml/min.

* All columns were tried under a variety of conditions. The retention time for the first dimer peak, and the resolution given here were obtained for isothermal operation at the stated temperature.

dimer isomers is expressed as the resolution R. The resolution between two peaks is defined for isothermal operation (88b) by:

$$R_{1,2} = \frac{2\Delta t}{(w_1 + w_2)}$$

where Δt is the distance between the maxima of the two peaks, and w is the base width found by extrapolation of tangents. The subscripts 1 and 2 refer to the two peaks for which the resolution is being measured.

None of the columns tried gave complete separation ($R_{1,2} > 1.5$) of the dimers. The best results with respect to resolution and speed were obtained with the 2% Apiezon L and the 2% Silicone Rubber columns. With Apiezon L all four dimers of 1,3-cyclohexadiene were visible in the order I, III, II, IV. The resolution was not sufficient to allow accurate measurement of at least one of the first three peaks. With the Silicone Rubber column three peaks were visible in the order I, II + III, IV. The latter column was used in the final analytical scheme. The packing of the 2% Silicone Rubber column was prepared from the 10% F & M product as follows: 15 g of 10% Silicone Rubber SE-30 on Diatoport WAW 60-80 mesh was added to 440 ml carbon tetrachloride and heated on a steam bath. 350 ml of the hot solvent was decanted and the remainder was evaporated on a steambath. The packing was further dried and the fines removed by bubbling 200 ml/min dry nitrogen gas through 2 g aliquots, contained in a glass tube of 1 cm i.d. The nitrogen flushing improved the performance of the column considerably by virtually eliminating peak tailing. In order to obtain good results it was necessary to condition the column for three days at 200°C.

C. Internal standard.

An internal standard (n-dodecane) was added to the samples prior to analysis for the following reasons:

It is not necessary to know accurately the volume injected.

Evaporation of solvent after the standard is added will not alter the relative amounts of the standard and the C_{12} products.

A change in the sensitivity of the g.c. will not change the G values measured.

Linearty of the detector response is required over a small range only.

Thus the need for calibration curves was eliminated, once it was established that the standard and the products gave identical signals for identical amounts, and that the detector response was linear over the region of interest.

In practice approximately 100 μl of a standard solution of n-dodecane in cyclohexane was placed in a small covered vial and carefully weighed. The sample bulb was then opened and the contents added to the n-dodecane solution, and weighed again. It was now possible to assign a "G value" to the n-dodecane in the sample:

$$\text{"G"} = \frac{W_o \times d \times N_o \times 100}{W_1 \times M_d \times D}$$

where W_o is the weight in g of the standard solution to which W_1 g of sample was added; d is the concentration of n-dodecane of the standard solution in g n-dodecane/g solution; M_d is the molecular weight of n-dodecane (170.33); N_o is Avogadro's number, and D is the total dose per gram received by the sample.

The G values of the products were measured by measuring the peak areas with an Ott planimeter and comparing the areas with the area of the standard. A typical gas chromatogram is shown in Fig. II-11.

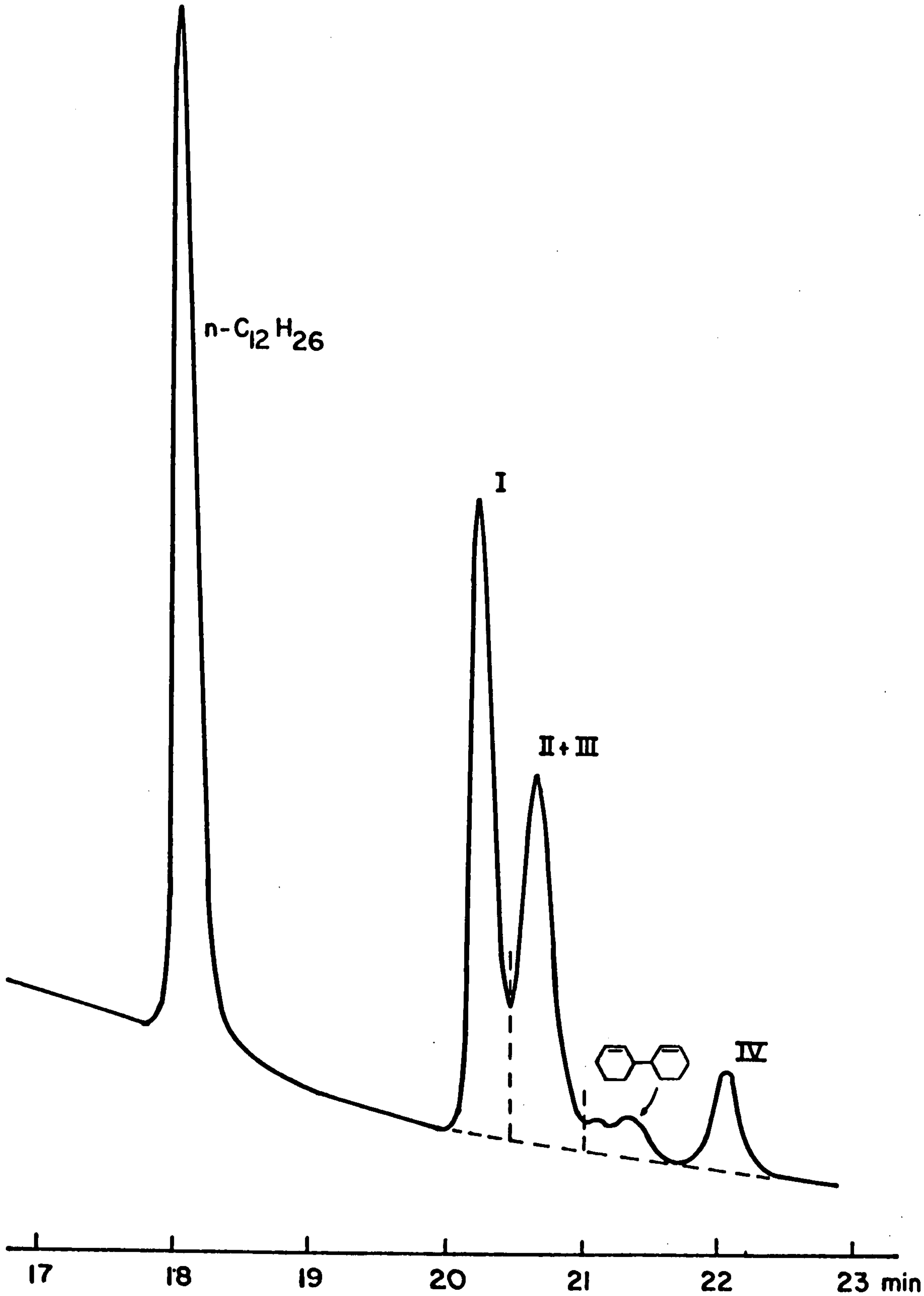


FIGURE II-11. Section of a gas chromatogram showing the C_{12} fraction of an irradiated sample with n-dodecane as internal standard. 2% Silicone Rubber SE-30 column.

III RESULTS

(A) Identification of C_{12} products.

Upon radiolysis of binary mixtures of CHD with benzene, cyclohexane, n-hexane, dipropylether, and ethanol, the major C_{12} products were four dimers of CHD. Two of these dimers were identical to those obtained when CHD was heated at 195°C in a closed tube. The other two dimers were identical to those obtained by photolysis of an isopentane solution of CHD containing β-acetonaphthone sensitizer.

Identification was done primarily by injections of mixtures of irradiated samples with authentic samples of thermal and photodimers on the g.c. Almost all the columns listed in Table II-4 were used in this identification.

The identification of the thermal dimers was supported by comparison of the nmr and ir spectra of the thermal product with those of the dimers isolated from 200 ml of a 1% CHD solution in cyclohexane, irradiated to a total dose of 1×10^{20} eV/g. The nmr spectra are shown in Fig. III-1. The agreement between the two spectra is good. It appears that the radiolysis sample contained some cyclohexane, as indicated by the extra absorption at $\tau = 8.562$. Literature lists $\tau = 8.564$ for cyclohexane (94). Fig. III-2 shows the ir spectra of the thermal and radiolysis products. Again extra absorptions are visible in the radiolysis product.

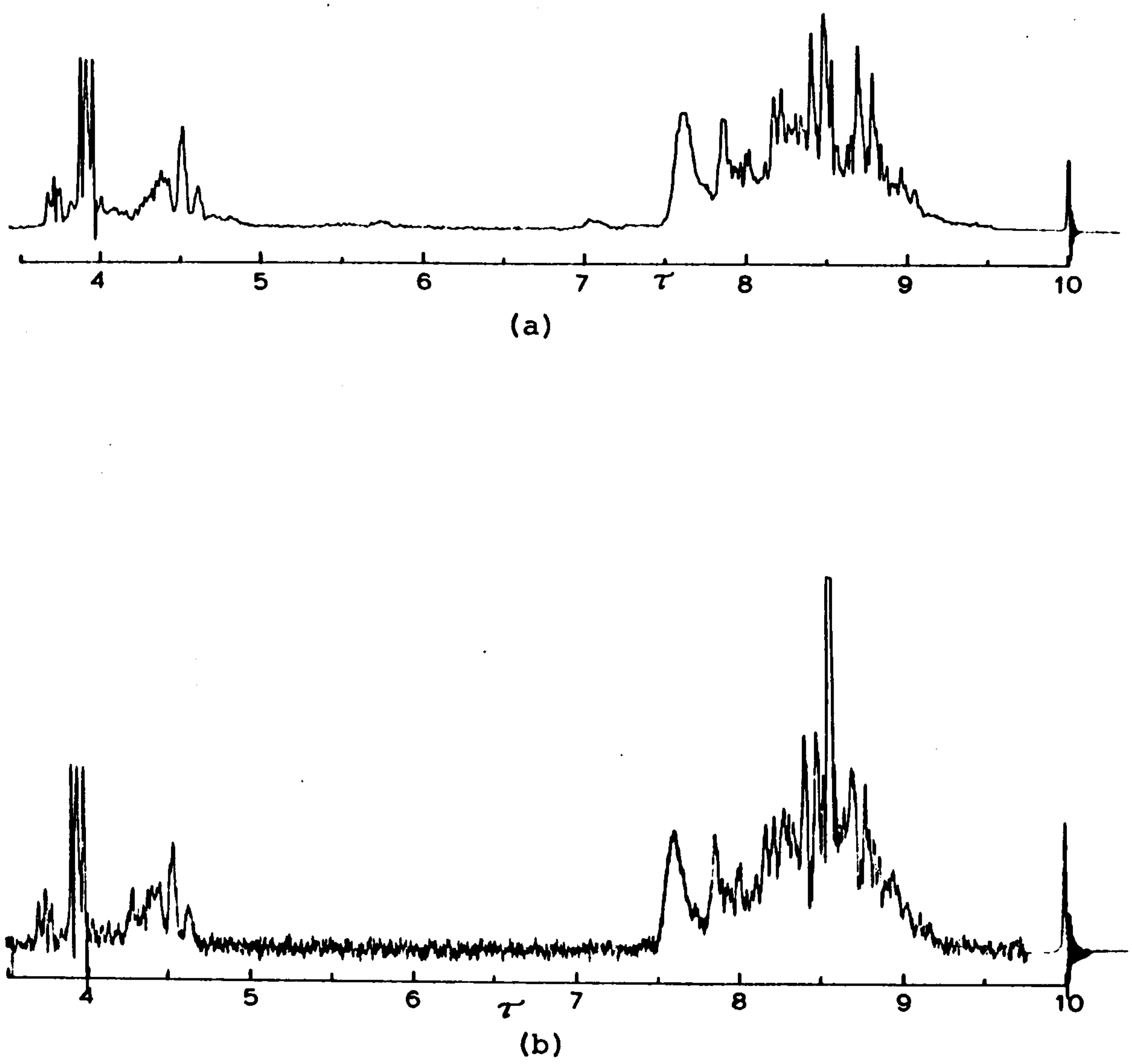


FIGURE III-1. Nmr spectrum of thermal dimers of 1,3-cyclohexadiene.

(a) Standard sample

(b) Radiolysis product.

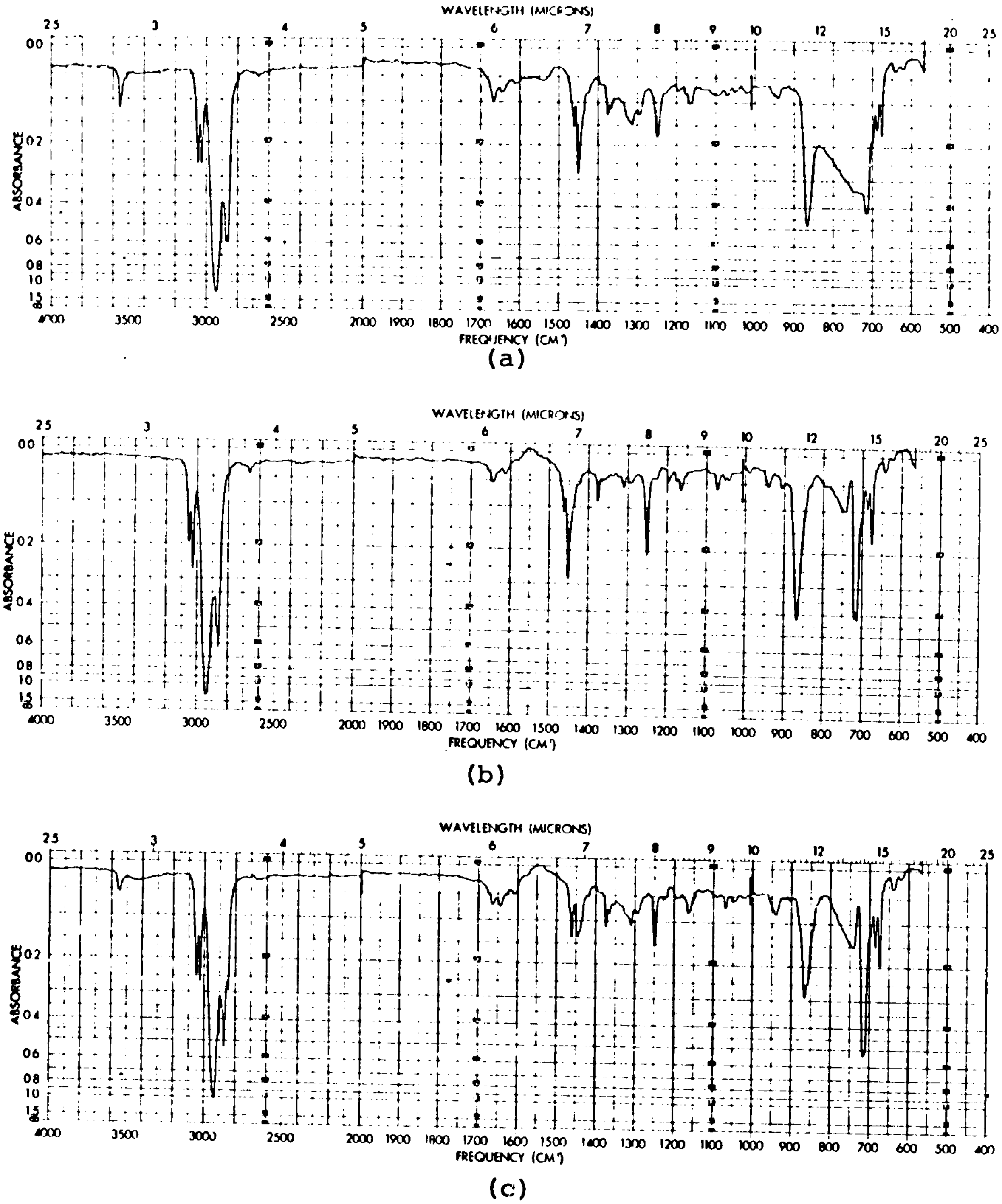


FIGURE III-2 ir spectrum of thermal dimers of 1,3-cyclohexadiene.

(a) Standard sample

(b) Radiolysis product

(c) Standard sample, after it was subjected to the same isolation procedure that was used for the radiolysis product.

At least some of these extra absorptions were introduced during the preparative gas-chromatography stage of the isolation procedure, as is illustrated by Fig. III-2C which shows the ir spectrum of the standard thermal product after it was subjected to the same procedure.

In dilute ethanol solutions the major C_{12} product was 2,2'-dicyclohexenyl. Identification was done by mixed injections on Silicone Rubber and Ucon columns. The dimer fraction was isolated from 100 ml of 4% CHD solution in ethanol irradiated to a total dose of 8×10^{20} eV/g. Fig. III-3 gives the nmr spectrum of the radiolysis product (recorded with a Varian HR-100) and that of an authentic sample (Varian A-60). The agreement between the two spectra is good.

In dilute solutions of CHD in cyclohexane there appeared an extra peak in the gas chromatogram, on the tail of the second CHD dimer peak. This product was identified by the mixed injection technique as dicyclohexyl. A minor peak appearing in almost all solvents was not identified beyond reasonable doubt. One compound which enhanced this peak upon mixed injection was cyclohexylcyclohexene. No attempt was made to get precise measurements of these minor products.

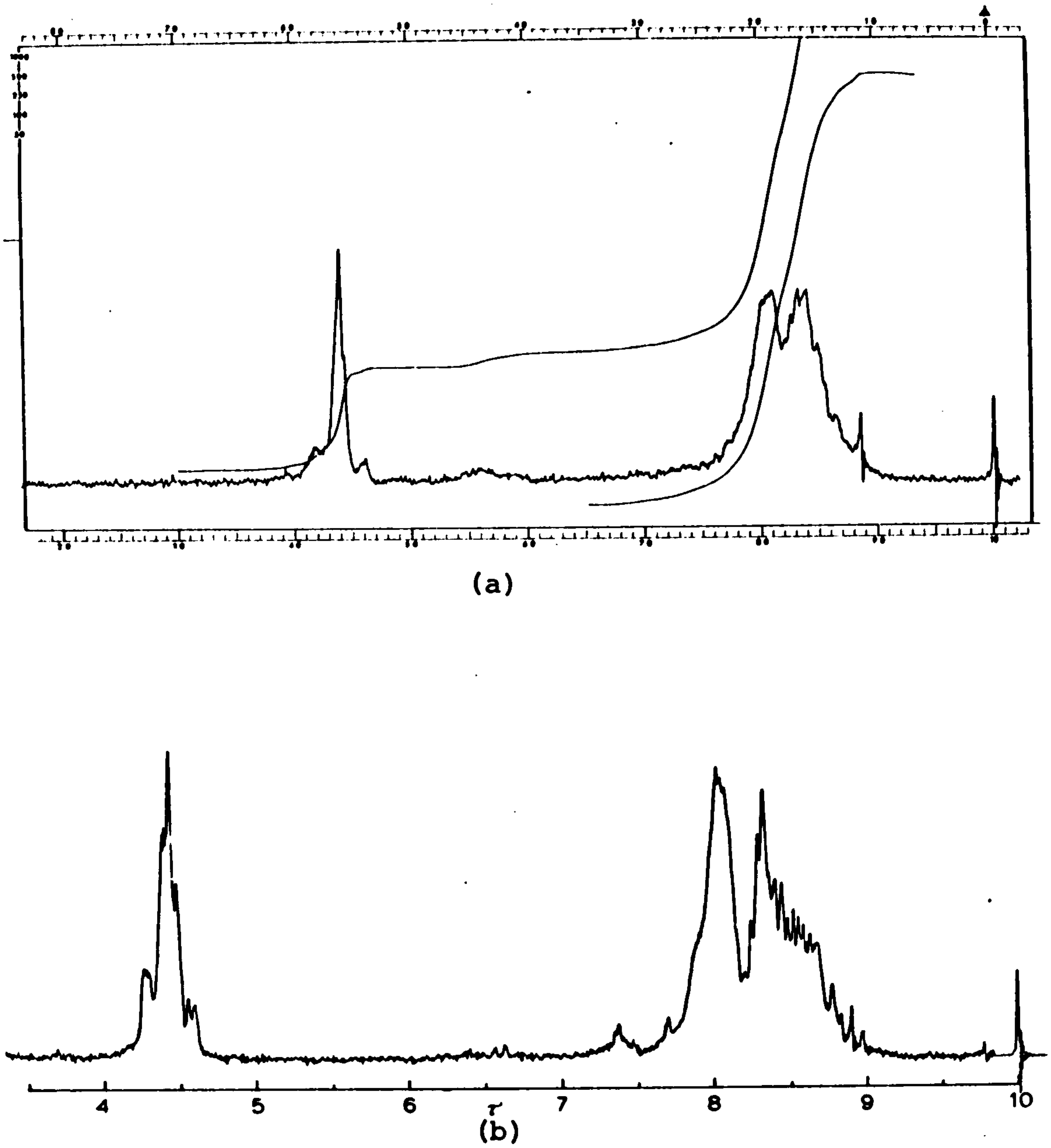


FIGURE III-3 Nmr spectrum of 2,2'-dicyclohexenyl.
(a) Standard sample
(b) Radiolysis product

B. Variation of total dose and radiation intensity.

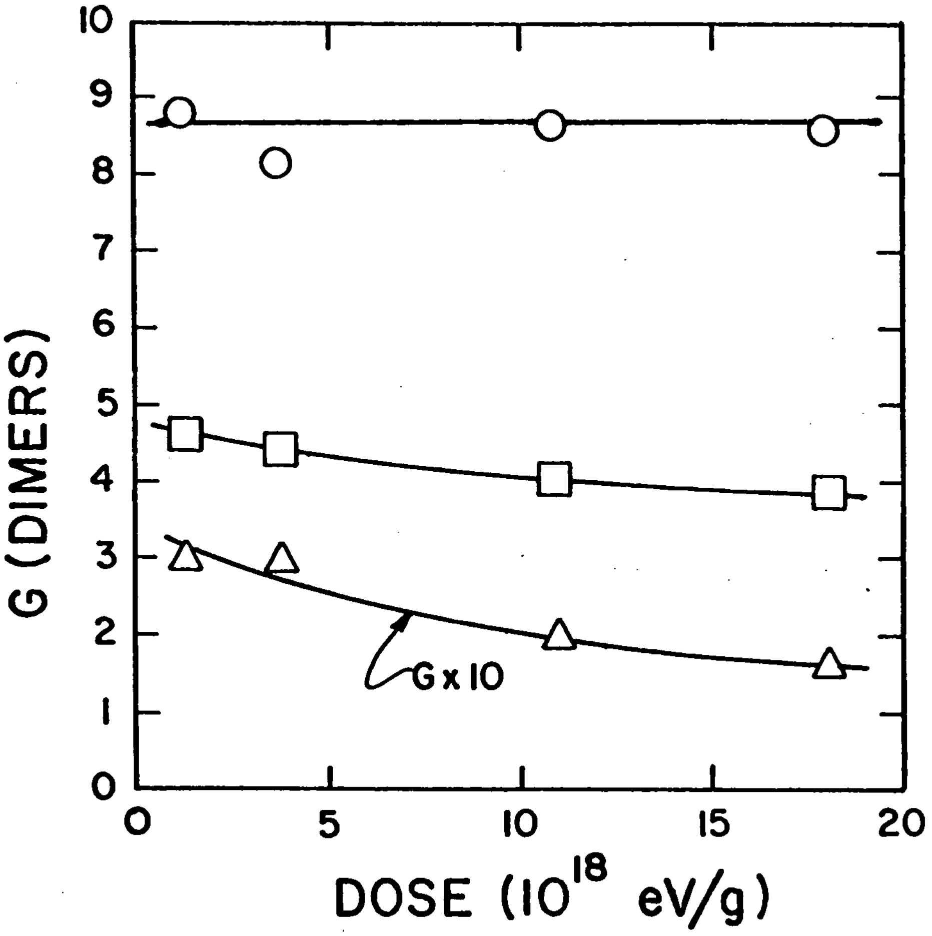
1. Effect of total dose.

