NATIONAL LIBRARY
OTTAWA

BIBLIOTHÈQUE NATIONALE
OTTAWA

CANADA

8458

NAME OF AUTHOR...Golinkin, Herbert Sheldon..................

TITLE OF THESIS..Piezochemistry of reactions in solution....

....

....

UNIVERSITY.......U. of C....................................

DEGREE FOR WHICH THESIS WAS PRESENTED.......Ph.D............

YEAR THIS DEGREE GRANTED...1966.............................

Permission is hereby granted to THE NATIONAL LIBRARY OF CANADA to microfilm this thesis and to lend or sell copies of the film.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

(Signed).....................

PERMANENT ADDRESS:

1038 Mill St.
Naperville, Illinois 60540
U.S.A.

DATED. April 5..........1971

NL-91 (10-68)

UNIVERSITY OF CALGARY

PIEZOCHEMISTRY OF REACTIONS IN SOLUTION

by

HERBERT SHELDON GOLINKIN

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

CALGARY, ALBERTA
AUGUST, 1966

UNIVERSITY OF CALGARY

FACULTY OF GRADUATE STUDIES

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

PIEZOCHEMISTRY OF REACTIONS IN SOLUTION

submitted by Herbert Sheldon Golinkin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

James B. Hyne
Supervisor

Frank G. Adams

Gale K. Billings

Wm. M. Laidlaw

Edward M. Arnett
External Examiner

Date 26 Aug 66.

The best and safest method of philosophizing seems to be, first, to inquire diligently into the properties of things and to establish those properties by experiments, and to proceed later to hypotheses for the explanation of things themselves. For hypotheses ought to be applied only in the explanation of the properties of things, and not made use of in determining them.

Sir Isaac Newton

ABSTRACT

The first order rate constants for the solvolysis of benzyl chloride in the series of aqueous methanol, ethanol, i-propanol and t-butanol solvent systems at various temperatures and pressures are reported.

The enthalpy of activation, ΔH^{*}, entropy of activation, ΔS^{*}, and the volume of activation ΔV_{0}^{*} are calculated from the rate data obtained. It is shown that it is both necessary and sufficient to allow for the pressure dependence of the activation volume when analyzing a set of rate data at various pressures. Values of $(\partial \Delta V^{*}/\partial p)_{T}$ are reported for the benzyl chloride solvolysis in the various solvent systems studied.

It is demonstrated that for benzyl chloride solvolysis the four aforementioned activation parameters, as well as the heat capacity of activation, ΔC_{p}^{*}, reported by Hyne, Wills and Wonkka,[106] exhibit extremum behavior as a function of solvent composition, and that the depth and position of the extrema are dependent upon the nature of the alcoholic solvent component. It is further demonstrated that the constant volume activation parameters, ΔU_{V}^{*} and ΔS_{V}^{*}, do exhibit extremum behavior contrary to previous reports,[135] and parallel the behavior of the more commonly used parameters.

The similarities between the activation parameter behavior and the thermodynamic parameters of mixing of the binary solvents are discussed both for the constant pressure and constant volume conditions.

The partial molal volume of benzyl chloride in each of the pertinent solvents is reported, and found to account for 50% to 100% of the extremum behavior in $\Delta V_o^{\neq}$.

It is established that the extremum behavior probably results from phenomena associated with the structural properties of the solvent, and is not due to concomitant hydrophobic-hydrophilic interactions.

The pressure dependence of the activation volume is observed to undergo a change in sign in highly aqueous media, and this phenomena may again be associated with structural changes in the solvent on addition of the alcoholic component.

ACKNOWLEDGEMENTS

I would like to take this opportunity to acknowledge the aid and assistance of some of the people who made this thesis possible. My sincere gratitude goes to the faculty members of the Department of Chemistry, University of Calgary for their advice and guidance--in particular to Dr. William G. Laidlaw for many helpful discussions with respect to the material in Chapter 6.

To the late Dr. Jim Young and the staff at Imperial Oil Research and Development Laboratories for advice in setting up the high pressure laboratory and permitting me the use of their compressibility apparatus.

To the staff of the University of Calgary Computing Centre for writing the Fortran programs used in this study.

To the personell of the University Machine Shop, particularly Mr. Fred Jarvis and Mr. Ron Keen, for the design, construction and maintenance of much of the high pressure equipment and related pieces of apparatus.