(a) Benzene solutions.

The yield of the dimers of CHD from CHD/benzene solutions at various doses is shown in Fig. III-4 and tabulated in Table III-1. The product yields are given as G-values, where G represents the molecules of product formed per 100 eV absorbed by the whole sample. The dose was varied between 1.25 and 18.0 x 10^{18} eV/g while the dose rate was constant at 3.62 x 10^{19} eV/g hr. At the highest dose employed the depletion of CHD, due to the dimer formation, was 4%. The yield of I remained constant and the yield of II + III and IV decreased with an increase in dose. The decrease of G(II + III) was 16% and that of G(IV) was about 45% over the dose range studied.

(b) Cyclohexane solutions.

The variation of yield of the dimers of CHD with dose is given in Fig. III-5 and Table III-2 for 1.5 mole % CHD solutions in cyclohexane. The dose was varied between 3.77 and 50.4 x 10^{18} eV/g at a constant dose rate of 3.79 x 10^{19} eV/ g hr. The results were similar to those obtained in benzene solutions: G(I) remained constant, G(II + III) decreased by about 15% and G(IV) by about 55% over the range employed.



<u>FIGURE III-4</u> Yield of CHD dimers from an 0.87 mole % CHD solution in benzene as a function of total dose.

Dose rate 3.62 x 10^{19} eV/ g hr.

○	dimer I
□	dimers II + III
△	dimer IV

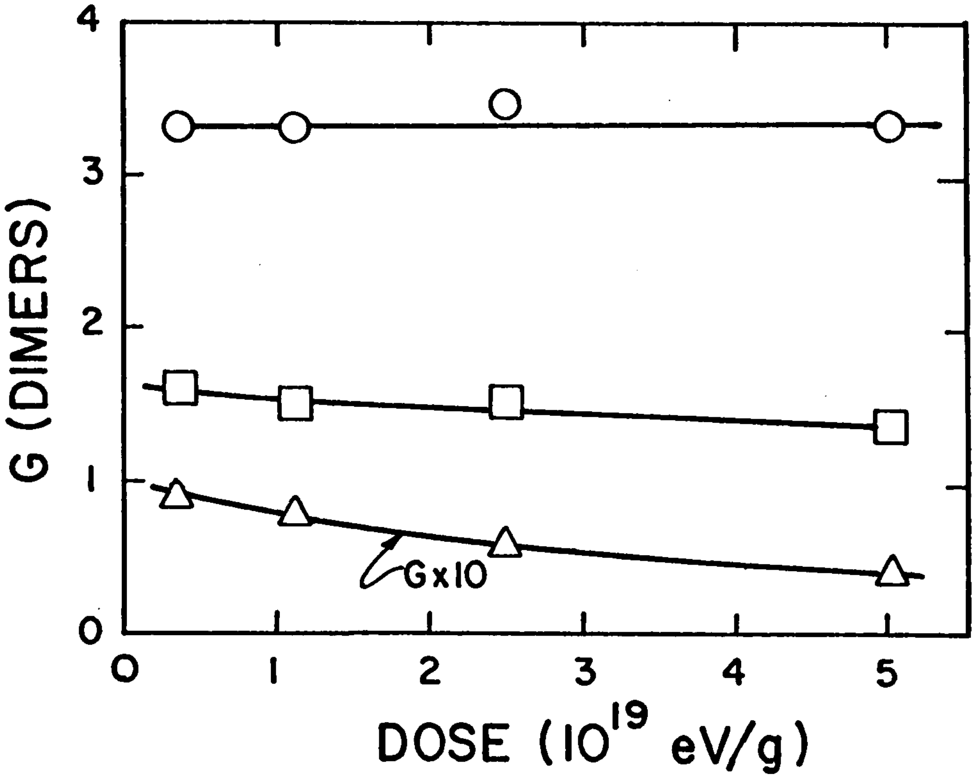


FIGURE III-5 Yield of CHD dimers from an 1.56 mole % CHD solution in cyclohexane. Dose rate is 3.79 x 10^{19} eV/g hr.

○	dimer I
□	dimers II + III
△	dimer IV

TABLE III-1

Yield of CHD dimers from benzene solutions* as a function of dose rate and total dose

Dose rate x 10^{-19} eV/g hr.	Total dose x 10^{-19} eV/g	G		
		I	II + III	IV
3.62	0.125	8.81	4.62	0.30
3.62	0.368	8.18	4.41	0.30
3.62	1.09	8.65	4.05	0.20
3.62	1.80	8.56	3.88	0.16
0.445	0.371	8.55	4.79	0.22
0.173	0.372	8.74	4.60	0.31
0.103	0.372	8.95	4.79	0.31

---

* CHD concentration = 0.87 mole %.

TABLE III-2

Yield of CHD dimers from cyclohexane solutions* as a function of dose rate and total dose.

Dose rate x 10^{-19} eV/ g hr	Total dose x 10^{-19} eV/ g	G		
		I	II + III	IV
3.79	0.377	3.31	1.62	0.09
3.79	1.13	3.31	1.50	0.08
3.79	2.52	3.46	1.52	0.06
3.79	5.04	3.32	1.38	0.04
0.464	1.13	3.80	1.68	0.08
0.180	1.13	3.70	1.76	0.10
0.107	1.13	3.63	1.61	0.06

*CHD concentration = 1.56 mole %

2. Effect of dose rate.

(a) Benzene solutions.

The yield of the dimers of CHD as a function of dose rate is shown in Fig. III-6 for an 0.87 mole % solution of CHD in benzene. The results are also tabulated in Table III-1. The dose rate was varied between 1.03 and 36.2 x 10^{18} eV/g hr at a constant total dose of 3.72 x 10^{18} eV/g. The value of G(I) at a dose rate 36.2 x 10^{18} eV/ g hr that was used in Fig. III-6 was interpolated from the graph of G(I) in Fig. III-4. The yields of dimers I and IV remained constant within the limits of error. Dimers II + III decreased by about 8% over the dose rate range studied.

(b) Cyclohexane solutions.

The variation in yield of the dimers of CHD with variation in dose rate is shown in Fig. III-6 and tabulated in Table III-2 for a 1.56 mole % solution of CHD in cyclohexane. The dose rate was varied between 1.0 and 37.9 x 10^{18} eV/g hr at a constant total dose of 11.3 x 10^{18} eV/g. The results show that dimer I and dimers II + III each decreased by about 10% when the dose rate was increased over the range studied. The scatter in the values of G(IV) does not permit conclusions with respect to the behaviour of dimer IV with change in dose rate.

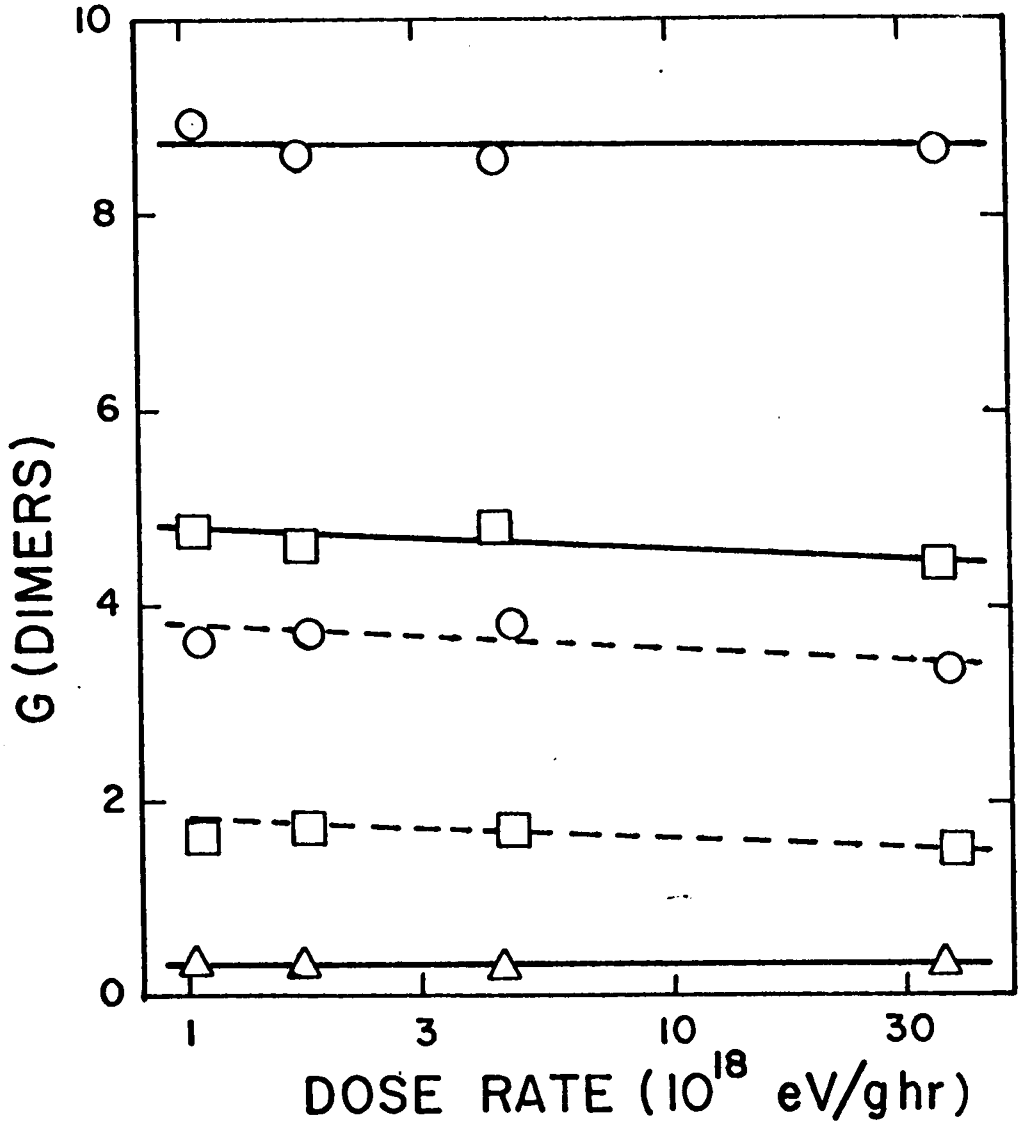


FIGURE III-6 Yield of CHD dimers as a function of dose rate.

—— 0.87 mole % CHD in benzene solvent. Total dose 3.72×10^{18} eV/g.

---- 1.56 mole % CHD in cyclohexane solvent. Total dose 1.13×10^{19} eV/g.

○ Dimer I

□ Dimers II + III

△ Dimer IV

The yields of dimer IV and of dimers II + III are sensitive to the total dose received by the sample. To eliminate variation of yields from a variation of total dose all samples were irradiated to a total dose of about 1.2×10^{19} eV/g where this was possible. Early experiments required larger doses because of the limited sensitivity of the g.c. The dependence of the yields on dose rate was so small, that the change in dose rate, due to the natural decay of the ^{60}Co γ-source over the time taken to complete this work was insignificant. It is thus sufficient to state that the dose rate in all solutions and throughout this work was $3.5 \pm 0.5 \times 10^{19}$ eV/g hr.

C. Radiolysis of 1,3-cyclohexadiene solutions.

(a) Pure 1,3-cyclohexadiene.

CHD of 99.4% purity was irradiated to a total dose of 1.20×10^{19} eV/g. The yields of the dimers were: G(I) = 1.43, G(II + III) = 3.44, and G(IV) = 0.83. In addition to these dimers 0.39 G units of other C_{12} compounds were detected.

(b) Benzene solutions.

The yield of thermal dimer (I) as a function of CHD concentration in the solvent benzene is presented in Fig. III-7A and in Table III-3. Upon addition of benzene

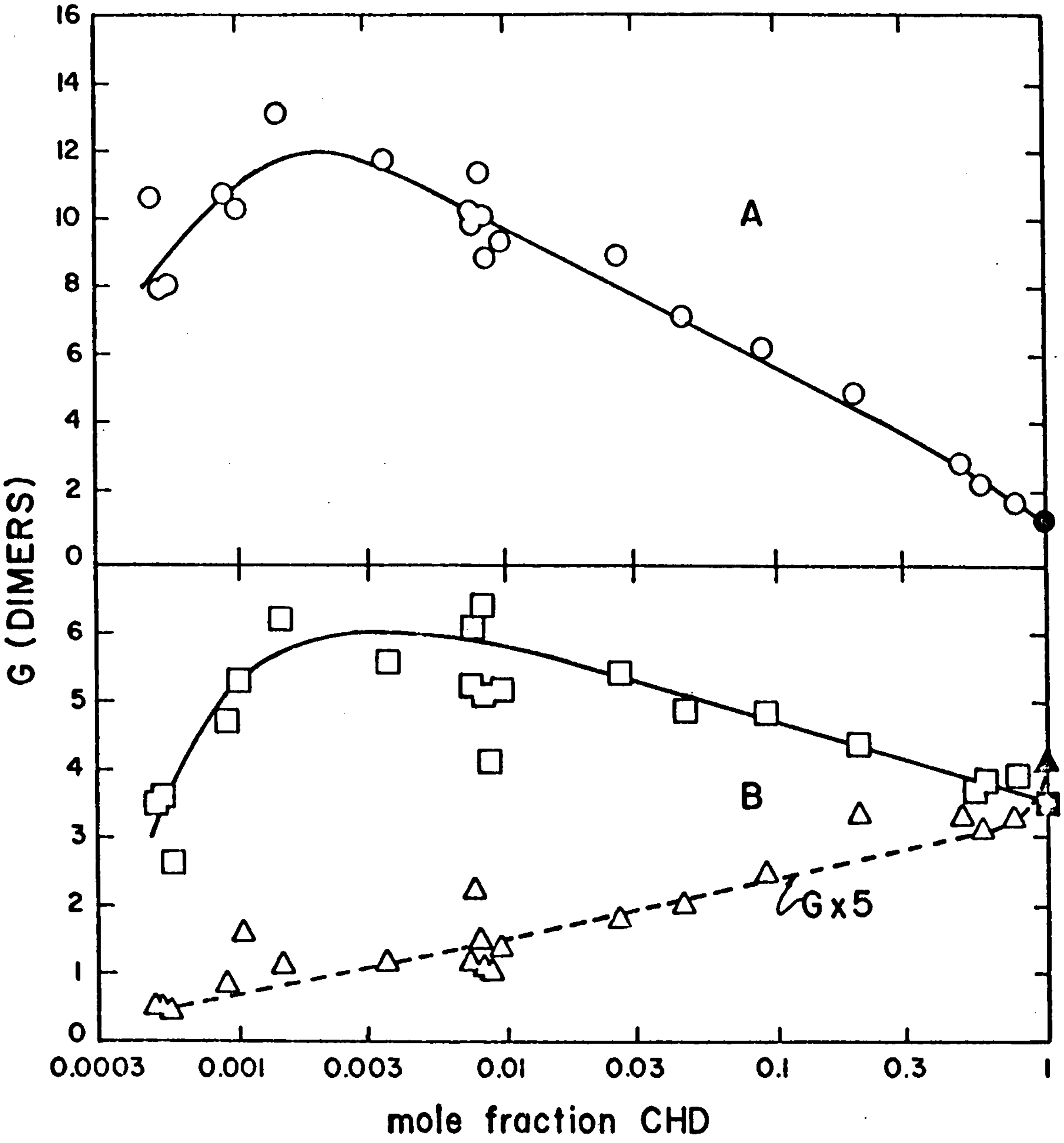


FIGURE III-7 Yield of CHD dimers from benzene solutions

A. Dimer I

B. □ Dimers II + III

△ Dimer IV.

TABLE III-3

Yield of 1,3-cyclohexadiene dimers from benzene solutions.

CHD		G			
Mole %	electron fraction	I	II + III	IV	total dose eV/g x 10^{-18}
0.0490	0.000513	10.7	3.5	0.11	2.20
0.0533	0.000559	7.9	3.6	0.09	1.37
0.0572	0.000600	8.0	2.6	0.08	4.21
0.091	0.000956	10.7	4.7	0.16	4.21
0.101	0.001062	10.4	5.3	0.31	1.37
0.147	0.00156	13.1	6.2	0.22	4.21
0.362	0.00379	11.8	5.6	0.23	16.0
0.755	0.00791	10.2	5.2	0.23	16.0
0.772	0.00800	9.9	6.1	0.44	3.65
0.804	0.00841	11.4	6.4	0.28	3.60
0.839	0.00881	10.1	5.1	0.21	39.9
0.871	0.00912	8.7	4.1	0.20	10.9
0.978	0.01023	9.3	5.2	0.28	16.0
2.68	0.0282	9.0	5.4	0.35	39.9
4.59	0.0491	7.2	4.8	0.39	39.9
9.19	0.0960	6.25	4.80	0.47	40.0
20.2	0.209	4.84	4.36	0.66	40.0
50.2	0.513	2.88	3.66	0.65	12.0
59.7	0.608	2.20	3.80	0.61	40.4
79.7	0.796	1.66	3.86	0.65	40.5

to CHD the yield of I increases until it reaches a maximum G value of 12 ± 1 at approximately 0.2 mole % CHD. Depletion of diene resulting from the formation of all C_{12} products was calculated for each sample. The concentrations listed in Table III-3 are averages between the initial and final concentrations. Only samples for which the conversion of CHD to dimer was less than 20% are included.

The yield of the mixed dimer gas chromatographic peak, (dimers II + III), as a function of CHD concentration is presented in Fig. III-7B, and in Table III-3. Upon addition of benzene to CHD the yield of II + III increases until it reaches a maximum G value of about 6 at approximately 0.4 mole % CHD. The cis-cis-cis photodimer (IV) which showed on the g.c. as a separate peak was difficult to measure below CHD concentrations of 1 mole %, because of its low yield relative to I and (II + III). Less weight should thus be given to the line below 1 mole %. The yield of dimer IV decreases with an increase in benzene concentration. A maximum is not observed. G(IV) is also given in Fig. III-7B and in Table III-3.

The reproducibility of the measured G values was approximately 15% from one batch of samples to another. Precision within one batch was 5%. For diene concentrations below 1 mole % the corresponding figures for dimer IV were 30 and 15% respectively.