To Mr. Tom Clement for construction and maintenance of the electronic equipment, and to Mr. Duncan Lindsay for construction of the glass apparatus.

To Dr. Ikchoon Lee for allowing me to use his data on the partial molal volume of benzyl chloride prior to publication, and to Mr. Gordon Weir for determining the solvent densities.

To the National Research Council of Canada for financial assistance.

To Professor James Bisset Hyne for his guidance and help throughout this project, and in matters normally extraneous to a thesis. Also for

allowing me to use the kinetic data on p-methylbenzyl chloride prior to publication.

To my parents, Abraham and Eva Golinkin, for their teaching, guidance and faith, I am truly grateful beyond the expression of mere words.

To my wife, Adrienne, goes my sincere gratitude for her patience and understanding when I was impossible, and for her encouragement and inspiration when I was depressed. I also wish to thank Adrienne for preparing the stencils of this manuscript.

TABLE OF CONTENTS

CHAPTER PAGE

PART I: INTRODUCTION AND REVIEW

PART III: STATIC MEASUREMENTS

CHAPTER PAGE

PART IV: DISCUSSION

PART V: APPENDICES

APPENDIX

LIST OF TABLES

LIST OF FIGURES

GLOSSARY OF SYMBOLS

A	area; empirical constant; Helmholtz free energy.
B	empirical constant.
C	empirical constant; heat capacity.
D	dielectric constant.
E	(sub.) excess.
$\underline{E}_n$	solvent nucleophilicity parameter.
F	Gibbs free energy.
H	enthalpy.
K	equilibrium constant.
M	molecular weight; (super.) mixing.
N	Avogardo's number.
P	steric factor in collision theory.
R	gas constant; electrical resistance.
S	entropy.
T	absolute temperature.
U	internal energy.
V	volume.
W	weight.
X	mole fraction; general parameter.
Y	Winstein solvent parameter.
Z	collision number; Kosower solvent parameter.

a	empirical constant.
a.d.	average deviation.
b	(sub.) bridge.
b	Swain and Dittmer solvent parameter.
bar	barometric pressure.
c	concentration in moles/liter; (sub.) compressibility cell; cell.
calc	calculated.
d	derivative; density.
e	electronic charge; Naperian logarithm base.
e	solvent electrophilicity parameter.
ex	(super.) expansion.
g	(sub., super.) initial state.
h	change in meniscus height; Planck's constant; (sub.) hydration.
k	rate constant.
k_b	Boltzmann's constant.
n	number of moles; (sub.) needle.
n	solvent nucleophilicity parameter.
o	(super.) degree; pure liquid; zero concentration; (sub.) atmospheric pressure; zero time.
obs	observed.
p	pressure; (sub.) compressibility pump; constant pressure.
pyr	pyrex.
r	radius.
rel	(sub.) relative.
s	(sub.) syringe; shunt.

s.d.	standard deviation.
t	time; centigrade temperature; (sub., super.) transition state.
v	(sub.) constant volume.
v_m	molal volume.
wd	withdrawn.
wts	weights.
α	thermal expansivity.
β	empirical parameter.
γ	activity coefficient.
δ	partial charge.
Δ	change in.
κ	isothermal compressibility.
Λ	electrical conductivity.
μ	dipole moment; ionic strength.
π	universal constant = 3.1415927....
∂	partial derivative.
ℓ	bond length.
*	activation process.
$-$	partial molal.
1	internal contribution; component 1.
2	solvent contribution; component 2.

PART I

INTRODUCTION AND REVIEW

CHAPTER 1

PIEZOCHEMISTRY

As will become apparent, this thesis is concerned with the study of the effect of hydrostatic pressure on the rate of neutral solvolysis. Nevertheless a brief review of general piezochemical phenomena, i.e. phenomena of high pressure chemistry, in solution is perhaps appropriate as a preparation for the more specific discussion of the effects of pressure on solvolytic reaction kinetics.

Many excellent reviews of high pressure chemistry are in print. Therefore no attempt will be made to present a compendium of piezochemistry. Instead a brief review of the pertinent aspects of this subject will be offered. The reader interested in more extensive treatments is directed to the works by Hamann[1] and Bradley[2] which are excellent digests. The latter also contains very extensive bibliographies. The review by Whalley[3] covers the field of pressure effects on reaction kinetics and the related mechanistic implications.