(c) Cyclohexane and hexane solutions.

The dimer yields from cyclohexane and from hexane solutions of CHD are given in Tables III-4 and III-5 respectively. The graphical results are shown in Fig. III-8 for dimer I. In cyclohexane solvent the maximum yield of I, G(I) = 6.4 ± 0.4, was reached at about 7 mole % CHD. This concentration is a factor of about 30 higher than the concentration of CHD at the maximum in benzene. The yield of the mixed dimers II + III is depicted in Fig. III-9. Initially the yield of II + III decreased when the CHD concentration was decreased through the addition of cyclohexane. A minimum G value of about 2.5 was reached at approximately 35 mole % CHD. When the CHD concentration was lowered further, the yield increased again to a maximum of about 2.9 at 8 mole % CHD. At first sight this behaviour might be surprising. However, the yield is the sum of the yields of two products, the curve thus reflects the different concentration dependences of the two products. The results for dimer IV are plotted in Fig. III-10. As was the case in benzene, the yield of IV decreased continuously with a decrease in CHD concentration.

When hexane was used as solvent the yields were similar to those obtained in cyclohexane. The results are plotted

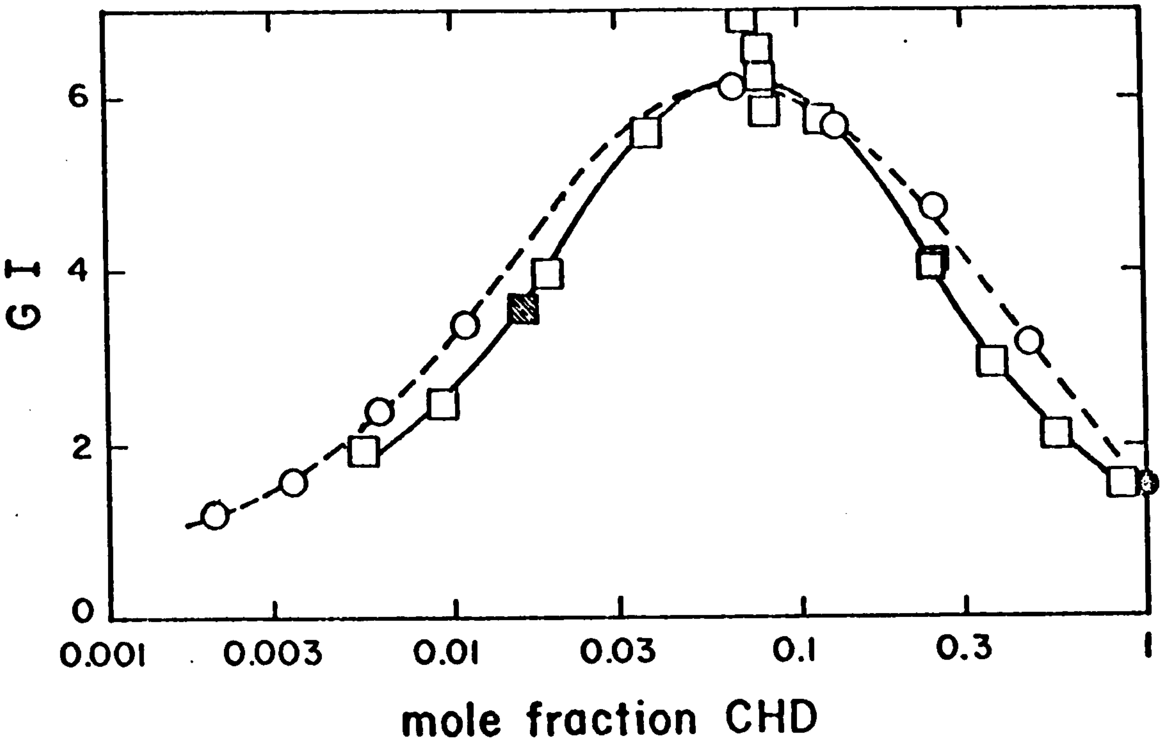


FIGURE III-8 Yield of dimer I from CHD/cyclohexane and CHD/hexane solutions.

O---- Solvent hexane

□ —— Solvent cyclohexane

▨ average of six measurements.

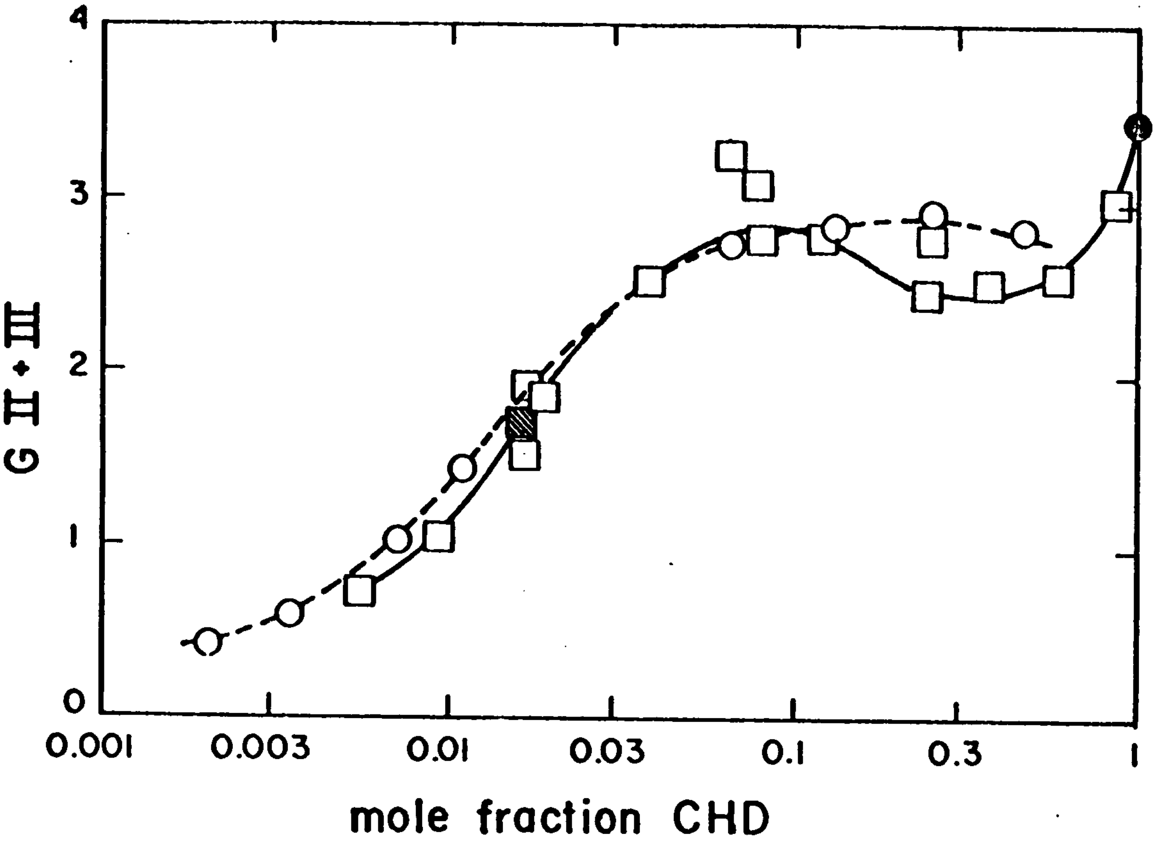


FIGURE III-9 Yield of dimer II + III from CHD/cyclohexane and CHD/hexane solutions.

O----	Solvent hexane
□——	Solvent cyclohexane
▨	Average of four measurements

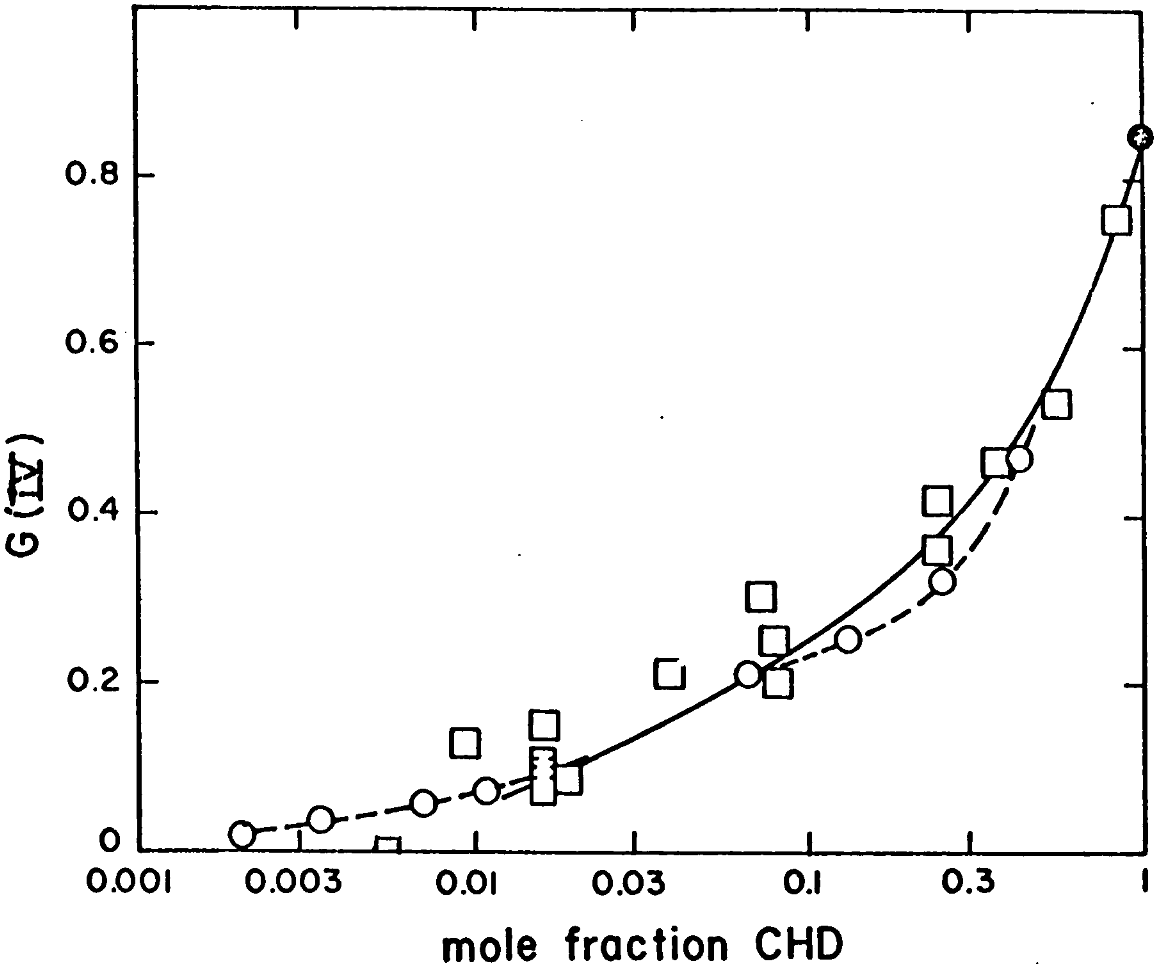


FIGURE III-10 Yield of dimer IV from CHD/cyclohexane and CHD/hexane solutions.

O----- Solvent hexane

□ —— Solvent cyclohexane

TABLE III-4

Yield of dimers of 1,3-cyclohexadiene from cyclohexane solutions.

CHD			G		
mole %	electron fraction	total dose eV/g x 10^{-19}	I	II + III	IV
0.548	0.00502	1.60	1.96	0.73	---
0.934	0.00857	1.60	2.43	1.05	0.13
1.61	0.0148	1.20	3.71	1.71	0.11
1.62	0.0149	1.20	3.78	1.71	0.09
1.64	0.0151	1.20	3.53	1.62	0.09
1.64	0.0151	1.21	3.24	1.49	0.07
1.64	0.0151	1.20	3.84	1.90	0.15
1.65	0.0152	1.20	3.25	1.84	0.09
1.89	0.0174	1.60	3.97	1.86	0.09
3.78	0.0347	1.60	5.59	2.53	0.21
7.07	0.0622	1.20	6.92	3.24	0.30
7.84	0.0723	1.20	6.54	3.65	0.36
7.92	0.0731	1.65	6.20	3.09	0.25
8.14	0.0751	1.65	5.81	2.79	0.20
12.1	0.112	1.65	5.74	2.79	0.27
24.7	0.232	1.64	3.96	2.44	0.36
24.9	0.234	1.21	4.02	2.75	0.42
37.2	0.352	1.63	2.94	2.51	0.46
56.0	0.538	1.62	2.08	2.56	0.53
87.2	0.862	1.60	1.50	3.01	0.75

TABLE III-5

Yield of dimers of 1,3-cyclohexadiene from hexane solutions

CHD		G		
Mole %	Electron fraction	I	II + III	IV
47.7	0.441	3.16	2.83	0.47
25.5	0.232	4.71	2.93	0.32
13.2	0.118	5.66	2.86	0.25
6.72	0.0596	6.11	2.75	0.21
1.10	0.00966	3.38	1.45	0.075
0.717	0.00630	2.40	1.02	0.060
0.350	0.00300	1.57	0.60	0.041
0.205	0.001804	1.20	0.43	0.022
0.0684	0.000602	0.85	0.17	not visible

Total dose $1.22 \pm 0.01 \times 10^{19}$ eV/g.

together with the cyclohexane results in Fig. III-8 for dimer I, in Fig. III-9 for dimers II + III and in Fig. III-10 for dimer IV. A noticeable difference between the two solvents occurred in solutions containing more than 10 mole % CHD. When the samples were irradiated to a total dose of 1.20 x 10^{19} eV/g the hexane solutions were opaque. After standing for one day the solutions were clear again. When the samples were subsequently poured from the sample tubes, the latter were coated on the inside by a clear polymer layer. When cyclohexane was used as solvent the samples remained clear and coating of the sample tubes was not observed. Whether this is an effect of a difference in the solubility of the polymer in the two solvents or of a difference in G(polymer) is not known.

(d) Di-propyl ether solutions.

When propyl ether is used as solvent the maximum yield of I is again shifted to higher concentrations of CHD. At the maximum, G(I) = 3.1 ± 0.1 and the CHD concentration is about 50 mole %, as is shown in Fig. III-11. The yields of the dimers of CHD in propyl ether solutions are given in Table III-6. To show the close relationship between the G values of the mixed dimers and dimer IV they were plotted together in Fig. III-12. For reasons of clarity, the graph for the mixed dimers is displaced by 0.5 G units along the ordinate.

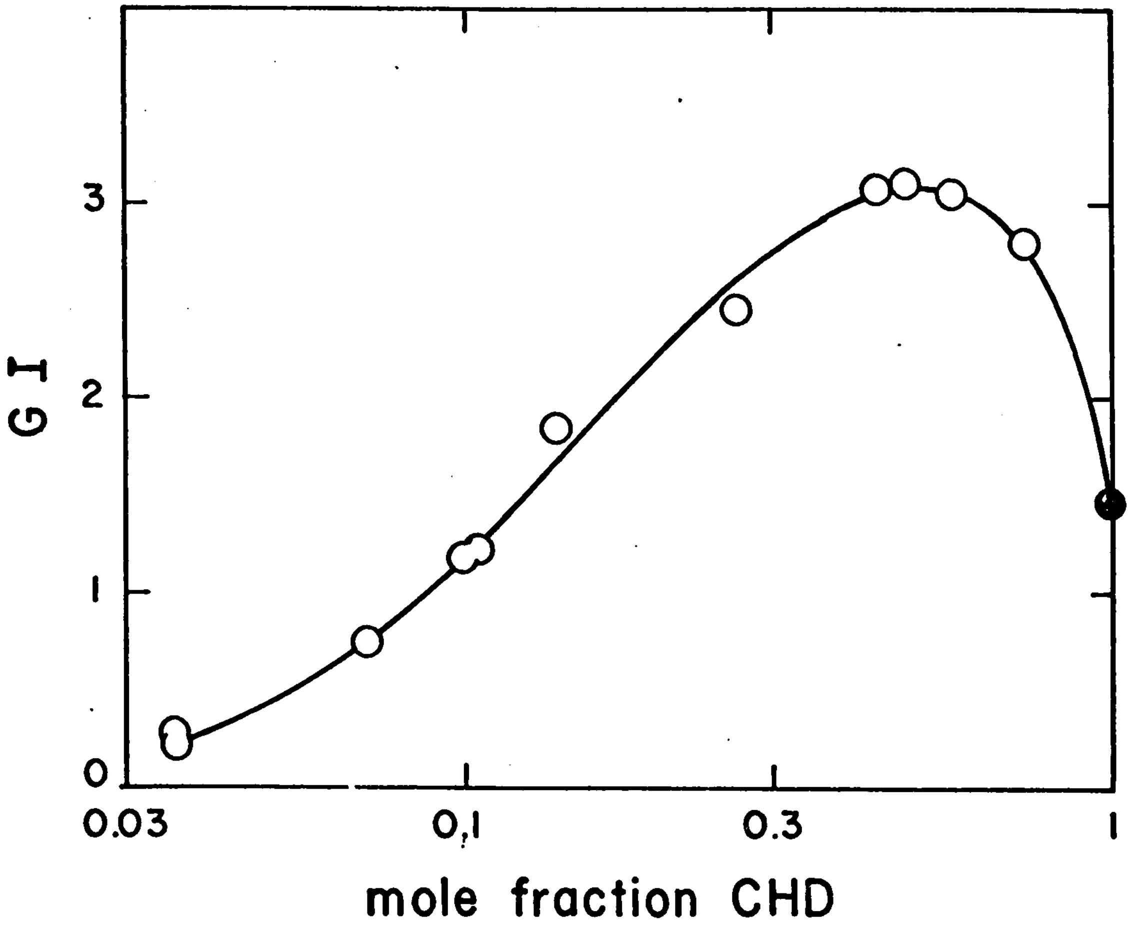


FIGURE III-11 Yield of dimer I from CHD/propyl ether solutions.

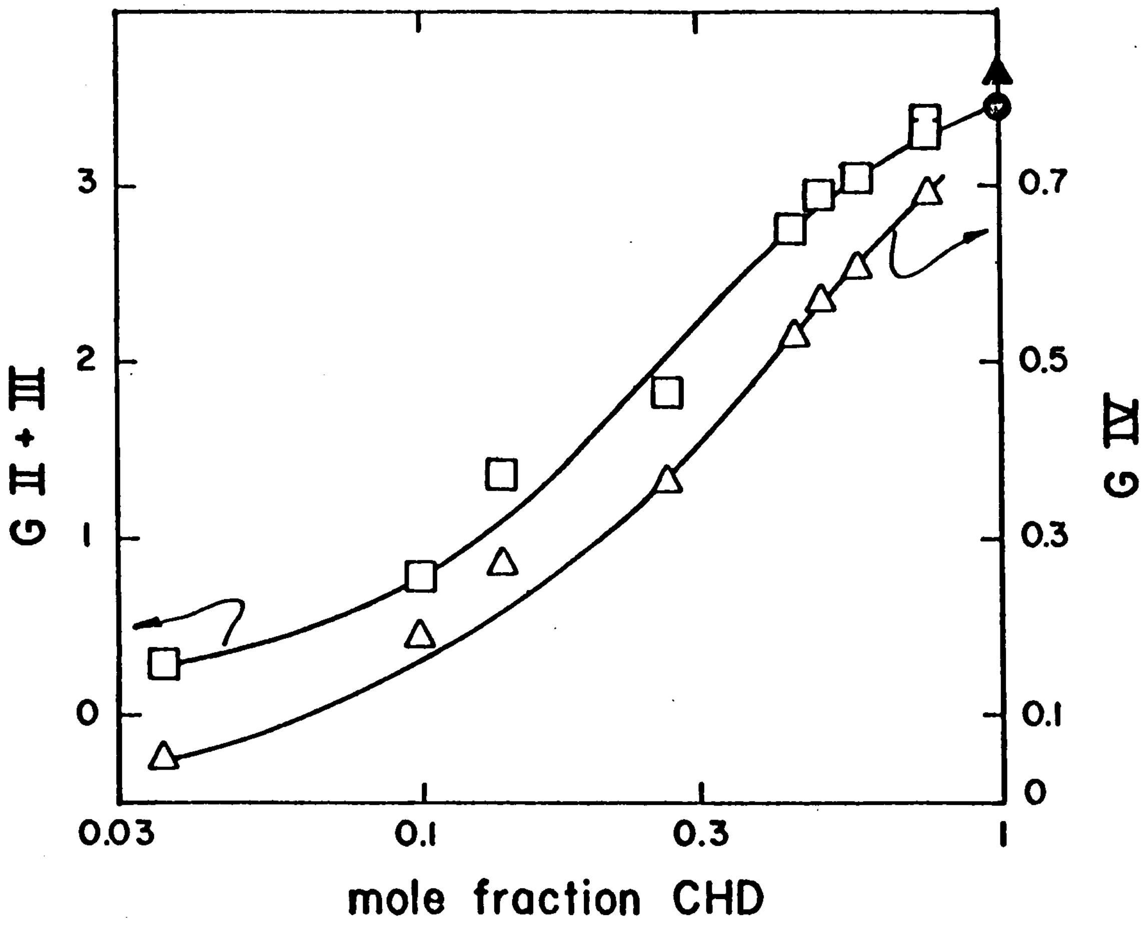


Figure III-12 Yield of CHD dimers from CHD/propyl ether solutions

☐ Dimers II + III

Δ Dimer IV

TABLE III-6

Yield of dimers of 1,3-cyclohexadiene from propyl ether solutions

CHD		G		
mole %	electron fraction	I	II + III	IV
74.6	0.691	2.78	3.38	0.69
57.2	0.500	3.02	3.04	0.61
49.0	0.422	3.10	2.95	0.58
44.0	0.373	3.06	2.76	0.53
26.7	0.216	2.44	1.84	0.36
13.9	0.1094	1.84	1.37	0.27
10.6	0.0825	1.21		
10.1	0.0782	1.18	0.79	0.19
7.12	0.0550	0.73		
3.60	0.0276	0.20	0.29	0.057
3.60	0.0276	0.29		

Total dose 1.22 ± 0.02 x 10^{19} eV/g.

(e) Ethanol solutions.

When ethanol was used as solvent the formation of CHD dimers was much less efficient than it was in the other solvents mentioned. No maximum in the yield of dimer I was observed. In Fig. III-13A and III-13B which shows the yield of IV, a dotted line is included to indicate the yield that would be "expected" on the basis of the electron fraction of CHD present with no interaction between the solute and solvent species. All three dimers were formed in less than "expected" amounts when ethanol was used as solvent. The yields were higher than "expected" for the solvents benzene, cyclohexane, hexane, and propyl ether. The dimer yields for ethanol solutions of CHD are given in Table III-7.

D. Radiolysis of 1,3-cyclohexadiene solutions with additives.

Samples containing CHD in various solvents and small amounts of an additive were irradiated. The solvents used were benzene, cyclohexane and propyl ether. The additives used were ethanol, propyl ether, carbon tetrachloride, nitrous oxide, sulfur hexafluoride and oxygen. The choice of CHD/solvent composition to which to add a third component was made on the basis of the results in the binary solutions. Selected were: (i) a concentration close to (or at) the maximum G(I) in cyclohexane and in propyl

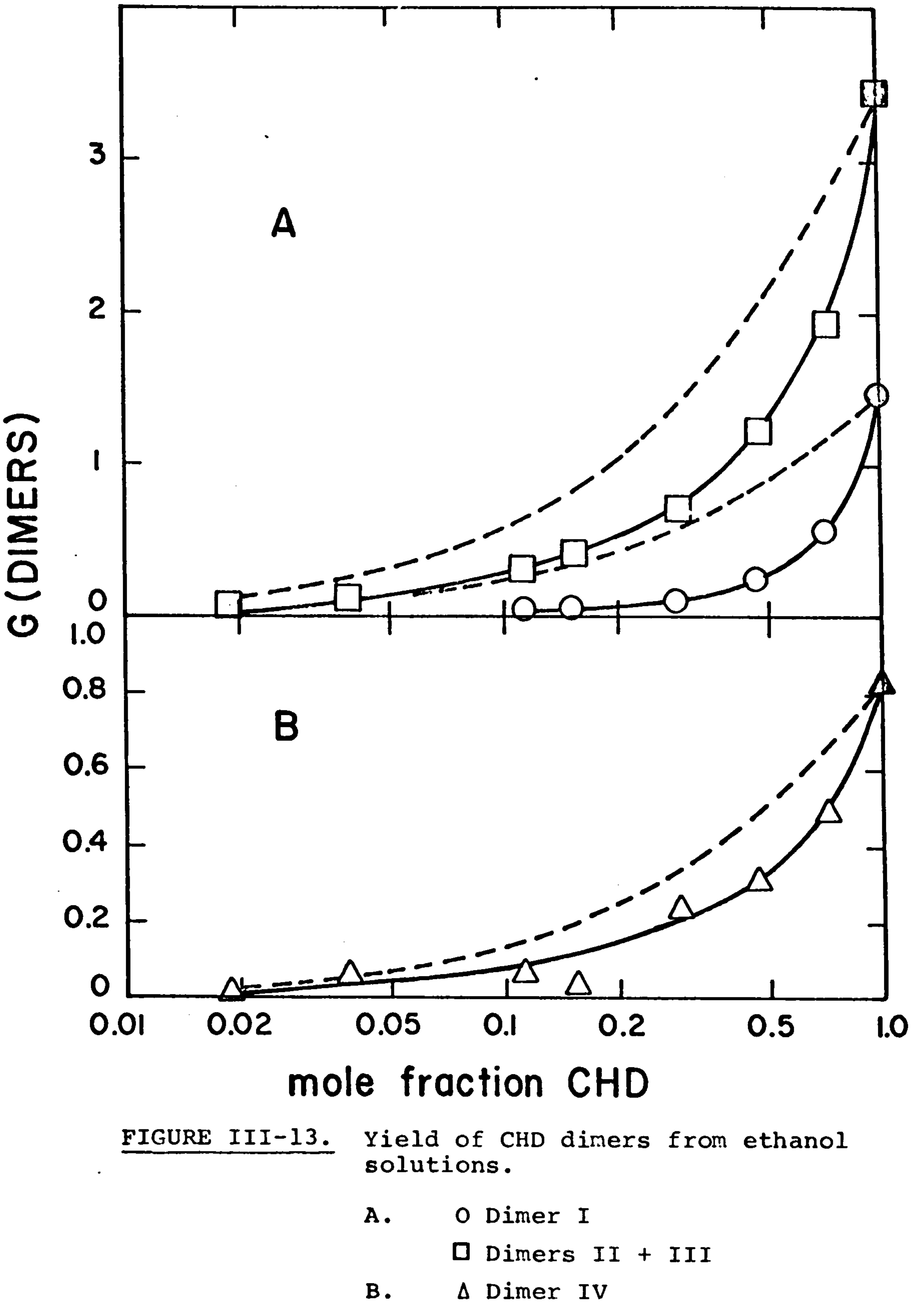


FIGURE III-13. Yield of CHD dimers from ethanol solutions.

A. ○ Dimer I

□ Dimers II + III

B. △ Dimer IV

TABLE III-7

Yield of dimers of 1,3-cyclohexadiene from ethanol solutions

CHD		G		
mole %	electron fraction	I	II + III	IV
71.50	0.7907	0.52	1.90	0.48
47.09	0.5972	0.23	1.22	0.30
29.10	0.4050	0.10	0.70	0.23
15.37	0.2335	0.04	0.41	0.02
11.46	0.1787	0.02	0.31	0.06
3.93	0.06461	*	0.12	0.06
1.90	0.03175	*	0.06	0.01
0.922	0.01553	*	0.02	0.01
0.490	0.00822	*	0.009	+
0.252	0.00424	*	0.006	*

* g.c. peak not visible.

\+ g.c. peak visible, but not measurable.

Total dose = $1.62 \pm 0.02 \times 10^{19}$ eV/g ether, (ii) a concentration well below the concentration of the maximum in cyclohexane and in propyl ether solvent, (iii) a concentration higher than the concentration of the maximum in cyclohexane and in benzene and (iv) the lowest possible concentration in benzene at which measurable results would still be obtained.

To facilitate a comparison between the effects of various additives, all additives were used with a 1.6 mole % CHD solution in cyclohexane. Carbon tetrachloride was used as additive in all three solvents, so that the solvents could be compared. The order of presentation of the results obtained with additives will be: (i) cyclohexane solutions with additives (except carbon tetrachloride), (ii) CCl_4 addition to various solvents and (iii) ethanol addition to benzene/CHD solution.

1. Solutions of 1,3-cyclohexadiene in cyclohexane with additives.

(a) Addition of ethanol.

Upon addition of ethanol to a solution of 1.6 mole % CHD in cyclohexane the yield of the dimers of CHD dropped sharply, as can be seen from Fig. III-14 and Table III-8. When CHD and ethanol were present in equal amounts the yield of I was 0.38 G units. Without ethanol, the yield of I at this concentration of CHD was 3.56 ± 0.09

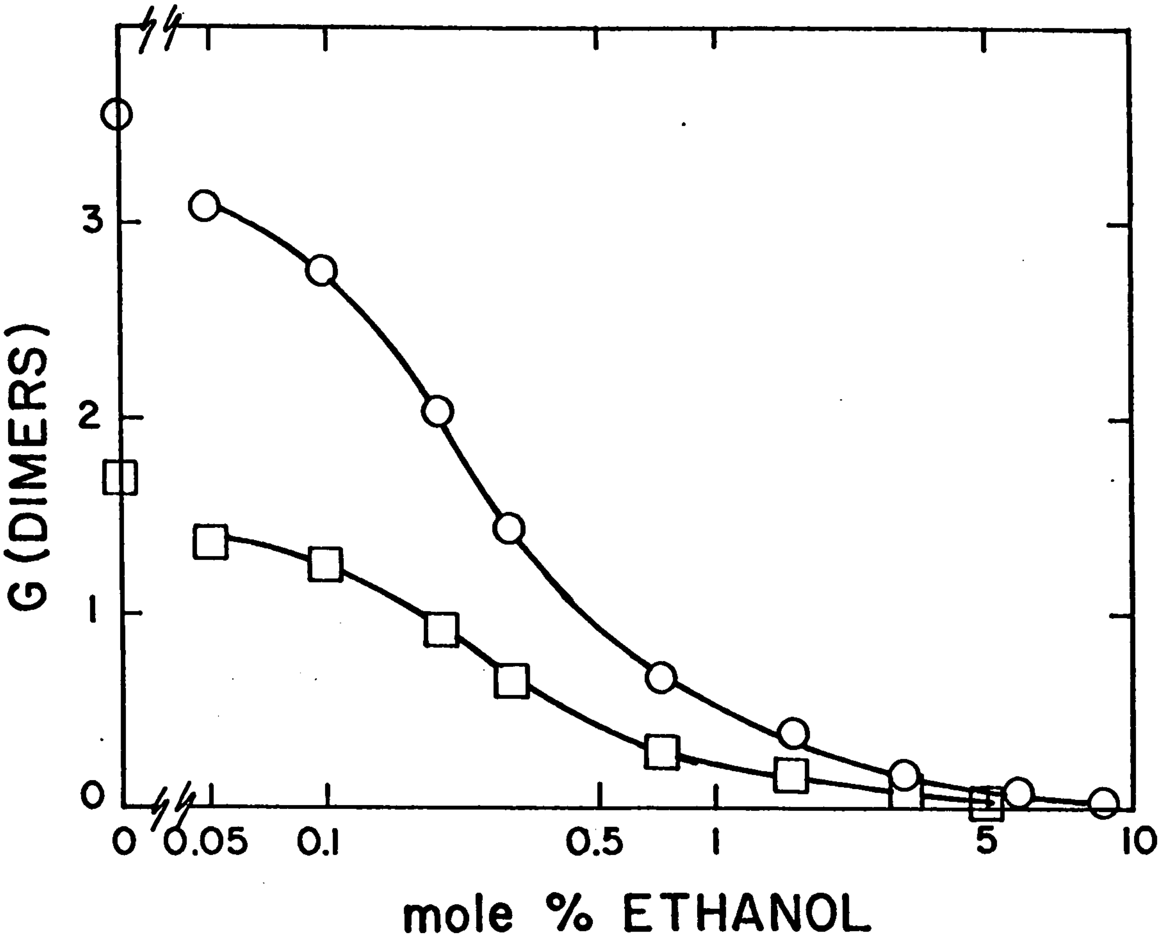


FIGURE III-14 Yield of dimers of CHD from 1.63 mole % CHD solutions in cyclohexane with ethanol additive.

○ Dimer I

□ Dimers II + III

TABLE III-8

Yield of CHD dimers from cyclohexane solutions* with ethanol additive.

Ethanol Mole %	G I	 II + III	 IV
0.0	3.78	1.71	0.09
0.0	3.53	1.62	0.09
0.050	3.09	1.36	0.08
0.10	2.73	1.24	0.06
0.20	2.01	0.91	0.06
0.30	1.42	0.65	----
0.74	0.65	0.29	0.03
1.62	0.38	0.18	0.03
3.18	0.19	0.09	0.02
6.06	0.09	0.05	0.03
9.93	0.03	----	0.02

* CHD concentration 1.63 mole %.

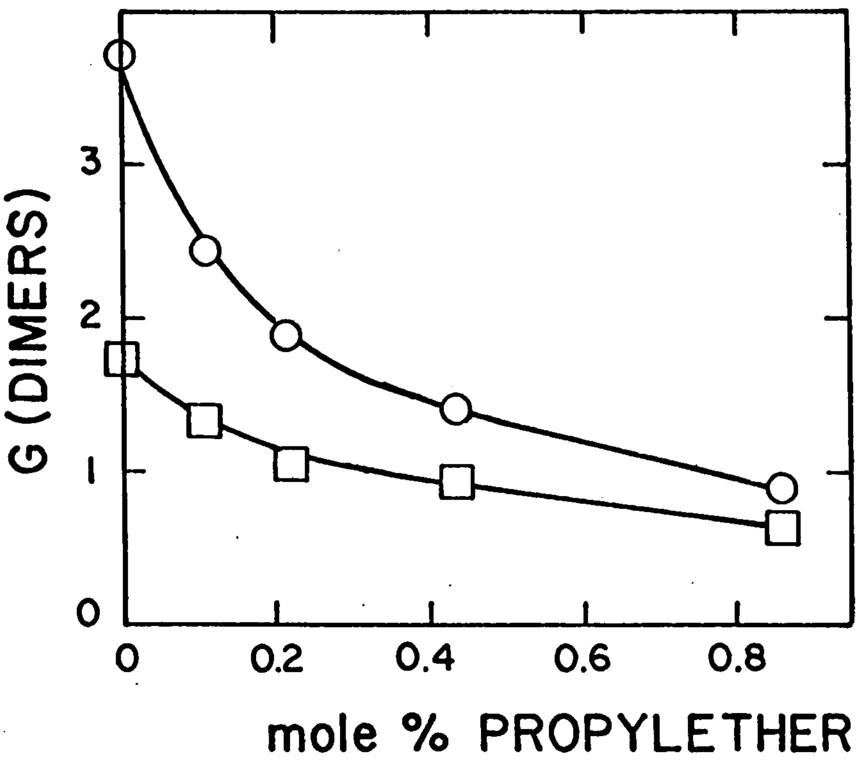
Total dose 1.20 x 10^{19} eV/g.

(mean of six measurements, with standard error). Similarly, the yield of II + III dropped from 1.71 ± 0.04 with no ethanol present to 0.18 G units when ethanol was present in an amount equal to that of CHD.

At 1.6 mole % in cyclohexane, the yield of dicyclohexyl was 0.30 ± 0.03 G units. Since a complete separation was not obtained between the g.c. peaks of dimers II + III and dicyclohexyl, they were measured together and a correction was applied afterwards. It was thus important to establish whether the addition of ethanol altered the yield of dicyclohexyl. To this end, four samples of cyclohexane containing various amounts of ethanol up to 3 mole % were irradiated. The yield of dicyclohexyl did not change significantly: (mole % ethanol--G(dicyclohexyl)) none--1.78; 0.74--1.82; 1.62--1.75; 3.18--1.74.

(b) Addition of propyl ether.

When propyl ether was used as additive the yield of I and II + III was lowered while the yield of dimer IV remained constant. At a propyl ether concentration half that of the CHD, G(I) was approximately 25% of the value obtained when propyl ether was absent. The results are plotted in Fig. III-15 and tabulated in Table III-9.



<u>FIGURE III-15</u> Yield of CHD dimers from 1.61 mole % solutions of CHD in cyclohexane with propyl ether additive.

○ Dimer I

□ Dimers II + III

TABLE III-9

Yield of CHD dimers from cyclohexane solutions* with propyl ether additive

Propyl ether mole %	G		
	I	II + III	IV
0.0	3.71	1.71	0.110
0.109	2.44	1.33	0.107
0.217	1.89	1.03	0.113
0.433	1.39	0.92	0.115
0.864	0.87	0.63	0.082

* 1.61 mole % CHD.

Total dose 1.20 x 10^{19} eV/g.

(c) Addition of nitrous oxide.

Nitrous oxide (N_2O) was added to 1.64 mole % CHD in cyclohexane and to 7.07 mole % CHD in cyclohexane. The latter concentration was close to the concentration of CHD where dimer I exhibited a maximum.

The variations of yield with N_2O concentration and with CHD concentration are given in Fig. III-16 and Table III-10. The yield of I and of II + III increased with increasing concentration of N_2O for the 1.6 mole % CHD solutions. For the 7 mole % CHD solutions plateau values were reached: about 8.2 G units for dimer I and about 3.6 for dimers II + III. The yield of dimer IV decreased by 0.05 G units (see Table III-10) in both solutions when 0.1 mole % N_2O was added; at higher N_2O concentrations the yield of IV remained constant at the lower value. Whether this initial decrease is real is not certain.

(d) Addition of sulfur hexafluoride

When sulfur hexafluoride was added to a 1.65 mole % CHD solution in cyclohexane, the results were similar to those of N_2O addition. Dimers I and II + III increased while dimer IV decreased with an increase in SF_6 concentration. The results are shown in Fig. III-17 and tabulated in Table III-11.

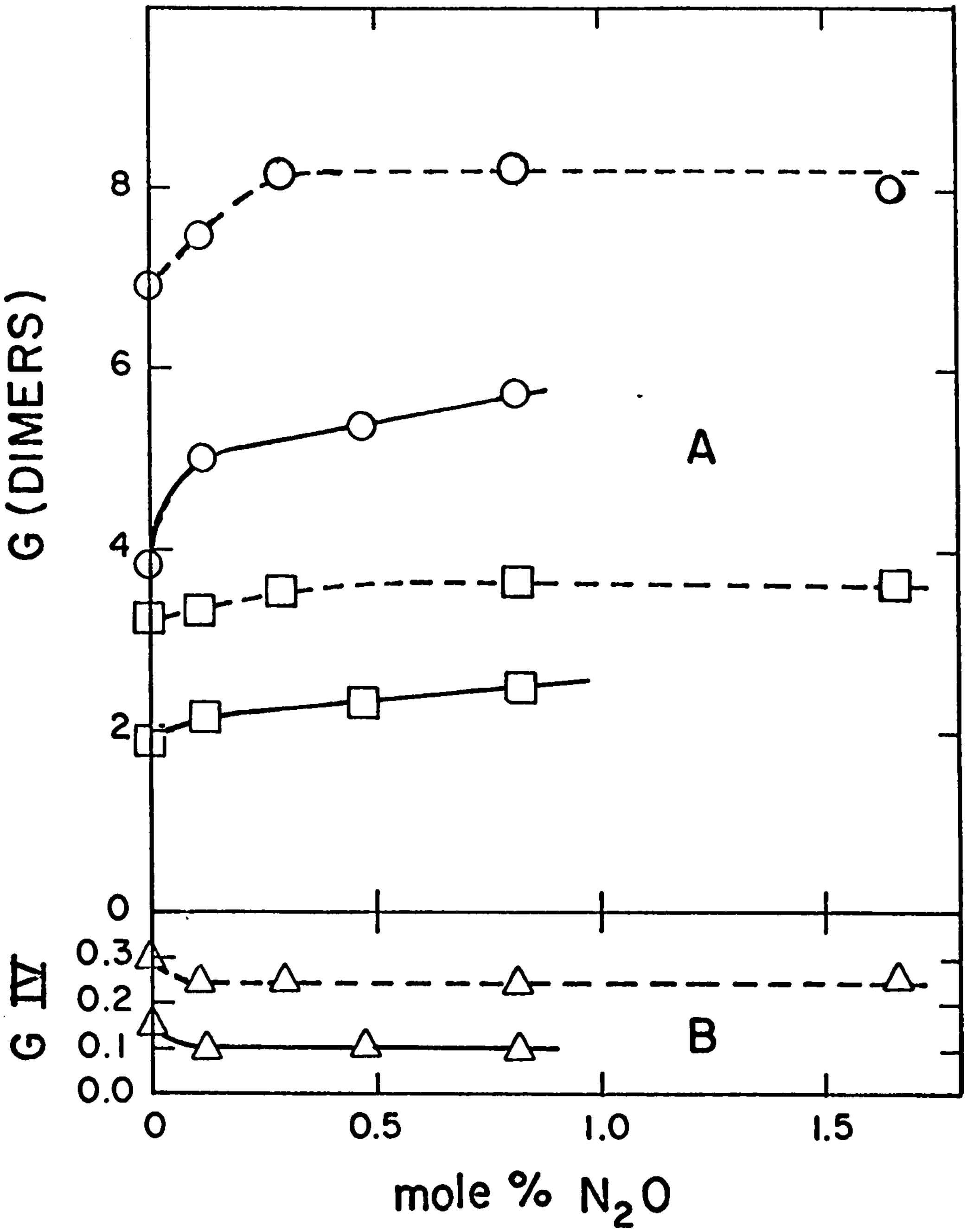


FIGURE III-16. Yield of CHD dimers from cyclohexane solutions with N_2O additive.