In solvolyses of organic and inorganic esters, a molecule of a protic acid is produced for every ester linkage which undergoes decomposition. In the case of the inorganic esters the acids are virtually completely ionized in aqueous media while the organic acids are frequently only partially ionized. The presence of these ionic species allow the use of an <u>in situ</u> conductimetric method for following the progress of the reaction. In anticipation of the use of this method, a summary of the effect of pressure on electrical conductivity in solution will be presented. Further, since there is an equilibrium between ionized and unionized species in these solutions, the electrical conductivity at various pressures also reflects the pressure dependence of this equilibrium. Consequently a survey of the piezochemistry of homogeneous equilibria is included. Finally the need for inclusion of a section on piezokinetics is obvious.

Homogeneous Equilibria

The first theoretical paper to be published on the effect of pressure on chemical equilibria was that of Planck in 1887.[4] He demonstrated that the relation between the equilibrium constant and pressure is

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta V}{RT} \qquad (1)$$

where ΔV is the total molar volume change accompanying the reaction. Apparently no further theoretical development occurred until 1941 when Owen and Brinkley[5] estimated the effect of pressure on the ionization constants of weak acids using the partial molal and ionic volumes of the species concerned along with their isothermal compressibilities. As an extension of this work these authors estimated the pressure dependence of the solubility product of various salts in both water and 0.725 molal aqueous sodium chloride. The calculations indicated three noteworthy trends. Firstly, ionization constants increase with increasing pressure. That is the ionic species as opposed to the unionized molecules are favored by increasing the pressure. Secondly, the sensitivity of the equilibrium to pressure decreases with increasing temperature. Thirdly, both the standard partial molal enthalpy and entropy, $\Delta\bar{H}^o$ and $\Delta\bar{S}^o$, become more negative at higher pressures.

The work of Buchanan and Hamann,[6] along with subsequent studies from Hamann's laboratory, afforded an understanding of the physical phenomena responsible for the observed trends of equilibria. Studying the ionization of ammonium hydroxide, these authors assumed that the main effect of pressure is to change the hydration free energy of the solvated ions; implying negligible pressure effects on the hydration free energy of non-ionic species, bond dissociation free energies, ionization potentials and electron affinities. Using the Born model (eq. 2) for the free energy of ionic hydration these authors calculated the variation in hydration

$$\Delta F_h = - \frac{Ne^2}{2(r + a)}\left(1 - \frac{1}{D}\right) \qquad (2)$$

free energy of the ammonium and hydroxide ions with pressure. Their results agreed surprisingly well with the experimental values. They concluded that the principal effect of pressure is to *lower the free energy of ionization* by lowering the solvation free energy of the ionic species. As a further test of this, the size of the cation was varied by replacing one of the protons by a methyl group.

The greater size of the methylammonium ion causes it to have a smaller hydration free energy than the ammonium ion since r + a is increased (see eq. 2). Therefore, if the solvation hypothesis is correct, the ionization of methylammonium hydroxide should be less sensitive to pressure than ammonium hydroxide (see eq. 3). This indeed is the case.

$$\left(\frac{\partial \Delta F_h}{\partial p}\right)_T = - \frac{Ne^2}{2(r + a)D^2}\left(\frac{\partial D}{\partial p}\right)_T + \frac{\Delta F_h}{(r + a)}\left(\frac{\partial r}{\partial p}\right)_T \qquad (3)$$

To test the generalization of the solvation hypothesis, Hamann and Strauss[7] determined the ionization constants of various weak acids up to pressures of 12,000 atm. They calculated the ionization curve for cesium fluoride as a reference. This salt was chosen because the radii of the ions are similar to those obtained from ammonium hydroxide, and the ionic compressibilities could be estimated from Bridgman's measurements.[8] They observed that the ionization free energy does decrease with increasing pressure in every case substantiating Owen and Brinkley's conclusion. However, the corollary regarding the relation of ionic size to pressure sensitivity was not borne out.

This corollary would predict that the pressure sensitivity of the various ammonium hydroxides is ammonium > methylammonium > dimethylammonium > trimethylammonium. In reality the positions of methylammonium and trimethylammonium hydroxides are interchanged. The explanation offered by the authors is that the assumption of the insignificance of the pressure dependence of the hydration free energy of unionized or undissociated species may be in error.