A	O	Dimer I
	□	Dimers II + III
B		Dimer IV
	----	7.07 mole % CHD
	——	1.64 mole % CHD

TABLE III-10

Yield of CHD dimers from cyclohexane solutions. N_2O additive.

		G		
CHD mole %	N_2O mole %	I	II + III	IV
1.64	0.0	3.84	1.90	0.15
1.64	0.122	5.01	2.17	0.10
1.64	0.475	5.35	2.30	0.11
1.64	0.820	5.71	2.49	0.10
7.07	0.0	6.92	3.24	0.30
7.07	0.114	7.46	3.31	0.24
7.07	0.298	8.16	3.54	0.25
7.07	0.823	8.20	3.65	0.24
7.07	1.66	8.00	3.60	0.25

Total dose 1.20×10^{19} eV/g.

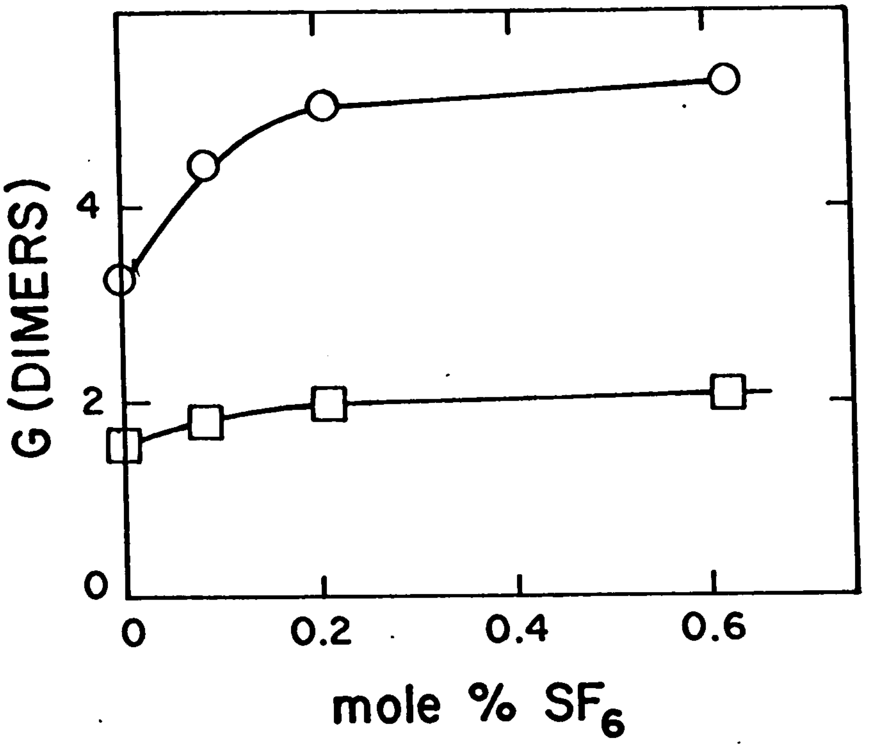


FIGURE III-17 Yield of CHD dimers from 1.65 mole % solution of CHD in cyclohexane with SF_6 additive.

○ Dimer I

□ Dimers II + III

TABLE III-11

Yield of CHD dimers from cyclohexane solutions* with SF_6 additive

mole % SF_6	G: I	G: II + III	G: IV
0.0	3.25	1.54	0.09
0.086	4.42	1.79	0.05
0.21	5.04	1.96	0.05
0.62	5.26	2.06	----

* 1.65 mole % CHD

Total dose 1.20×10^{19} eV/g

(e) Addition of oxygen.

The addition of 0.5 mole % oxygen to a 7.84 mole % solution of CHD in cyclohexane increased the yield of dimer I by about 0.8 G units, while the yield of dimers II + III was lowered by approximately this amount. Dimer IV could not be measured in the oxygen containing solutions because many additional products were formed and dimer IV was "lost" in a multitude of peaks on the gas chromatogram. A blank sample containing about 3 atmosphere oxygen was left at room temperature while the other samples were being irradiated. This sample did not show peaks on the g.c. indicating that the interference was caused by radiolysis products. The results are given in Table III-12. After radiolysis the samples were opaque due to the formation of polymer.

2. Addition of carbon tetrachloride to 1,3-cyclohexadiene solutions in various solvents.

(a) Cyclohexane solutions.

Carbon tetrachloride was used as an additive in various amounts up to 1 mole % at two CHD concentrations: 1.64 and 24.9 mole %. The yields of the dimers as a function of CCl_4 concentration are depicted in Fig. III-18. Dimer I increased steadily with increasing CCl_4 concentration. The dimers II + III increased with an increase in CCl_4 con-

TABLE III-12

Yield of CHD dimers from cyclohexane solutions* with O_2 additive.

O_2		G		
total in sample mole %	liquid phase mole %	I	II + III	IV
0.0	0.0	6.54	3.65	0.36
1.83	0.46	7.23	3.08	a
1.78	0.47	7.07	2.84	a
2.02	0.51	7.34	2.85	a

* CHD concentration 7.84 mole %

a not measurable because of interference by other products (see paragraph III-D-1e)

Total dose 1.20 x 10^{19} eV/g.

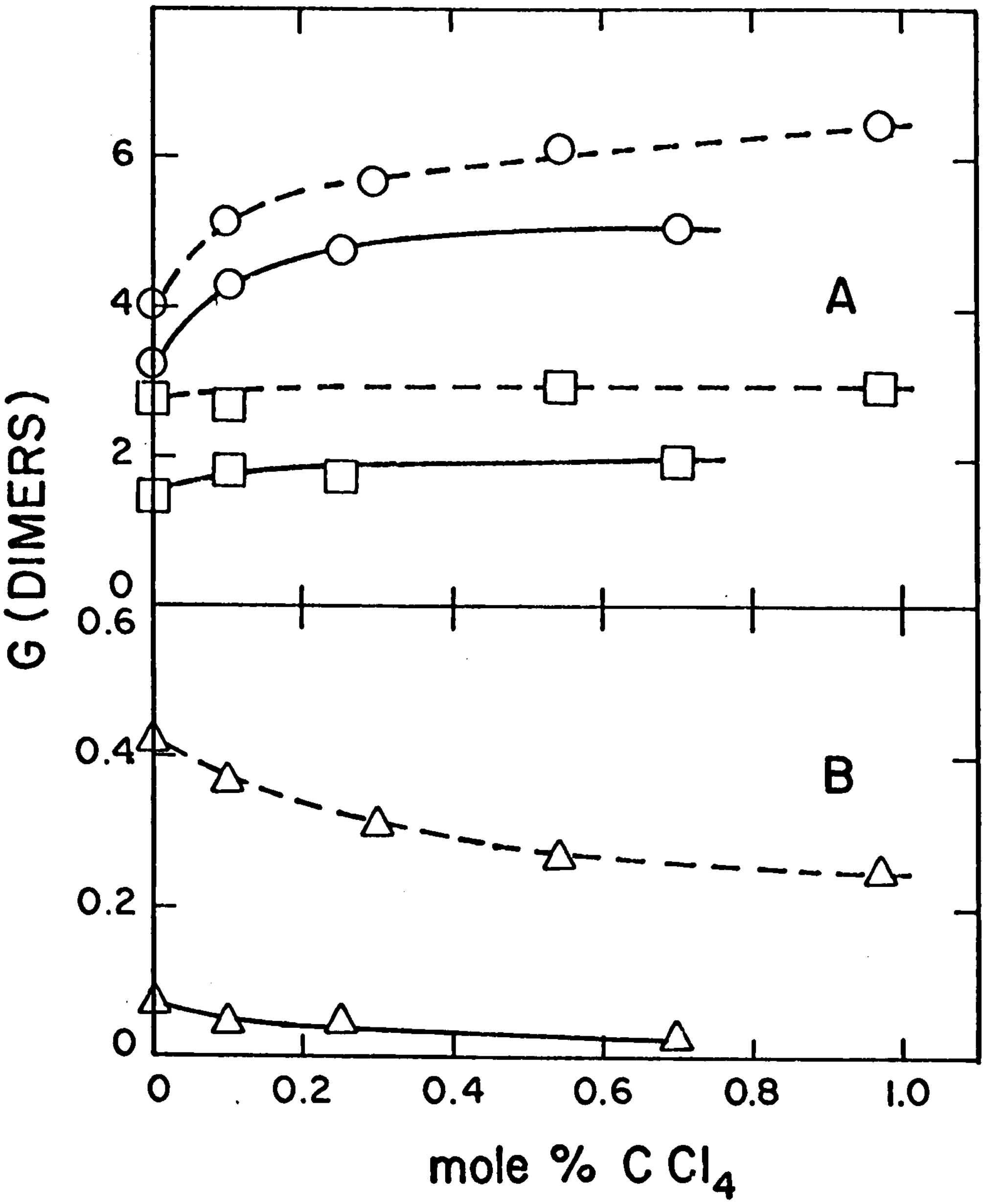


FIGURE III-18 Yield of CHD dimers from cyclohexane solutions with carbon tetrachloride additive.

----- 24.9 mole % CHD

——— 1.64 mole % CHD

A ○ Dimer I

☐ Dimers II + III

B Dimer IV.

centration for the 1.64 mole % CHD solutions, while for the 24.9 mole % CHD solution G(II + III) remained constant after a slight initial increase of 0.2 G units. The yield of dimer IV decreased steadily with an increase in CCl_4 concentration for both solutions. To test the effect of CCl_4 in concentrated solutions of CHD, one sample containing 67.8 mole % CHD and 0.95 mole % CCl_4 was irradiated. When the results of this sample are compared with the G values of the products from the cyclohexane solutions without additives (see Table III-4) it appears that G(I) increased, G(II + III) remained constant and G(IV) decreased with the addition of 0.95 mole % CCl_4. The results are summarized in Table III-13.

(b) Di-propyl ether solutions.

Carbon tetrachloride was added to two sets of solutions of CHD in di-propyl ether. The CHD concentration of the first set was 10.1 mole %, a concentration well below that where the maximum yield of dimer I occurs (Fig. III-11). The other set had a CHD concentration (49.0 mole %) close to that where the maximum yield of dimer I occurs. The variations in the yield of the dimers with CHD and with CCl_4 concentration are given in Fig. III-19, and in Table III-14.

TABLE III-13

Yield of CHD dimers from cyclohexane solutions, CCl_4 additive.

		G		
mole % CHD	mole % CCl_4	I	II + III	IV
1.64	0.0	3.24	1.49	0.074
1.64	0.10	4.30	1.82	0.045
1.64	0.25	4.79	1.73	0.046
1.64	0.70	5.08	1.98	0.024
24.9	0.0	4.02	2.75	0.42
24.9	0.098	5.16	2.69	0.37
24.9	0.293	5.69	2.94	0.31
24.9	0.54	6.14	2.96	0.27
24.9	0.97	6.48	2.97	0.25
67.8	0.0	1.78*	2.72*	0.61*
67.8	0.95	4.27	2.76	0.49

* Interpolated from Table III-4

Total dose 1.21 ± 0.01 x 10^{19} eV/g.

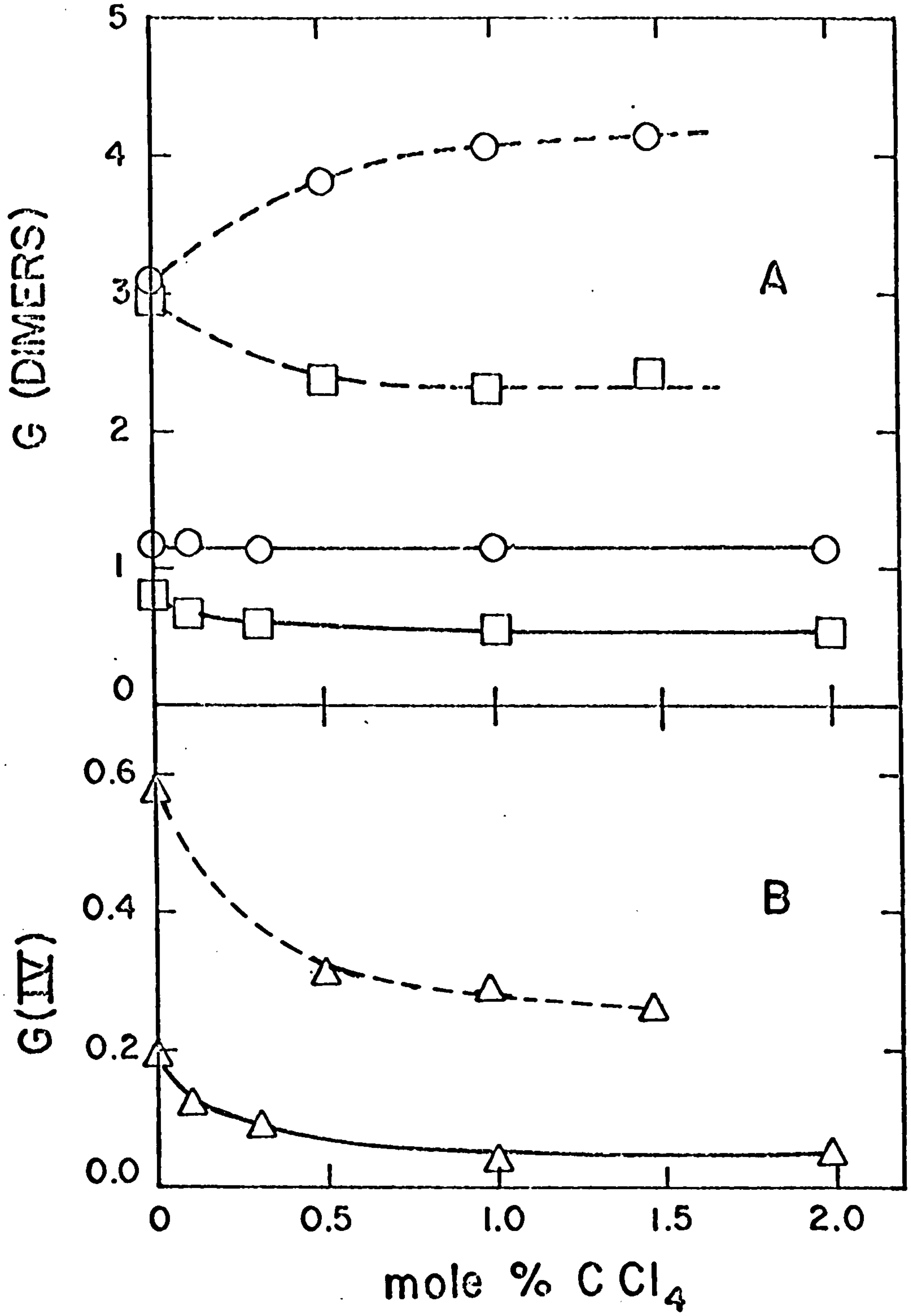


FIGURE III-19 Yield of CHD dimers from CHD/propyl ether solutions with carbon tetrachloride additive.

---- 49.0 mole % CHD

—— 10.1 mole % CHD

O Dimer I

Dimers II + III

Δ Dimer IV

TABLE III-14

Yield of CHD dimers from propyl ether solutions CCl_4 additive

CHD mole %	CCl_4 mole %	G I	 II + III	 IV
10.1	0.0	1.18	0.79	0.19
10.1	0.105	1.20	0.72	0.12
10.1	0.306	1.14	0.61	0.09
10.1	1.00	1.15	0.55	0.04
10.1	1.99	1.13	0.51	0.05
49.0	0.0	3.10	2.95	0.58
49.0	0.501	3.84	2.37	0.31
49.0	0.978	4.07	2.30	0.29
49.0	1.46	4.14	2.41	0.26

Total dose 1.21×10^{19} eV/g

For the 10.1 mole % CHD series the yield of I was constant over the CCl_4 concentration range used. The yield of II + III was decreased by 35% and G(IV) was decreased by 75% by the time 1 mole % CCl_4 was added.

In the more concentrated CHD solution the yield of I increased and the yield of II + III and of IV decreased with an increase in CCl_4 concentration.

(c) Benzene solutions

Carbon tetrachloride was added to three different CHD concentrations in benzene solvent; one (0.049%) was below, one (0.77%) slightly above, and the other (50%) much above the concentration at the maximum in the G(I) curve in Fig. III-7.

Fig. III-20 depicts the results obtained with the 0.049% mole % CHD solution for dimer I and dimers II + III. Upon addition of CCl_4, the yield of II + III decreased slightly. The changes in G(I) and G(IV) are within the limits of the experimental error, so that conclusions with respect to the influence of CCl_4 on the yield of these dimers cannot be drawn.

Fig. III-21 gives the results obtained with the 0.772 mole % CHD solution. The yield of I was constant within the limits of the experimental error. The decrease in G(II + III) and G(IV) with an increase in CCl_4 concentration might be real.

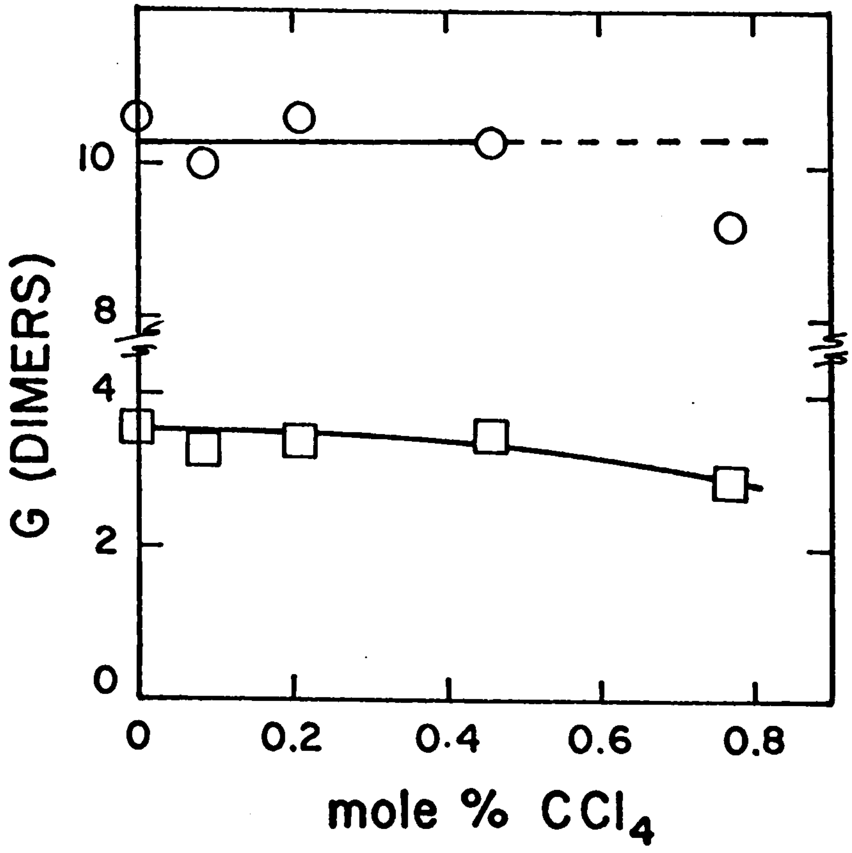


FIGURE III-20 Yield of CHD dimers from 0.049 mole % CHD solutions in benzene with carbon tetrachloride additive.