In summary it is apparent that increasing the hydrostatic pressure on a liquid system increases the extent of ionization of ionizable species. Therefore, determining the concentration of an ionizable species in solution by measuring the conductance of its ions would not be expected to be hindered by the application of pressure.

Electrolytic Conductance

The history of piezochemical studies dates back to 1827 when Colladon and Sturm studied the conductance of nitric acid and ammonia to 30 atm.[9] This work is only of historical interest as the accuracy was limited.

Introduction of the alternating current conductance bridge facilitated accurate conductance measurements, and Fink[10] used it to measure the conductances of electrolyte solutions to 500 atm. Lusanna[11] extended the pressure range to 1000 atm., Tammann to 3700 atm.[12] and Zisman reached 11,000 atm.[13] More recently Hamann and Strauss studied both aqueous and methanolic solutions to 12,000 atm.,[14] and Franck has explored electrolytic solutions in supercritical steam.[15]

It has been observed that the effect of pressure on electrolytic conductance is strongly dependent upon the concentration.[1] At finite concentrations ions of opposite charge may interfere with one another's movement in the applied electric field, and the formation of ion pairs or neutral molecules also serves to reduce the conductivity. Both of these effects are pressure dependent. It is therefore desirable to consider the cases of infinite dilution and finite concentration separately.

Infinite Dilution

Wall and Gill observed that transport numbers are not greatly affected by pressure,[16] leading to the conclusion that any large change in molar conductance must be due to variation of the ionic mobilities.

Since the ionic mobilities are dependent upon the viscosity of the medium, the existence of a parallel effect of pressure on conductance and viscosity was expected. Hamann compared the relative molar conductance of potassium chloride with the inverse relative viscosity of pure water over 12,000 atm.[1] From the similarity of the two dependencies above 1000 atm. it appeared that the decrease in Λ^{o} for the salts as the pressure is increased is a consequence of the rise in viscosity of the solvent. Below this pressure the abnormal behavior in Λ^{o} was thought to be a reflection of a similar abnormality which appears in the viscosity of water at lower temperatures and the same pressure. This was attributed to electrostriction of the solvent about the ions.

The molal conductances of strong acids and bases have been observed to be reduced to a lesser extent by pressure than those for strong salts.[1] This was shown to be due to an <u>increase</u> in the excess conductances of the hydronium and hydroxyl ions. Using Bell's model for the energetics of proton transfer[17] Hamann and Strauss[7] suggested that pressure assists this process by overcoming some of the repulsion energy between the oxygen atoms of adjacent water molecules. Thus the oxygen atoms are brought into closer proximity to one another. Proton transfer could thereby occur more readily resulting in an increase of the excess conductances of the hydrogen and hydroxyl ions.

Finite Concentrations

Kohlrausch[18a] suggested that eq. 4 be used for the extrapolation of conductivity data of strong electrolytes to infinite dilution. In

$$\Lambda = \Lambda^{o} - B\sqrt{c} \qquad (4)$$

order for the conductance at finite concentration to have the same pressure dependence as Λ^{o}, $B\sqrt{c}$ would have to be independent of pressure. Because of the non-zero compressibility of the solvent, concentration is not a pressure independent variable. The value of B for potassium chloride in water was observed to decrease by 28% between 1 and 3000 atm.[14] Consequently Λ and Λ^{o} cannot have the same pressure dependence.

In the case of weak electrolytes complete dissociation occurs only at infinite dilution. Since the dissociation increases with pressure it is to be expected that the conductance will increase as the pressure is increased due to the greater ionic strength. This is indeed observed[1] in contrast to the behavior of the strong electrolytes. A decrease in conductance of a weak electrolytic solution due to increasing viscosity of the solvent has apparently never been observed. It is to be expected that under sufficiently high pressure a weak electrolyte could become completely dissociated, and strong electrolyte behavior observed. However, freezing of the solvent has prevented such observations.