○ Dimer I

□ Dimers II + III

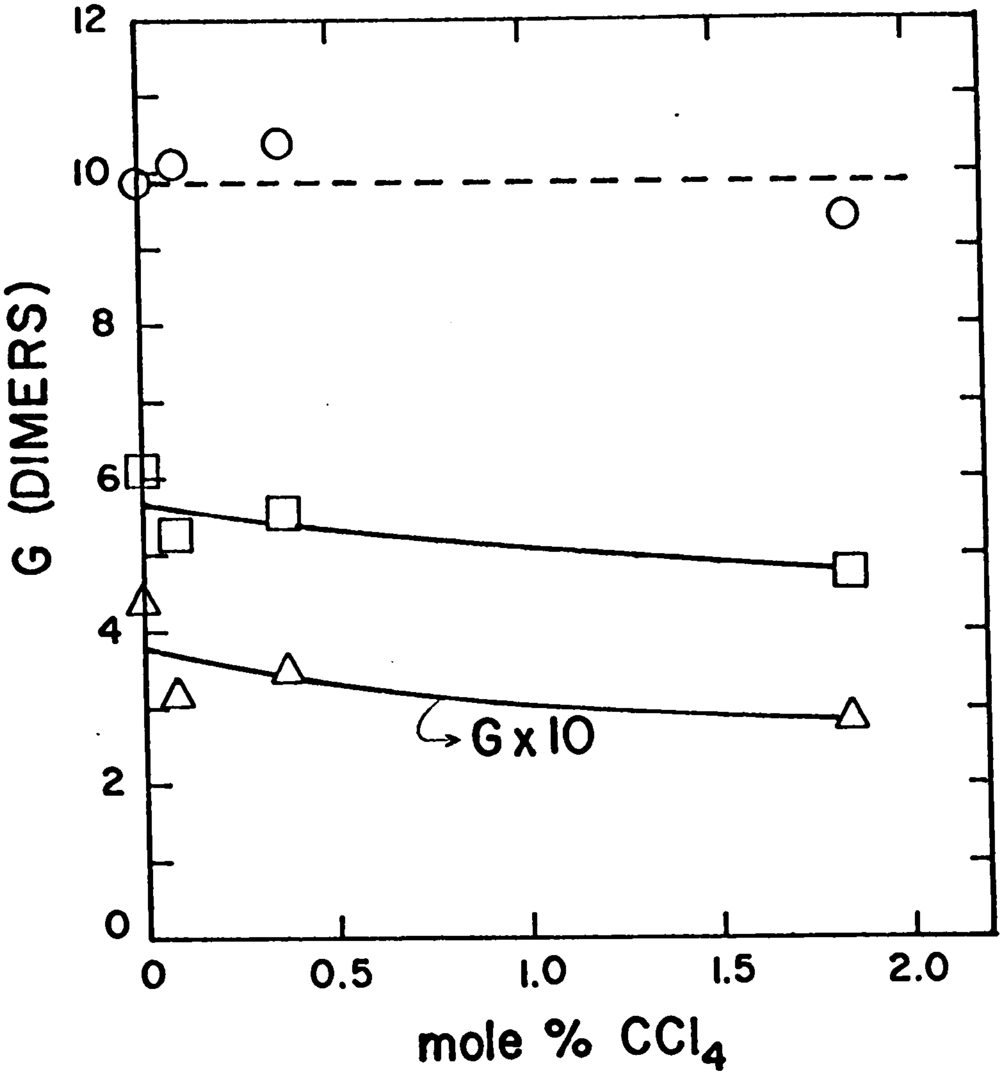


FIGURE III-21 Yield of CHD dimers from 0.772 mole % CHD solutions in benzene with carbon tetrachloride additive.

○ Dimer I

Dimers II + III

Δ Dimer IV

When CCl_4 was added to a 50 mole % CHD solution in benzene the results, shown in Fig. III-22, were more definite than those of the dilute CHD solutions, although a large amount of scatter remained in the G values. G(I) increased while G(II + III) and G(IV) decreased with an increase in CCl_4 concentration.

The results are tabulated in Table III-15.

3. Addition of ethanol to benzene solutions of 1,3-cyclohexadiene.

Addition of small amounts of ethanol to benzene containing 0.80 mole % CHD lowered G(I) considerably, as is shown in Fig. III-23 and Table III-16. At an ethanol concentration of 0.4 mole % the yield was only 5% of the yield of I without any ethanol present. In contrast, the yield of IV remained constant and the yield of II + III decreased by 70%.

E. Summary of Results.

The yield of dimer I exhibited a maximum in the solvents benzene, cyclohexane, hexane, and propyl ether. A maximum was not observed in ethanol solutions. Dimer IV increased with an increase in CHD concentration in all solvents.

The changes of the yields of dimer I and of dimer IV with a change of total dose, dose rate, CHD concentration,

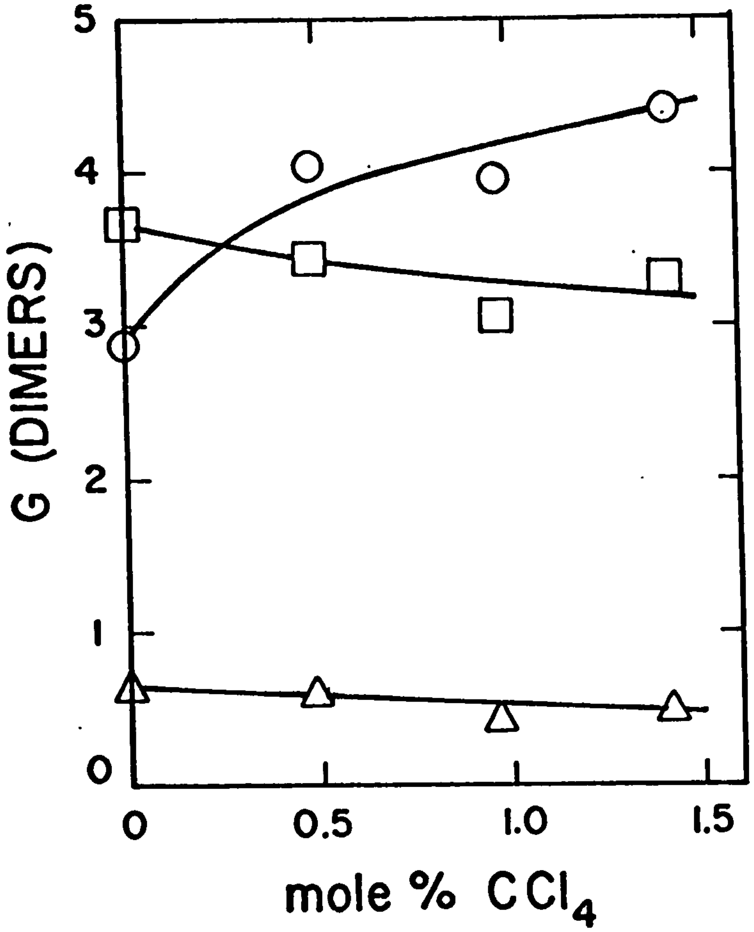


FIGURE III-22. Yield of CHD dimers from 50.2 mole % CHD solutions in benzene with carbon tetrachloride additive.

○ Dimer I

□ Dimers II + III

Δ Dimer IV

TABLE III-15

Yield of CHD dimers from benzene solutions. CCl_4 additive.

CHD mole %	CCl_4 mole %	total dose eV/g x 10^{-18}	G		
			I	II + III	IV
0.049	0.0	2.20	10.6	3.54	0.11
0.049	0.083	2.20	10.0	3.28	0.10
0.049	0.21	2.20	10.6	3.39	0.12
0.049	0.46	2.20	10.3	3.44	0.14
0.049	0.77	2.20	9.2	2.84	0.10
0.772	0.0	3.65	9.9	6.10	0.44
0.772	0.092	3.65	10.1	5.28	0.32
0.772	0.37	3.65	10.4	5.54	0.35
0.772	1.84	3.65	9.4	4.76	0.28
50.2	0.0	1.20	2.88	3.66	0.65
50.2	0.480	1.20	4.04	3.44	0.59
50.2	0.956	1.20	3.96	3.06	0.42
50.2	1.413	1.20	4.40	3.30	0.47

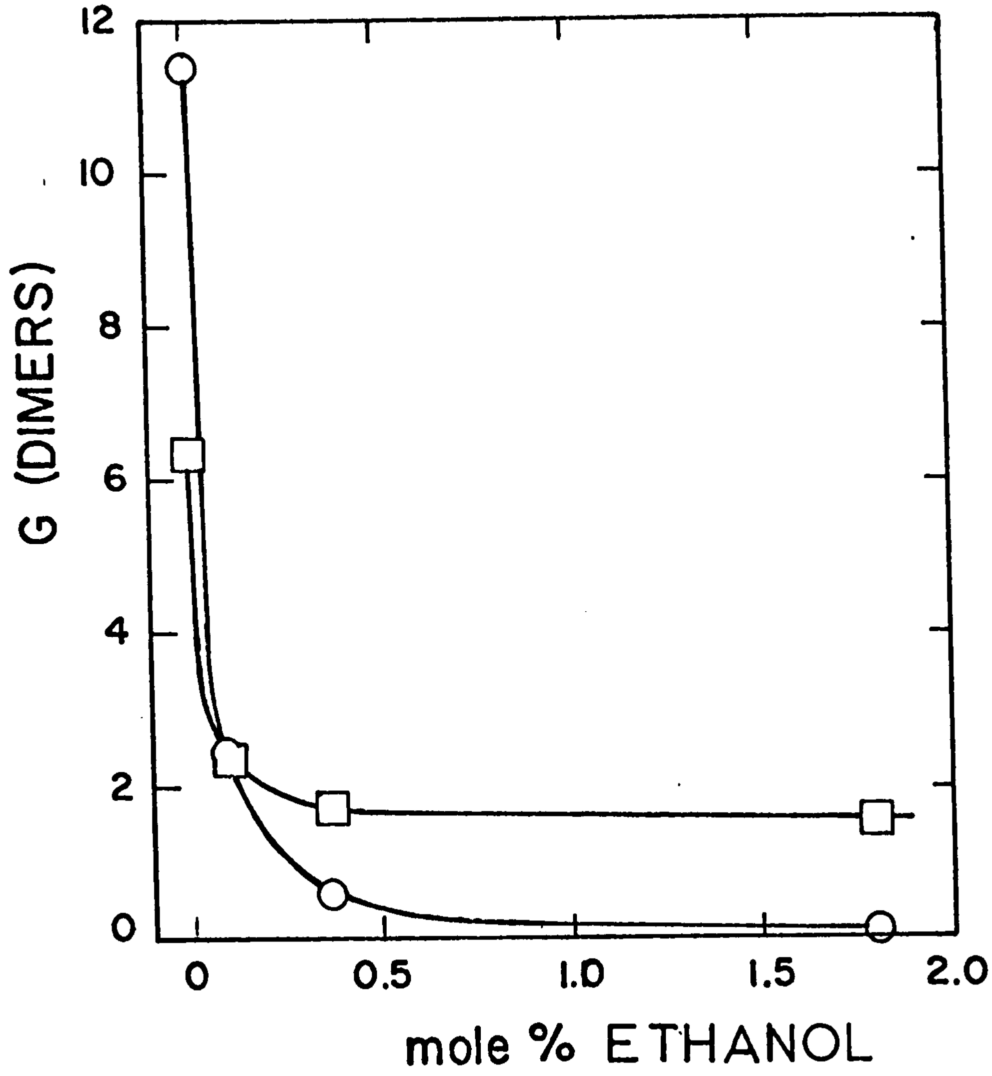


FIGURE III-23 Yield of CHD dimers from an 0.80 mole % CHD solution in benzene with ethanol additive.

○ Dimer I

□ Dimers II + III

TABLE III-16

Yield of CHD dimers from benzene solutions* with ethanol additive

	G		
ethanol mole %	I	II + III	IV
0.0	11.4	6.36	0.28
0.092	2.46	2.35	0.30
0.365	0.60	1.70	0.30
1.80	0.11	1.53	0.29

* concentration CHD 0.80 mole %

Total dose 3.60×10^{18} eV/g.

and additive are summarized in Table III-17. The effect of these variables on the yield of the dimers II + III is not included in Table III-17 because the composite nature of the g.c. peak makes the net effect dependent on the magnitude of the individual effects.

TABLE III-17

Summary of Results.

Solvent	CHD mole %	increase of or addition of	dimer I	dimer IV
benzene	0.87	total dose	O	-
	0.87	dose rate	O	O
cyclohexane	1.56	total dose	O	-
	1.56	dose rate	$\underline{O}$	O
	1.63	ethanol	-	-
	1.61	propyl ether	-	O
	1.64	N_2O	+	$\underline{O}$
	7.07	N_2O	+	$\underline{O}$
	1.65	SF_6	+	$\underline{O}$
	7.84	O_2	+	?
	1.64	CCl_4	+	-
	24.9	CCl_4	+	-
	67.8	CCl_4	+	-
propyl ether	10.1	CCl_4	O	-
	49.0	CCl_4	+	-
benzene	0.049	CCl_4	$\underline{O}$	O
	0.772	CCl_4	O	-
	50.2	CCl_4	+	-
	0.80	ethanol	-	O

+ = increase; -= decrease; O = no change; $\underline{O}$ = slight decrease.

IV DISCUSSION

(A) Mechanism of formation of the thermal dimers

(1) Positive ion chain reaction

The curves of the yield of dimer I vs the concentration of CHD exhibit maxima at 7 mole % CHD in cyclohexane and in hexane solvent with $G(I)_{max} = 6.4$, at ∿0.2 mole % in benzene with $G(I)_{max} = 12$, and at 50 mole % in propyl ether with $G(I)_{max} = 3.1$. The high yield in benzene and, to a lesser extent, the yields in cyclohexane and hexane strongly indicate a chain reaction. Ethanol was a much less efficient solvent for the formation of I. Small amounts of ethanol were added to an 0.8 mole % solution of CHD in benzene. The yield dropped from G = 11.4 with no ethanol present to G(I) = 0.6 with 0.4 mole % ethanol present. Similarly a decrease in G(I) was observed when ethanol or propyl ether was added to a 1.6 mole % solution of CHD in cyclohexane. Ethanol can act as a positive ion scavenger in cyclohexane, presumably through proton abstraction from a positive ion (95). The proton affinity (PA) of an ether is higher than the PA of the corresponding alcohol. This might be attributed to the inductive effect of the alkyl group, which tends to increase the negative charge density on the oxygen atom of alcohols and ethers. Compare the decrease in acid strength in the series formic acid, acetic acid, propionic acid; the decrease in ionization potential in the series water, methanol, ethanol, propanol and in the series dimethyl ether, diethyl ether, dipropyl ether.

The PA of ethanol is 193 ± 8 kcal/mole (96), and that of propyl ether can be estimated at 200 kcal/mole. A possible ion scavenging reaction of ethanol and propyl ether in cyclohexane is reaction [2] (95). The PA of the

$$c\text{-}C_6H_{12} \rightsquigarrow c\text{-}C_6H_{12}^{+} + e \qquad [1]$$

$$c\text{-}C_6H_{12}^{+} + C_2H_5OH \rightarrow c\text{-}C_6H_{11} + C_2H_5OH_2^{+} \qquad [2]$$

cyclohexyl radical is 179 kcal/mole.

The effect of ethanol and of propyl ether in cyclohexane solutions can thus be interpreted as positive ion scavenging.

The increased yields when the electron scavengers N_2O, SF_6 and CCl_4 were added lead to the same conclusion, namely that positive ions are involved in the formation of I. The reasoning however, in this case is indirect: an electron or anion is not the precursor of I, otherwise the yield would have been lowered by these compounds.

Addition of oxygen led to a slight increase in G(I). This virtually rules out a radical mechanism for I.

The positive ion chain reaction proposed here for the formation of the Diels-Alder dimers of 1,3-cyclohexadiene has charge scavenging by CHD as the initiation step and the dimerization and subsequent charge transfer to CHD as propagation steps. Termination may occur by neutralization, charge transfer to an impurity, and by a reaction with CHD itself. The latter reaction is postulated to account for the low yield of I in pure CHD, in other words, to explain the maxima in the G(I)-CHD concentration curves. Since it is expected that a chain reaction would be more efficient at high than at low CHD concentrations, the observation of the reverse trend in the yields leads to the postulate that CHD itself is an inhibitor of the chain reaction. To satisfy the general shape of the yield vs concentration curves the inhibiting reaction is either of the first order in CHD in competition with a reaction not involving CHD, e.g. a rearrangement of an intermediate, or, of the second order in CHD in competition with a propagation step that is of the first order in CHD. The following mechanism assumes a rearrangement of an intermediate, reaction [7].

$$\mathrm{M} \rightsquigarrow \mathrm{M}^{+} + e^{-} \qquad [3]$$

$$\mathrm{CHD} \rightsquigarrow \mathrm{CHD}^{+} + e^{-} \qquad [4]$$

$$\mathrm{M}^{+} + \mathrm{CHD} \rightarrow \mathrm{CHD}^{+} + \mathrm{M} \qquad [5]$$

$$\mathrm{CHD}^{+} + \mathrm{CHD} \rightarrow \mathrm{D}^{+*} \qquad [6]$$

$$\mathrm{D}^{+*} \rightarrow \mathrm{I}^{+} \qquad [7]$$

$$\mathrm{D}^{+*} + \mathrm{CHD} \rightarrow \mathrm{Trimer}^{+} \qquad [8]$$

$$\mathrm{I}^{+} + \mathrm{CHD} \rightarrow \mathrm{CHD}^{+} + \mathrm{I} \qquad [9]$$

$$(\mathrm{M}^{+}, \mathrm{CHD}^{+}, \mathrm{D}^{+*}, \mathrm{I}^{+}) + \mathrm{N}^{-} \rightarrow \text{neutralization} \qquad [10]$$

$$(\mathrm{M}^{+}, \mathrm{CHD}^{+}, \mathrm{D}^{+*}, \mathrm{I}^{+}) + \mathrm{Z} \rightarrow \text{chain termination} \qquad [11]$$

where M is the solvent, M^+ is an ion capable of charge transfer to CHD (reaction [5]), D^{+*} is an intermediate that rearranges (reaction [7]) to the thermal dimer positive ion I^+, N^- is an anion or electron, and Z is any molecule that can react with a chain carrier (reaction [11]) in such a manner that afterwards the charge cannot be transferred to CHD. Reaction [11] offers an explanation for the variation in G(I) with solvent, in particular for the solvent ethanol. The chain consists of reactions [6], [7] and [9]. The termination reactions are [8], [10] and [11].

If inhibition of formation of I occurs by the second above mentioned type of competition, rather than by competition between [7] and [8], reactions [6], [7] and [8] would be replaced by the competitive reactions [12] and [13]:

$$CHD^+ + CHD \rightarrow I^+ \qquad [12]$$

$$CHD^+ + 2\ CHD \rightarrow Trimer^+ \qquad [13]$$

This pair of reactions leads to the same type of kinetic expression (see Appendix) for the yield of I as does the original set of three reactions. Only the interpretation of the various parameters would differ. However, true termolecular reactions are rare.

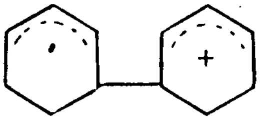
(2) Energetics of the dimerization.

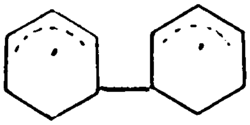
For the chain to occur it is necessary that the heat of reaction of the overall dimerization is sufficiently large to overcome the difference in the ionization potentials of CHD and I. If the thermal dimer is considered to be a substituted cyclohexene (ionization potential of 4-methylcyclohexene is 8.91 eV (25)), this difference is about 0.5 eV (12 kcal/mole); the ionization potential of CHD being 8.40 eV. The product is a tricyclic unsaturated molecule with strong non-bonding interactions between several groups. It is expected that a considerable amount of strain energy is present in I. The magnitude of this strain in I may be compared to the strain in III, as the former compound isomerizes to III at room temperature under certain circumstances (77). An estimate of the strain energy of III is 24 kcal/mole, the usual strain of a cyclobutane ring (40d).

Using the following values for the bond energies C-C bond 83 kcal/mole, C=C bond 146 kcal/mole, discrepancy energy for hydrogenation of CHD 1.8 kcal/mole, and strain energy in the product 24 kcal/mole, the net exothermicity of the overall neutral dimerization is calculated to be $2 \times 83 - 2(146 - 83) - 2 \times 1.8 - 24 \approx 12$ kcal/mole. The net effect might be more or less, depending on whether an extra strain energy is assigned to CHD (80) over and above the strain energy in the cyclohexene rings in III (106).

The overall cationic dimerization is thus approximately thermoneutral. With reference to the proposed mechanism it seems necessary that each of reactions 5 and 6 is thermoneutral when the overall process is thermoneutral.

The proposed intermediate D^{+*} (reaction 6) could be of a structure V, by analogy with that (VI) suggested by Valentine et al (77) to account for the isomerization


V


VI

of photodimers to thermal dimers at temperatures above 160°. To assess whether V is reasonable as intermediate an estimate of the resonance energy and the ionization potential of V will have to be made, and these estimates may then be compared with known values of comparable compounds. An estimate of the resonance energy of VI (and presumably also of V) can be made on the basis of the known activation energy of the isomerization III→I (36.8 kcal/mole) (77). Using the same bond energy values as before the resonance energy of VI is 83 - 24 - 36.8 = 22 kcal/mole.

The value of the ionization potential of VI, which causes reaction [6] to be thermoneutral is then:

$$83 - 2 \times (146 - 83) + \text{IP(CHD)} + 22 = \text{IP (VI)}$$
$$= 173 \text{ kcal/mole } (7.5 \text{ eV}).$$

This latter value may be compared to the ionization potential of the 2-buten-1-yl radical, 7.71 eV (26). The resonance energy of the allyl radical is about 18 kcal/mole (40c). An intermediate with structure VI, does not require unreasonable values for its resonance energy and ionization potential in order to make reactions [6] and [7] thermoneutral. Before one can have confidence in the calculated energetics of any of these reactions more exact information is required about the strain energy in the products.

(3) Mechanism of the Diels-Alder reaction

The mechanism of the Diels-Alder reaction has been reviewed by J. Sauer (97). In the majority of cases, the Diels-Alder reaction is regarded as one step reaction. An ionic-two-step mechanism is discussed in connection with the catalytic influence of Lewis Acids (98). No catalysis by Lewis acids has been observed in systems with no polar groups, i.e. with purely olefinic components. However, a two step Diels Alder reaction is also proposed for those adducts that give a Woodward-Katz rearrangement. This rearrangement appears to be confined to adducts in which both components possess diene character (99), as is the case under consideration here.