Reaction Kinetics

Apparently the first study of the effect of pressure on chemical reactions in the liquid phase was published in 1862. Berthelot and Pean de Saint Gilles observed that the rate of esterification of acetic acid with ethanol did not change significantly up to 100 atm. pressure.[19]

The first systematic study was that of Röentgen on the inversion of sucrose.[20] This work and that of Stern[21] demonstrated that the effect produced by increasing pressure was dependent upon the nature of the catalyst. The rate was observed to be retarded at higher pressures when strong acid catalysts were used, but was increased in the presence of weak acids. Similar behavior also was observed in acid catalyzed ester hydrolyses[22] wherein weak acids exhibited a greater increase in rate with pressure than strong acids.

The reason for this anomalous behavior of acid catalysts is to be found in the previous section on equilibria. The greater the pressure the greater the degree of ionization of weak acids. Therefore the greater the concentration of the proton catalyst and the faster the reaction rates. This behavior is of course absent in strong acids due to complete dissociation.

Theories of Pressure Effects

Van't Hoff was the first to demonstrate the connection between reaction rate dependencies on pressure and a change in volume during the reaction.[23] However, his formulation included an undefined constant and hence the treatment had only empirical value. In 1935 Evans and Polanyi related these volume changes to transition state theory by eq. 5,[24] where

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = - \frac{\Delta V^{\ddagger}}{RT} \qquad (5)$$

$\Delta V^{\ddagger}$ is the difference in the partial molal volumes of the initial and transition states.

The physical significance of volumes of activation ($\Delta V^{\ddagger}$), or of pressure dependencies of rate constants, was not understood until recent years, but several hypotheses had been previously presented. In 1926 Cohen came to the conclusion that the influence of pressure on the rate of a reaction is specific[25]--that is to say, the pressure dependence of reaction rates is not due to secondary influences such as alteration of solvent association. In 1934 Fawcett and Gibson offered the suggestion that "the velocity would also be influenced by pressure if the potential energy gained by the system as a result of isothermal compression is available as part of the activation energy necessary for reaction."[26]

Evans and Polanyi considered activation volumes as being separable into two components.[24] The first being that due to alterations in the internal structure of reacting substrate molecules ($\Delta_1 V^{\ddagger}$), and the second being due to changes in solute-solvent interactions ($\Delta_2 V^{\ddagger}$) during the activation process. Later workers ignored consideration of the second component.

Perrin classified reactions into three groups as they were found to be affected by pressure.[27] Slow reactions had small values for their pre-exponential factors and were greatly accelerated by pressure. Normal reactions exhibited only slight acceleration when the pressure was increased, and had normal pre-exponential factors. The third class was represented by only one example--decomposition of phenylbenzylmethylallylammonium bromide in chloroform. The rate was retarded by increasing pressure.

In 1941 Stearn and Eyring proposed a quantitative theory based upon Perrin's classification.[28] They assumed that no change occurs in solute-solvent interactions during activation, and that the partial molal volumes, isothermal compressibilities and thermal expansivities of the reactants in solution are the same as in the pure liquid. Eqs. 6 for unimolecular reactions and 7 for bimolecular reactions were developed. The ℓ_i are the bond lengths taken in the direction of the

$$\Delta V^{\ddagger} = -\frac{0.1\ell^{\ddagger}}{\sum_i \ell_i + r_1 + r_2 + 1} V \tag{6}$$

$$\Delta V^{\ddagger} = -\frac{1}{\sum_i \ell_i + \sum_j r_j + 2} \Sigma V \tag{7}$$

reaction, the r's are covalent or ionic radii and the V's are the molal volumes of the reactants.

Buchanan and Hamann demonstrated the invalidity of the Stearn-Eyring theory with respect to ionic reactions.[6] The volume decrease due to partial formation of the nitrogen to carbon bond in Menschutkin reactions was adequately considered in this theory, but the simultaneous volume increase due to the stretching of the carbon to halogen bond was omitted. The agreement with experiment obtained by Stearn and Eyring can only lead to one of two conclusions. Either the agreement was fortuitous or the carbon to halogen bond is unaffected in the attainment of the transition state. If the latter were correct then variation of the halogen atom would not affect the reaction rate. Such an effect is not observed,[27] consequently the former conclusion must hold.