Woodward and Hoffmann (100) in their theoretical studies of cycloaddition reactions, characterized orbital symmetry relationships as determinants in concerted intermolecular cycloaddition reactions. Their selection rules can be summarized for the dimerizations of CHD as follows: 1,4-cycloaddition is thermally allowed and 1,2-cycloaddition is photochemically allowed. An extension of the rules states: "the relationships apply to ionic components as well as to neutral molecules". This implies that reactions proceeding through positive ions give the same products as thermal reactions, and that negative ions give the same products as electronically excited molecules.

With respect to an intermediate Woodward and Hoffmann made two remarks which differ from each other in the degree to which intermediates are formed. First of all the rules apply to all concerted cycloaddition reactions, even though there may be considerable asymmetry in the rate at which the various different newly forming σ bonds are established. This refers in particular to the two-step Diels-Alder reaction for those adducts that give a Woodward-Katz rearrangement (99). Secondly, the selection rules need not apply to multistep cycloaddition reactions which proceed through discrete diradical or dipolar intermediates, containing a single newly formed σ bond.

The mechanism proposed for the formation of the thermal dimers during radiolysis might involve an intermediate of the second kind. It is for this reason that the Woodward-Hoffmann rules are not used as an argument in support of the ionic-chain mechanism.

The rules are mentioned here merely to show that the γ-ray induced dimerizations support the theoretical considerations of Woodward and Hoffmann.

(4) Kinetic considerations.

Since the major contribution to the yield comes from the longest lived ions, especially in dilute solutions, the free ions make a larger contribution to the reaction than do those that undergo geminate neutralization. Thus the application of steady state homogeneous kinetics is allowed. Assuming a steady state for all ionic species in reactions [3]-[11], the expression obtained for the yield of thermal dimer I is eq. IV-1:

$$G(I) = \frac{\frac{k_7}{k_8} C^2 G(CHD^+)\varepsilon_c + \frac{k_7}{k_8} \frac{C^3}{C+\alpha} G(M^+)\varepsilon_m}{C^3 + (\beta+\gamma+\delta)C^2 + \{(\gamma+\frac{k_7}{k_8})(\beta+\delta) + \beta\delta\}C + \beta\delta(\gamma+\frac{k_7}{k_8})} \tag{IV-1}$$

(see Appendix for the derivation of this equation)

where α, β, γ and δ are constants of the form

$$\frac{k_{10}[N^-] + k_{11}[Z]}{k_j} \qquad \text{(IV-2)}$$

with j = 5 for α, 6 for β, 8 for γ and 9 for δ, C is the concentration of CHD in moles/l, and ε_m and ε_c are the electron fractions of the solvent and CHD respectively.

In dilute solutions the approximation may be made that the contribution of the direct radiolysis of CHD (reaction [4]) is negligible, compared to the sensitized formation of CHD^+ by reaction [5]. Thus ε_m is taken as 1.0 and eq. IV-1 reduces to eq. IV-3 (see also Appendix d)

$$\begin{aligned} G(I) = {} & \frac{k_7}{k_8} C^3 \, G(M^+) [C^4 + (\alpha+\beta+\gamma+\delta)C^3 + \{\alpha(\beta+\gamma+\delta) + \\ & (\gamma+\frac{k_7}{k_8})(\beta+\delta) + \beta\delta\}C^2 + \{[(\beta\delta+\alpha(\beta+\delta)](\gamma+\frac{k_7}{k_8})\}C + \\ & \alpha\beta\delta(\gamma+\frac{k_7}{k_8})]^{-1} \end{aligned} \qquad \text{(IV-3a)}$$

or

$$G(I) = \frac{a\,C^3}{C^4 + bC^3 + dC^2 + eC + f} \qquad \text{(IV-3b)}$$

It is shown in the Appendix that e and f are small compared to C and a reduction to three parameters is obtained (eq. IV-4):

$$G(I) = \frac{aC}{C^2 + bC + d} \qquad \text{(IV-4)}$$

Values of the three parameters a, b, and d cannot be chosen at random. The following three relationships hold: The maximum in the curve is reached for $C_{max} = d^{\frac{1}{2}}$; the yield at the maximum is $G(I)_{max} = a/(2C_{max} + b)$ and the initial slope is $\left(\frac{\partial G}{\partial C}\right)_{C=0} = \frac{a}{d}$.

For solutions of CHD in cyclohexane, the best fit with the experimental points is obtained with:

$$G(I) = \frac{14.5C}{C^2 + 1.0C + 0.44} \qquad \text{(IV-5)}$$

The considerable scatter in the results obtained for the benzene solutions makes the identification of $G(I)_{max}$, and C_{max} very difficult (Fig. III-7). Indeed it can be questioned whether the fall-off in the curve of G(I) vs CHD at the low concentration side has been reached. Nevertheless for dilute solutions (< 1M) of CHD in benzene the equation:

$$G(I) = \frac{12\ C}{C^2 + 1.0C + 0.001} \qquad \text{(IV-6)}$$

describes the observed yields within an error of about 10%.

Propyl ether as solvent is different from the other solvents employed in that the yields in > 4 M CHD solutions are higher than in the other solvents. These high yields are especially surprising when the inhibiting effect of propyl ether in dilute solutions of CHD in cyclohexane is considered. Analysis of the G(I) vs CHD concentration curve reveals another difference from the solvents benzene and cyclohexane in the initial slope at low diene concentrations. The initial slope is finite in benzene and in cyclohexane, but zero in propyl ether. The mathematical expression of the yield must then contain in the numerator the diene concentration to a power one unit higher than in cyclohexane or benzene, assuming the denominator to be of the same form.

The mechanistic equivalent of this statement is that charge transfer from propyl ether to CHD, reaction [5], does not occur; $G(M^+) = 0$ (in eq. IV-1); dimer I is the product of direct radiolysis of CHD. The ionization potential of propyl ether, 9.27 eV (25) is 0.9 eV higher than the ionization potential of CHD. The failure of propyl ether to transfer charge to CHD in dilute solutions may be caused by the ion-molecule reaction [14], which lowers the energy of the ion by the bond dissociation energy

$$C_3H_7OC_3H_7^+ + C_3H_7OCH_2C_2H_5 \rightarrow (C_3H_7OC_3H_7)H^+ + C_3H_7OCHC_2H_5 \qquad [14]$$

of the α C-H bond in ether, about 90 kcal/mole (3.9 eV).

Equation IV-1 rearranges to eq. IV-7, when it is

$$G(I) = \frac{\frac{k_7}{k_8} C^2 \, G(CHD^+) \varepsilon_c}{C^3 + (\beta+\gamma+\delta)C^2 + \{(\gamma+\frac{k_7}{k_8})(\beta+\delta) + \beta\delta\}C + \beta\delta(\gamma+\frac{k_7}{k_8})} \quad \text{(IV-7)}$$

assumed that no charge transfer from propyl ether positive ions to CHD occurs. The best fit with the experimental results below 2 M CHD solutions is obtained with the equation:

$$G(I) = \frac{28.9 \; C \; \varepsilon_c}{C^2 + 0.04C + 0.84} \quad \text{(IV-8)}$$

Comparison of this equation with the one that describes the dilute cyclohexane solutions, gives the interesting result that the constant a is a factor 2 larger in propyl ether than in cyclohexane. The reason for this might be that G(free ions) in propyl ether is expected to be higher than in cyclohexane. G(free ions) is roughly proportional to the dielectric constant of the medium (14). The dielectric constants of propyl ether and of cyclohexane are 3.39 (101) and 2.02 respectively (102). Freeman (19) gives an approximate rate constant k_{10} for random neutralization:

$$k_{10} = 2 \times 10^{10}/\varepsilon\eta, \text{ l/mole sec}$$

where η is the viscosity in poise and ε the dielectric constant of the medium. The lifetimes of the ions are then proportional to the dielectric constant. The increased ion lifetimes would explain the fact that G(I) in concentrated CHD solutions is higher in propyl ether than in the other solvents.

An alternative explanation is offered by the ratio of rate constants k_7/k_8 which form part of the constant a. A solvent dependence of these rate constants, in the sense that the ratio increases in propyl ether solution, compared with cyclohexane or benzene solutions, would also lead to an increase in the constant a.

The numerical expression for the yield in benzene can be used to make estimates of the rate constants of reactions [6] to [9]. Benzene is chosen because of the high yield in dilute solutions compared to cyclohexane or hexane as solvents; the influence of side reaction [11] is thus minimal in benzene. As will be seen later, the G values obtained for dimer I must be multiplied by a factor of about 1.3 to give the total yield of thermal dimer. The following expressions are obtained by combining eq IV-6 with eq IV-3:

$$15.6 = \frac{k_7}{k_8}\ G(M^+)_o \qquad \text{(IV-9)}$$

$$1.0 = \alpha + \beta + \gamma + \delta \qquad \text{(IV-10)}$$

$$0.001 = \alpha(\beta + \gamma + \delta) + (\gamma + \frac{k_7}{k_8})(\beta + \gamma\ ) + \beta\delta \qquad \text{(IV-11)}$$

Taking $G(M^+) = 0.1$ in eq. IV-9 the value derived for k_7/k_8 is about 160. The second term in eq IV-11 is the largest single term when k_7/k_8 is 160. This gives a value of

$10^{-3}/160 = 6 \times 10^{-6}$ M for $(\beta + \delta)$. The constants β and δ are associated with the specific rates of reactions [6] and [9] respectively Reaction [6] is the formation of D^{+*} and reaction [9] is charge transfer from I^+ to CHD. If $k_6 = k_9$ then $\beta = \delta = 3 \times 10^{-6}$M. The average lifetime of the free ions is calculated to be about 8×10^{-3} sec, using G(free ions) = 0.1, dose rate = 1×10^{16} eV/cc sec and $k_{10} = 10^{12}$ l/mole sec. Substitution of the average ion lifetime into β and δ gives: $k_6 = k_9 = 4 \times 10^7$ l/(mole sec).

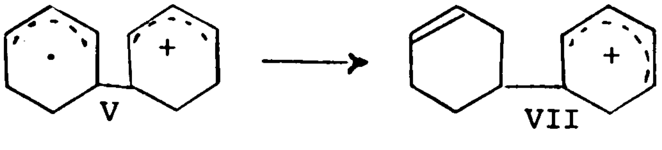
The constant α was assumed to be small (see Appendix), the value for γ found from eq IV-10 is then $\gamma = 1.0$. Again using 8×10^{-3} sec as the average lifetime of the ions k_8 is found to be about 1.2×10^2 l/mole sec, and from this value and the ratio $k_7/k_8 = 160$ M, the value of k_7 is found to be 1.9×10^4 sec^{-1}. The average lifetime of the intermediate $= \frac{1}{1.9 \times 10^4} = 5 \times 10^{-5}$ sec.

It should perhaps be emphasised that the rate constants obtained in this manner are only tentative. If reaction [11] participates in the chain termination to the extent that $k_{11}[Z] = h\,k_{10}[N^-]$, $h \gg 1$, all rate constants must be multiplied by the factor h. Also the value of G(free ions) used in the calculation has a bearing on the values obtained (see eq IV-9).

For the solvent cyclohexane, a similar treatment gives $\gamma = 1$ M, $k_7/k_8 = 190$ M, $\beta = \delta = 1.2 \times 10^{-3}$M. The reason for the lower yields in cyclohexane compared to benzene must thus be sought in the constants β and δ. A reaction between CHD^+ or I^+ and the solvent (reaction [11]) could cause the constants β and δ to increase.

The numbers obtained from the equation describing the propyl ether solutions are, assuming that the ratio k_7/k_8 is the same as in cyclohexane: $\beta = \delta = 2.2 \times 10^{-3}$M and $\gamma = 0.035$M.

The large value found for γ as compared to that of $(\beta + \delta)$ in the solvents cyclohexane and benzene, can be rationalized in two ways. The first way is by referring to the definition of γ and simply stating that reaction [8] is a slow reaction. The second possibility is to assume another unimolecular rearrangement of D^{+*}, in such a way that the product will not be able to transfer its charge to CHD, e.g an intramolecular H^+ or H transfer, reaction [15]. The product VII is a substituted 1,3-cyclohexadiene that presumably is not able to transfer its charge to CHD. The chain is thereby terminated. Thus $\gamma = \frac{k_{15}}{k_8} = 1$ M. The ion VII is able to enter into another

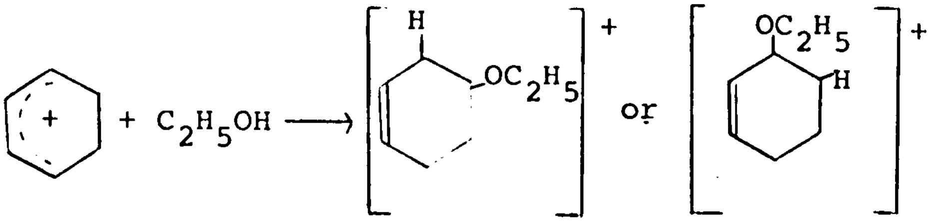


[15]

addition reaction with CHD to give polymer; in this way it would escape detection. A consequence of this postulate is that any definite information with regard to the numerical values of k_7 and k_8 is lost. Reaction 15 also offers an explanation for the lack of dose rate dependence of G(I). In the expression for the yield in benzene only the constant d is left as a dose rate dependent term. In 0.1 M solution, where the effect of dose rate was studied, the denominator in eq IV-6 changes from 0.111 to 0.116 when the dose rate is increased by a factor of 36. The yield of dimer I consequently changes only by 5%, which is within the limits of error in G(I).

(5) The effect of scavengers

Some of the interpretations of the effect of scavengers have already been given in the previous paragraphs. The decrease in yield of dimer I with the addition of ethanol and propyl ether was interpreted as scavenging of positive ions. The yields observed in propyl ether solutions led to the postulate that propyl ether cannot efficiently scavenge the ions involved in the chain propagation reactions. The proton affinity of the cyclohexadienyl radical is calculated from a Born-Haber cycle to be > 197 kcal/mole, possibly as high as 205 kcal/mole. Proton abstraction is then probably not possible by either propyl ether (PA ≃ 200 kcal/mole) or ethanol (PA = 193 kcal/mole) from the cyclohexadiene positive ion. This immediately poses the question: how then does ethanol inhibit in benzene solutions or when it functions as solvent? The answer might be found in the addition of ethanol to CHD^+, by analogy



[16]

with the addition of alcohols to olefins as mentioned in the Introduction (p.23). This reaction has not been observed with ethers, thus making the ether a better solvent than ethanol.

The effects of electron scavengers (CCl_4, SF_6, N_2O and O_2) on the yield of I are difficult to explain. The problem is not so much the lack of influence in dilute benzene solution, but that they increase the yield of I in cyclohexane and in concentrated CHD solutions in both benzene and propyl ether. A slow down of the neutralization reaction has been proposed to account for an increase in the yield of propane from the radiolysis of solutions of cyclopropane in saturated hydrocarbons to which electron scavengers were added (103). A decrease in the rate of neutralization cannot be used in the present system for various reasons.

The first reason is that CHD itself might be an electron scavenger (17). The second reason is a kinetic one. In dilute solutions in cyclohexane the increase in yield could be described by a decrease in the constants b and d. For 25% CHD in cyclohexane the same explanation is just possible with both b and d equal to zero at the highest yield obtained. But in the 69 mole % CHD solution this same treatment is no longer possible; a 2.5 fold increase in a is necessary to account for the observed yield.

If the electron scavengers do not increase the overall lifetime of the ions, it seems necessary to postulate that the neutralization reaction itself is responsible for the higher yields. It is possible that the short lived ions contribute to the yield in the more concentrated solutions. In agreement with this idea is the observation in concentrated solutions, that the yields are higher than those calculated from the numerical expressions eq IV-5, 6 and 8. The differences are about 0.2 to 0.5 G units, which indicates that only 10 to 20% of the yield at these concentrations is contributed by the short lived ions.

Assume that the ring closure of D^{+*} (reaction [7]) is the slow step in the dimerization. Then, for the short lived ions, the neutralization will take place almost exclusively with D^{+*}. The influence of an electron scavenger might thus be considerable when the neutralization is changed in character. When a chain carrier is neutralized by an electron or CHD negative ion, a thermal dimer is not formed, but when it is neutralized by a negative ion of an additive a thermal dimer is formed.

The photodimers are also formed from ionic precursors (see later), and it appears that the sum of the increase in the yield of thermal dimers and the yield of photodimers is larger than the total yield of ions available in 70 mole % CHD in cyclohexane. Part of the increase in thermal dimers must thus be attributed to an increased lifetime of the (short lived) ions. More experiments, especially in concentrated CHD solutions, are needed before the details of the effects of electron scavengers can be filled in.

B. Mechanism of formation of the photodimers.

From an examination of the summary of results, Table III-17, it can be concluded that there are no additives which effectuate an increase in dimer IV, whereas the yield of dimer I is increased by several additives. Dimer IV is therefore taken as representative of the photodimers i.e. a set of dimers which is formed by another mechanism than dimer I. Dimer I was taken as representative of the thermal dimers, on the ground that it was not formed in the photosensitized dimerization of CHD. The set of photodimers might include part of the yield of dimer II.

The yields of the photodimer IV in solutions of CHD in the solvents benzene, cyclohexane, hexane and propyl ether are higher than the yields expected from the electron fraction of CHD present in the solutions. These solvents sensitize the dimerization reaction. When ethanol is used as solvent the opposite is found; ethanol inhibits dimer formation.

The photochemical formation of the photodimers in isopentane solutions of CHD containing a triplet sensitizer points to a triplet state molecule as a possible precursor of the photodimers. CHD is also an efficient quencher of singlet excited states (104). The quenching action apparently does not lead to product formation from CHD, in particular dimers were not observed. This indicates that the dimerization of CHD involves CHD molecules in the triplet excited state. According to the theory of Woodward and Hoffman the photodimers could be formed from a CHD negative ion, in addition to formation from an electronically excited CHD molecule. Electron scavenging followed by dimerization seems unlikely as a possible mechanism, because this mechanism could lead to a chain reaction analogous to the cis → trans isomerization of

$$\mathrm{CHD}^- + \mathrm{CHD} \rightarrow \mathrm{IV}^- \qquad [17]$$

$$\mathrm{IV}^- + \mathrm{CHD} \rightarrow \mathrm{CHD}^- + \mathrm{IV} \qquad [18]$$

cis-stilbene (see P.19). From what is known about electron affinities it seems likely that an electron could transfer from the photodimer negative ion to CHD (reaction [18], because the dimer does not contain conjugated double bonds. No sign of a chain reaction with respect to the formation of photodimers was observed.

Carbon tetrachloride lowered the yield of IV by 20 - 75% in all solutions for which precise data are available. This is a sign of an involvement of negatively charged species in the dimer formation. Since it is unlikely that the negative ion of CHD itself forms the dimer it is concluded that the photodimers are formed after neutralization, or as a result of the neutralization reaction. It is thus safe to state that the nature of the positive ion involved in the neutralization reaction is a determining factor in the formation of photodimers.

The failure of ethanol to inhibit dimer IV formation in dilute CHD solutions in benzene is explained by the non-occurrence of a reaction between the benzene positive ion and ethanol (cf. paragraph IV-A-5). Neutralization of $C_6H_6^+$ by an electron could produce an electronically excited (singlet or triplet) benzene molecule which might transfer its excitation to CHD, followed by dimerization. Neutralization by CHD^- could likewise lead to an electronically excited CHD molecule. It is not sufficient to state that triplet state benzene has been established to occur in radiolysis systems independent of ionization processes, and that ethanol should thus not have an effect. Since CCl_4 decreased the yield of photodimers by 35% (Fig. III-21) in solutions where ethanol had no effect, the charged species are involved in the dimerization in benzene solutions.

The yield of IV in benzene solutions shows a continuous increase with an increase in CHD concentration. No plateau value was reached, as was the case in the benzene sensitized isomerization of 2-butene (51). In 0.1 M solutions G(triplet olefin) was about 3.0 for 2-butene in benzene. G(photodimers) for 0.1 M CHD in benzene is 1.8 and at least 35% of this yield has ionic precursors. The lack of a plateau in dilute solutions, and the participation of at least two precursors prohibit an estimate of the contribution of triplet excited benzene to the yield of photodimers.

Ethanol completely inhibited the formation of IV in cyclohexane solutions (Table III-8). Propyl ether had no effect. It was postulated in sections IV-A-4 and 5 that ethanol and propyl ether could react with a cyclohexane positive ion, and that ethanol could react with a CHD positive ion, while propyl ether failed to do so. The neutralization reaction leading to triplet CHD molecule in cyclohexane thus involves a CHD positive ion, and not a cyclohexane positive ion. The cyclohexane positive ions are of course precursors to the CHD positive ions. Propyl ether is then expected to have an effect on the photodimer yield, through competition with CHD for the solvent positive ions. The fact that it has no effect might be due to the competition being heavily in favor of CHD, since electron abstraction from CHD might be faster than proton abstraction by propyl ether.