Buchanan and Hamann pointed out the fact that the classification proposed by Perrin was actually a classification according to the electrical nature of the reactions.[6] The slow reactions were ionogenic in nature, while the normal reactions were all negative ion replacements involving no net change in the number of ions. The unimolecular decomposition involved a destruction of ionic species. The reactions of the slow class all showed fairly large negative entropies of activation[27] representative of greater electrostriction of solvent molecules about the partially charged transition state.[6] Conversely the large positive activation entropy observed for the decomposition of the quaternary ammonium salt arises from the release of solvent molecules by the partial neutralization of the ionic charges. These authors concluded that "reactions in which the transition state is more highly ionic, and hence more extensively 'solvated', than the initial state are greatly accelerated by pressure; those in which the transition state is less ionic and less 'solvated' than the initial state are retarded by pressure."[6] From studies on ionic equilibria (*vide supra*) they concluded that the main effect of pressure is to increase the solvation free energy of electrically charged groups. This hypothesis was substantiated by the observation that the rates of unimolecular solvolyses of alkyl halides are increased with increasing pressure, i.e. $\Delta V^{\ddagger} < 0$.[6]

Non-ionic Reactions

In order to obtain some idea of the magnitude of the solvent electrostriction contribution to activation volumes, it is necessary to determine the contribution to be expected from $\Delta_1 V^{\neq}$ (the internal structure volume change). This can be found from studies of reactions which do not involve major change in the electrical properties of the reactants on activation.

Homolytic dissociation of a molecule involves a transition state having an elongated bond. It is to be expected that such a reaction is retarded by the application of pressure. This is indeed the case.

Ewald observed a twofold decrease in the rate of pentaphenylethane decomposition between 1 and 1500 atm.[29] This corresponds to an activation volume of about +13 cc./mole. The decomposition of azo-isobutyric acid α,α'-dinitrile, however, was seen to involve a volume of activation of only +3.8 cc./mole.[29]

The decomposition of benzoyl peroxide has been studied by several workers--the popularity of this compound resulting from its use as an initiator of free radical polymerizations. Walling and Pellon studied the pressure effect on this system in acetophenone at 80°C. and found an activation volume of +4.8 cc./mole.[30] Nicholson and Norrish, working in carbon tetrachloride solution at 60° and 70°C., showed that three processes occur:[31] decomposition of the peroxide into two benzoyl radicals, recombination of the radicals accompanied by loss of carbon dioxide to give phenyl benzoate, and attack of benzoyl radical on benzoyl peroxide to give phenyl benzoate, carbon dioxide and benzoyl radical. The value for the activation volume of the initial decomposition was found to be about +10 cc./mole.[31] Ewald measured this peroxide decomposition in toluene solution in the presence of diphenylpicrylhydrazyl which serves as a trap for the benzoyl radicals.[32] He observed a smaller effect of pressure than did Nicholson and Norrish corresponding to an activation volume parameter of +5 cc./mole.

Walling and Metzger found that the determined activation volume depended upon the nature of the solvent.[33] In toluene a value of +5 cc./mole was obtained for the peroxide decomposition, and a similar value of +7 cc./mole was found in cyclohexane. On the other hand in benzene or carbon tetrachloride a value of +13 cc./mole was obtained. The authors suggested that the difference arises because toluene and cyclohexane are readily attacked by the radicals so that the reaction is completed within the solvent cage. However, in benzene and carbon tetrachloride the radicals must escape from the cage to react further so that a competition between recombination and diffusion exists. Thus the observed activation volume becomes a composite quantity. Both Ewald[29] and Walling and Metzger[33] pointed out that the observed difference between the so-called direct method and that employing a scavenger (vide supra) is probably also due to a cage effect.

The combination of two free radicals in solution is an extremely fast process, and the reaction rate is often determined by the rate at which the combining radicals can diffuse together.[34] An increase in pressure might therefore be expected to decrease the rate since the viscosity of the solvent increases with pressure. Nicholson and Norrish indeed found that the rate of the termination step in the polymerization of styrene decreases rapidly up to 1000 atm., and then decreases more slowly.[35]

The Diels-Alder reaction is one which has resisted man's desire for mechanistic elucidation. In the hope of unraveling the nature of the elusive transition state the kinetic effect of pressure on this system has been studied. Raistrick, et al., found a very marked effect in the dimerization of cyclopentadiene, amounting to a decrease of 25 cc./mole in the activation process.[36] Since this value is close to the total volume change for the reaction, Gonikberg and Vereshchagin concluded that the transition state structure is very close to that of the dimer.[37a] This conclusion implies that the transition state is a cyclic structure.

Walling and Peisach found that the dimerization of isoprene is also accelerated by pressure, but that the activation volume is only half that of the overall volume change.[38] They concluded that the transition state cannot be cyclic, but may be a biradical precursor. Benson and Berson criticized this conclusion on the basis that the method used to calculate $\Delta V^{\ddagger}$ was incorrect.[39] Instead these authors used the Tait equation[18b] to represent the compressibilities of both the initial and transition states (vide infra). They obtained values for the activation volume considerably more negative than those reported by Walling and Peisach, and concluded that the values are as consistent with a cyclic transition state as with a biradical structure.

Brower studied the Claisen rearrangement of p-cresyl allyl ether in an attempt to determine whether the transition state involved a predominance of formation of the new bond or rupture of the old one.[40] It was known that this reaction occurs with retention of configuration, and the negative entropy of activation suggests a cyclic transition state.[41] Brower found that the activation volume was virtually independent of the solvent, its value in 65% ethanol being -15 ml./mole while that in benzene is -18 ml./mole. He concluded that the transition state is virtually nonpolar, and that it is a cyclic structure.

Ionic Reactions

In order to make inferences concerning the nature of the transition state of ionic reactions from activation volumes, some means of separating $\Delta_1V^{\ddagger}$ and $\Delta_2V^{\ddagger}$ (vide supra) is required. The author knows of no instance wherein such a separation has been experimentally achieved, however, several authors have proposed models from which estimates can be made. We have already considered that of Stearn and Eyring[28] for estimating the internal volume contribution, $\Delta_1V^{\ddagger}$.

A detailed calculation of the solvent electrostriction contribution requires both a quantitative solution theory and knowledge of the electrostatic character of the transition and initial states. Except for the electrostatic character of the initial state this knowledge is not presently obtainable. Consequently only an empirical estimate of the electrostatic contribution to activation volumes is possible.

Hamann,[1a] using Born's dielectric continuum model for the solvent (eq. 2), concluded that the electrostatic volume decrease for the development of a full electronic charge on a small spherical molecule ranges from 10 to 30 ml./mole. Couture and Laidler[42] obtained the value for $\Delta_2V^{\ddagger}$ of - 26 ml./mole in water.

Hamann[1a] concluded that the solvation term will predominate in all reactions involving ionic species, but later modified this to be only a working hypothesis.[2a] Gonikberg[1b] questioned the effort spent in model calculations of molecular and solvent effects since none of the methods used take account of the change in molecular packing during the activation process.

The kinetics of Menschutkin reactions have been widely studied as a function of pressure. The various data available lead to several generalizations.[1c] These reactions are strongly accelerated by an increase in pressure, and have activation volumes in the range of -20 to -40 ml./mole at atmospheric pressure. The value of ΔV^{*} for a given example varies with the solvent, and decreases in magnitude with increasing pressure. These observations are consistent with a highly solvated transition state. Hamann and Teplitzky[43] have shown that these values of ΔV^{*} decrease in magnitude as the size of the halogen atom increases. The authors attributed this behavior to a decrease in the electric field strength around the charged atom in the transition state. It is known that such a field varies as the inverse of the atomic diameter.

As a further test of the importance of solvation to ionic reactions Burris and Laidler[44] studied three bimolecular displacement reactions. The basic hydrolysis of the bromopentammine cobaltic ion was shown to have an activation volume of +8.5 ml./mole. Since the transition state formation involves the partial neutralization of ionic charges, a decrease in solvent electrostriction is to be expected; this is consistent with the observed volume increase. The second reaction, that of bromoacetate with thiosulphate, showed a value of -4.8 ml./mole for the activation volume while the neutral methyl bromoacetate gave a value of +3.2 ml./mole on reaction with the same reagent. It is not surprising that the solvent is electrostricted to a higher degree in the former since a triply charged complex is formed. The reduction of the electrical field intensity in the latter would be expected to result in a decreased amount of solvent electrostriction, as is apparent.

It is well known that the entropy of activation of ionic reactions also reflects the solvent behavior,[45] and Burris and Laidler[44] undertook a study to determine whether there is a parallel behavior between $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$. They corrected the activation entropy for the contribution due to changes in the number of species in solution. For example in a bimolecular reaction the formation of one mole per liter of transition state complex from two moles per liter of reactant produces a negative entropy change due to the unmixing of one mole per liter of material (in water this amounts to -7.9 cal./deg. mole). After carrying out such a correction a good correlation of $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ was found, the signs being the same in each instance.