At 7 mole % CHD in cyclohexane, addition of only 0.3 mole % N_2O gave the maximum effect on the yields of all dimers. An increase to 1.7 mole % N_2O did not further change the G values. It seems necessary to postulate that neutralization by a negative ion of N_2O also leads to an electronically excited CHD. Hertzberg (105) places the energy of the triplet state of N_2O at 60 - 70 kcal/mole. There is then a possibility that a neutralization reaction between N_2O^- and CHD^+ produces a triplet excited CHD molecule, perhaps via a triplet excited N_2O. The energy of the lowest triplet state of CHD is 53 kcal/mole (64).

It is unfortunate that the G values of dimer IV are subject to considerable scatter. It is not possible to extract quantitative information with respect to lifetimes of excited states or scavenging efficiency of CHD for positive ions from the data.

C. Total G values of thermal dimers and photodimers

Since it was not possible to find a gas chromatography column that separated all four dimers of CHD, it is necessary to use an approximation in the calculation of total G values for the thermal dimers and the photodimers.

One approach would be to use the ratio of II: I obtained in the thermal dimerization of CHD. This ratio is $\frac{II}{I} = 0.29$. Multiplication of I by 1.29 then gives the total thermal dimer yield, and the remainder of the dimers is photodimer. Another approximation is offered by the ratio of the photodimers as obtained from the photolysis of CHD in isopentane solution. The ratio is $\frac{II + III}{IV} = 4.35$. The total photodimer yield is then given by 5.35 G(IV), and the remainder of the dimers constitute the thermal dimers. When both ratios are tried on a set of results the values obtained for the total thermal dimer yield and the total photodimer yield do not agree with each other. The discrepancy varies but is for the photodimers in some cases as high as 90%.

Schenck et al. (83) claim that the ratios of the yields of the various dimers is dependent on the solvent, the sensitizer, the temperature, and the type of radiation employed. Extrapolation of the results from the thermal dimerization and the photolysis in isopentane to the radiolysis at room temperature in various solvents would thus be meaningless.

An empirical approach to each separate eystem seemed in order. Assume that the ratio of the thermal dimers $\frac{II(t)}{I} = r$, and the ratio of the photodimers $\frac{II(p) + III}{IV} = p$ are constant in a particular system. Dimer II, which was formed in the photolysis as well as in the thermal dimerization is divided over these two ratios in some unknown manner. The second gas chromatographic peak is the sum of the minor thermal dimer (II) and the major photodimer. The area of this peak can be expressed in the areas of the peak of the major thermal dimer (I) and the minor photodimer IV:

$$II(t) + \{II(p) + III\} = rI + pIV$$

Dividing by IV gives

$$\frac{II + III}{IV} = r\frac{I}{IV} + p.$$

The equation of a straight line with slope r and intercept p. An example of a plot of (II + III)/IV vs I/IV is given in Fig. IV-1. The ratio of the photodimers p = 3.3 and the ratio of the termal dimers r - 0.33. In order to find accurate values of p and r the values of IV must be accurate. This is not always the case. For this reason only a few accurate values of p and r were obtained.

The ratio of the photodimers found from the intercept (3.3) is much lower than the ratio found from the photolysis

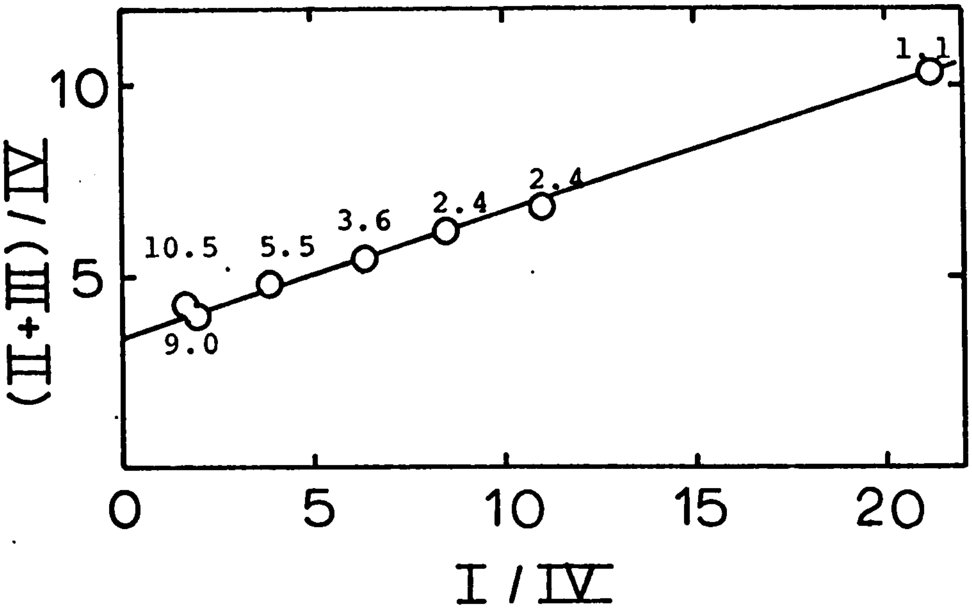


Figure IV-1 Ratios of the peak areas of the CHD dimers.

The numbers near the points give the CHD concentration in moles/l. Solvent cyclohexane.

in isopentane (4.4). Schenck et al. report for photolysis of pure CHD without a sensitizer the following composition of the dimer mixture: II-33%, III-44%, and IV-23%. The corresponding ratio p is then $\frac{33 + 44}{23} = 3.35$, in good agreement with the above value.

It appears that the ratio of the photodimers is subject to change from one system to another. If this is the case even the above derived method is subject to a systematic error since for CHD/solvent mixtures extrapolation occurs always towards pure CHD. An intercept of about 3 will thus be found, but this intercept (ratio p) does not necessarily describe the ratio of the photodimers in dilute solutions. The results of scavenger studies in dilute solutions, in particular ethanol in benzene and propyl ether in cyclohexane, have been treated by the above method and it appears that the ratio of photodimers might be as high as 5.0 in dilute solutions. The constant r varies between 1.22 (propyl ether) and 1.39 (benzene).

The possibility of a systematic error, and the lack of accuracy in dimer IV, limited the discussion to dimer I and dimer IV. Total G values were not calculated.

D. Summary of conclusions.

The Diels-Alder (thermal) dimers are formed in a positive ion chain reaction, initiated by charge transfer from the solvent in benzene, cyclohexane and hexane solutions. In ethanol and in dilute solutions of CHD in propyl ether charge transfer from the solvent does not occur.

The chain proceeds through an intermediate that can either react with CHD to form trimer or form a Diels-Alder positive ion in a unimolecular reaction.

In 0.7% of the cases the intermediate may undergo an intramolecular H atom or H^+ transfer reaction. Such a reaction explains the dose rate independence of the yields.

Chain carrier positive ions may undergo an addition reaction with ethanol. Such a reaction does not occur with propyl ether.

Electron scavengers may change the neutralization reaction in such a way that Diels-Alder dimers are formed.

Electronically excited (triplet) benzene molecules formed directly by the radiation and by ion neutralization might be precursors to the photodimers in benzene solution.

The photodimers are formed during neutralization or as a result of neutralization in cyclohexane solutions. Neutralization involving a cyclohexane positive ion does not lead to a photodimer.

Neutralization of CHD^+ by a negative ion of N_2O may lead to a triplet excited CHD molecule, perhaps via a triplet excited N_2O.

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APPENDIX

(a). Derivation of equation IV-1 of page 136.

Application of steady state homogeneous kinetics to the reactions [3] to [11]

$$\mathrm{M} \rightsquigarrow \mathrm{M}^+ + e^- \qquad [3]$$

$$\mathrm{CHD} \rightsquigarrow \mathrm{CHD}^+ + e^- \qquad [4]$$

$$\mathrm{M}^+ + \mathrm{CHD} \rightarrow \mathrm{CHD}^+ + \mathrm{M} \qquad [5]$$

$$\mathrm{CHD}^+ + \mathrm{CHD} \rightarrow \mathrm{D}^{+*} \qquad [6]$$

$$\mathrm{D}^{+*} \rightarrow \mathrm{I}^+ \qquad [7]$$

$$\mathrm{D}^{+*} + \mathrm{CHD} \rightarrow \mathrm{Trimer}^+ \qquad [8]$$

$$\mathrm{I}^+ + \mathrm{CHD} \rightarrow \mathrm{CHD}^+ + \mathrm{I} \qquad [9]$$

$$(\mathrm{M}^+, \mathrm{CHD}^+, \mathrm{D}^{+*}, \mathrm{I}^+ + \mathrm{N}^-) \rightarrow \text{neutralization} \qquad [10]$$

$$(\mathrm{M}^+, \mathrm{CHD}^+, \mathrm{D}^{+*}, \mathrm{I}^+ + \mathrm{Z}) \rightarrow \text{chain termination} \qquad [11]$$

leads to the following set of simultaneous equations (for definition of symbols see p.138).

$$\frac{d[\mathrm{M}^+]}{dt} = G(\mathrm{M}^+)\varepsilon_m - [\mathrm{M}^+](k_5C + k_{10}[\mathrm{N}^-] + k_{11}[\mathrm{Z}]) = 0$$

$$= G(\mathrm{M}^+)\varepsilon_m - k_5[\mathrm{M}^+](C+\alpha) \tag{A-1}$$

$$\text{where } \alpha = \frac{k_{10}[\mathrm{N}^-] + k_{11}[\mathrm{Z}]}{k_5}$$

$$\frac{d[\mathrm{CHD}^+]}{dt} = G(\mathrm{CHD}^+)\varepsilon_c + k_5[\mathrm{M}^+]C + k_9[\mathrm{I}^+]C - [\mathrm{CHD}^+](k_6C + k_{10}[\mathrm{N}^-] + k_{11}[\mathrm{Z}]) = 0$$

$$= G(\mathrm{CHD}^+)\varepsilon_c + k_5[\mathrm{M}^+]C + k_9[\mathrm{I}^+]C + k_6[\mathrm{CHD}^+](C+\beta) \tag{A-2}$$

where $\beta = \dfrac{k_{10}[N^-] + k_{11}[Z]}{k_6}$

$$\frac{d[D^{+*}]}{dt} = k_6[CHD^+]C - [D^{+*}](k_8C + k_7 + k_{10}[N^-] + k_{11}[Z]) = 0$$

$$= k_6[CHD^+]C - k_8[D^{+*}](C + \frac{k_7}{k_8} + \gamma) \qquad \text{A-3}$$

where $\gamma = \dfrac{k_{10}[N^-] + k_{11}[Z]}{k_8}$

$$\frac{d[I^+]}{dt} = k_7[D^{+*}] - [I^+](k_9C + k_{10}[N^-] + k_{11}[Z]) = 0$$

$$= k_7[D^{+*}] - k_9[I^+](C + \delta) \qquad \text{A-4}$$

where $\delta = \dfrac{k_{10}[N^-] + k_{11}[Z]}{k_9}$

From eq A-1 to A-4 the expressions for the concentrations of each of the ions of the chain are derived:

$$[M^+] = \frac{G(M^+)\varepsilon_m}{k_5(C + \alpha)} \qquad \text{A-5}$$

$$[CHD^+] = \frac{G(CHD^+)\varepsilon_c + k_5[M^+]C + k_9[I^+]C}{k_6(C + \beta)} \qquad \text{A-6}$$

$$[D^{+*}] = \frac{k_6[CHD^+][C]}{k_8(C + \gamma + \frac{k_7}{k_8})} \qquad \text{A-7}$$

$$[I^+] = \frac{k_7[D^{+*}]}{k_9(C + \delta)} \qquad \text{A-8}$$

Substitution of A-6 into A-7 and substitution of the result into A-8 gives:

$$[I^+] = \frac{k_7}{k_9(C+\delta)} \cdot \frac{k_6 C}{k_8(C+\gamma+\frac{k_7}{k_8})} \cdot \left[\frac{G(CHD^+)\varepsilon_c + k_5[M^+]C}{k_6(C+\beta)} + \frac{k_9[I^+]C}{k_6(C+\beta)} \right] \qquad \text{A-9}$$

or after rearrangement and substitution of A-5

$$[I^+] = \frac{k_7 C\{G(CHD^+)\varepsilon_c + \frac{G(M^+)\varepsilon_m C}{C+\alpha}\}}{k_8 k_9 (C+\beta)(C+\delta)(C+\gamma+\frac{k_7}{k_8}) - k_7 k_9 C^2} \qquad \text{A-10}$$

The thermal dimer is formed in reaction [9]

$$G(I) = k_9[I^+]C \qquad \text{A-11}$$

Substitution of A-10 to A-11 gives the yield of thermal dimer equation A-12:

$$G(I) = \frac{k_7 C^2\{G(CHD^+)\varepsilon_c + \frac{G(M^+)\varepsilon_m C}{C+\alpha}\}}{k_8\{(C+\beta)(C+\delta)(C+\frac{k_7}{k_8}+\delta) + \frac{k_7}{k_8}C^2\}} \qquad \text{A-12}$$

A final rearrangement gives eq. IV-1.

$$G(I) = \frac{\frac{k_7}{k_8} C^2\{G(CHD^+)\varepsilon_c + \frac{G(M^+)\varepsilon_m C}{C+\alpha}\}}{C^3 + (\beta+\gamma+\delta)C^2 + \{\beta\delta + (\gamma+\frac{k_7}{k_8})(\beta+\delta)\}C + \beta\delta\,(\gamma+\frac{k_7}{k_8})} \qquad \text{IV-1}$$

(b) Reduction to three parameters

The number of data available and their precision are not sufficient to allow a calculation of all five parameters. To decide which parameters can be neglected in the calculations a trial calculation was done. For C = 1 M in cyclohexane solutions G(I) = 5.8. Substition of these values in eq. IV-3b gives: a = 5.8 (1 + b + d + e + f). Combination with eq. IV-3a gives:

$$\frac{k_7}{k_8} G(M^+) = 5.8 \left(1 + b + \frac{k_7}{k_8}(\beta + \delta) + \frac{k_7}{k_8}\alpha(\beta + \delta) + \frac{k_7}{k_8}\beta\delta + \frac{k_7}{k_8}\alpha\beta\delta + \text{rest terms not including } \frac{k_7}{k_8}\right).$$

whence:

$$\frac{k_7}{k_8}\{G(M^+) - 5.8\,(1 + \alpha)(\beta + \delta + \beta\delta)\} = 5.8\,(1 + b + \text{rest terms}).$$

Since all constants are > 0, a solution can only be found for

$$G(M^+) > 5.8\,(1 + \alpha)(\beta + \delta + \beta\delta).$$

Taking a maximum value of $G(M^+) = 4.0$ the result is

$$(1 + \alpha)\,(\beta + \delta + \beta\delta) < 0.69$$

A similar calculation for C = 0.1 M, G(I) = 2.0 in cyclohexane gives:

$$(1 + 10\alpha)(\beta + \delta + 10\beta\delta) < 0.2$$

Independent of the value of α the upper limit for $\beta + \delta +$

$10\beta\delta$ is 0.2. For a given sum of $(\beta + \delta) < 1$, the product $\beta\delta$ is maximal for $\beta = \delta$ thus $2\beta + 10\beta^2 < 0.2$ and $\beta = \delta < 0.07$. Neglecting the term $\beta\delta$ in the constant e the ratio $\frac{f}{e} = \frac{\beta\delta}{\beta + \delta}$. The maximum value of this ratio is: $\frac{0.0049}{0.14} = 0.03$. Thus in 0.1 M solution in cyclohexane the contribution of f to the denominator is maximal 30% of the contribution of the term eC. When a more realistic value of $G(M^+)$ is taken, i.e. $G(M^+) = G(\text{free ions}) = 0.1$ the ratio $\frac{f}{e}$ is found to be 10^{-3}, the contribution of f is thus 10% of the contribution of eC to the denominator when C is 0.1 M.

Considering the mechanism, the reaction [5] determining α, and the reaction [9] determining δ are of the same type: charge transfer from M^+ or I^+ to CHD. It may be assumed that the rates of these reactions are of the same order of magnitude. The constants α and δ are then of the same order of magnitude. To explore the maximum values of α, β and δ, they are assumed to be equal. Thus, with $G(M^+) = 4$,

$$\alpha + 15\alpha^2 + 50\alpha^3 < 0.1 \quad \therefore \alpha < 0.05$$

With $G(M^+) = 0.1$ a value of $\alpha < 0.002$ is obtained. The ratio of the constants e and d is thus found to be $\frac{e}{d} < 0.05$.

The assumption that α is of the same order of magnitude as δ leads to the conclusion that $e << d$. It was demonstrated that $f < eC$. A reduction to three parameters may thus be obtained by neglecting the last two terms in the denominator of eq IV-3b:

$$G(I) = \frac{aC}{C^2 + bC + d} \qquad \text{IV-4}$$

(c) Derivation of the kinetic expression for the mechanism with competition between a bimolecular and a termolecular reaction.

$$\mathrm{CHD}^+ + \mathrm{CHD} \rightarrow \mathrm{I}^+ \qquad [12]$$

$$\mathrm{CHD}^+ + 2\mathrm{CHD} \rightarrow \mathrm{Trimer}^+ \qquad [13]$$

Upon application of steady state homogeneous kinetics to the reactions [3] - [5] and [9] to [13], the following equations are obtained for the concentrations of the ionic species:

$$[M^+] = \frac{G(M^+)\varepsilon_m}{k_5(C + \alpha)} \qquad \text{A-13}$$

$$[\mathrm{CHD}^+] = \frac{G(\mathrm{CHD}^+)\varepsilon_c + k_5[M^+]C + k_9[I^+]C}{k_{12}(C + \frac{k_{13}}{k_{12}}C^2 + k_{10}[N^-] + k_{11}[Z])}$$

$$= \frac{G(\mathrm{CHD}^+)\varepsilon_c + k_5[M^+]C + k_9[I^+]C}{k_{12}(C + \frac{k_{13}}{k_{12}}C^2 + \eta)} \qquad \text{A-14}$$

$$\text{where } \eta = \frac{k_{10}[N^-] + k_{11}[Z]}{k_{12}}$$

$$[I^+] = \frac{k_{12}[CHD^+]C}{k_9(C + \delta)} \qquad \text{A-15}$$

The yield of thermal dimer is given by:

$$G(I) = k_9[I^+]C = \frac{k_{12}C^2[CHD^+]}{(C + \delta)} \qquad \text{A-16}$$

Substitution of A-15 and A-13 into A-14 gives:

$$[CHD^+] = \frac{G(CHD^+)\varepsilon_c + \frac{G(M^+)\varepsilon_m}{C + \alpha} + \frac{k_{12}C^2[CHD^+]}{C + \delta}}{k_{12}(C + \frac{k_{13}}{k_{12}} C^2 + \eta)} \qquad \text{A-17}$$

After rearrangement and substitution of the result into A-16 the expression for the yield of thermal dimer obtained is:

$$G(I) = \frac{C^2}{C + \delta} \left[\frac{G(CHD^+)\varepsilon_c + \frac{G(M^+)\varepsilon_m C}{C + \alpha}}{(\frac{k_{13}}{k_{12}} C^2 + C + \eta) - \frac{C^2}{C + \delta}} \right] \qquad \text{A-18}$$

$$G(I) = \frac{C^2(G(CHD^+)\varepsilon_c + \frac{G(M^+)\varepsilon_m C}{C + \alpha})}{(C + \delta)(\frac{k_{13}}{k_{12}} C^2 + C + \eta) - C^2}$$

or

$$G(I) = \frac{\frac{k_{12}}{k_{13}} C^2(G(CHD^+)\varepsilon_c + \frac{CG(M^+)\varepsilon_m}{C + \alpha})}{C^3 + \delta C^2 + \frac{k_{12}}{k_{13}} (\eta + \delta)C + \frac{k_{12}}{k_{13}} \eta\delta}$$

(d). The use of the complete formula eq. IV-1 in the trial calculation of appendix b reduces the limits found for β, δ and α by 1%. In concentrated solutions ($C>>\alpha$) where the assumption $\varepsilon_m = 1.0$ cannot be used a reduction of the numerator of eq. IV-1 to:

$$\frac{k_7}{k_8} \; C^2\{G(M^+)\varepsilon_m + G(CHD^+)\varepsilon_c\}$$

is obtained.

The assumption $\varepsilon_m = 1.0$ may now be supplanted by the assumption $G(M^+) = G(CHD^+)$, in order to keep the number of parameters down to three:

$$\frac{k_7}{k_8} \; C^2G(M^+)(\varepsilon_m + \varepsilon_c) = \frac{k_7}{k_8} \; C^2G(M^+)$$

The latter assumption is not unreasonable since equation IV-1 was derived for the long lived ions (free ions). The proper value of $G(M^+)$ and of $G(CHD^+)$ to be substituted in the formula is thus G(free ions) = 0.1 in all the hydrocarbon solvents used.