Brower studied the effect of solvent polarity on the pressure dependencies of various reactions.[46] He observed that reactions which involve no change of polarization have essentially the same volume of activation in polar and non-polar solvents. However, the variation of activation volume for reactions in which ions are created or destroyed amounts to a substantial fraction of the variation of partial molal volumes of electrolytes among the same solvents. This is in accord with the above observation for the pressure dependencies of Menschutkin reactions.

Baliga and Whalley[47] have observed that the acid catalyzed hydration of propylene has an activation volume of -9.6 ml./mole while that for isobutylene has a value of -11.5 ml./mole. Since there is no net change in the total number of ionic charges during the slow step of the reaction, only a very small pressure dependence is to be expected. These authors attributed the large volume changes to incorporation of a water molecule into the transition states.

Buchanan and Hamann[6] studied the solvolyses of t-butyl chloride and benzotrichloride in 80% ethanol. The results obtained were mainly used to demonstrate the importance of solvation phenomena to activation volumes. The authors thought the actual numbers to be in error in view of the fact that the two rate vs. pressure curves intersected.[48] The Stearn-Eyring theory[28] predicted a value of +2.8 ml./mole for the activation volume for t-butyl chloride solvolysis, and therefore a decrease in rate with increasing pressure. In fact the reaction was enhanced by the application of pressure substantiating the importance of solute-solvent interactions in ionic reactions.

David and Hamann[49] extended the previous study to include both neutral and alkaline solvolyses of alkyl halides using both hydroxide and methoxide as the attacking base. It was found that the solvation phenomena predominated in determining the effect of pressure on the reaction rates. In each case the reaction proceeded faster at higher pressures. This is contrary to the observation of Burris and Laidler[44] (vide supra) for the reaction of thiosulphate with methyl bromoacetate.

Here the reaction was retarded by pressure supposedly because of dispersion of the electrical field. In the alkaline solvolyses studied by David and Hamann a charge dispersal undoubtedly occurs. However, it is possible that the total charge on the transition state is greater than one electronic unit even though the net charge is not increased. This could be the case if a partial positive charge develops on the reacting carbon atom.

In support of the observations made by David and Hamann, the following can be cited. Gibson, et al.,[50] showed that the rate of the reaction of ethyl iodide with sodium ethoxide increased by 60% as the pressure was increased by 3000 atm., while the alkaline hydrolysis of chloroacetate ion increased in rate by 89% over the same pressure range.[51] The value for the activation volume for these reactions is around -10 ml./mole, which is close to the estimate made by Gonikberg[37c] for $\Delta_1 V^{\ddagger}$. The latter author presumed that the value is likely to be even more negative, and attributed the smaller value to a positive contribution from $\Delta_2 V^{\ddagger}$.

Several studies on the hydrolyses of carboxylic esters have been conducted under pressure. Laidler and Chen[52] observed activation volumes of about -10 ml./mole for the alkaline hydrolyses of methyl and ethyl acetates. The corresponding amides were observed to have volume changes on activation of close to -15 ml./mole. These values were attributed to solvation phenomena related to the change in substrate polarization.

Le Noble and Yates[53] have recently measured a stereochemical effect using piezokinetics. They solvolyzed both the exo- and endo-2-norbornyl brosylates and found the former to have an activation volume of -14.3 ml./mole while the latter was 3.5 ml./mole more negative. Thus it would appear that activation volume data may be useful in distinguishing the reactivity of one isomer from another.

CHAPTER 2

SOLVOLYSES

Several reviews concerning the mechanism of solvolyses reactions are in print,[54-56] and every textbook concerned with reaction mechanisms has one or more chapters dealing with the subject.[41,57-59] It is therefore deemed inappropriate to present yet another comprehensive review of this subject especially in view of the fact that the mechanism of solvolytic reactions is only indirectly related to the main thesis of this work. The role played by the solvent in these reactions is the principal interest in this work and therefore in this short review the main emphasis will be placed on this aspect. A detailed account of the knowledge of the mechanism by which the substrate of interest to this study decomposes solvolytically will also be included.

Mechanism

Since the appropriate mechanism applicable to benzyl chloride solvolysis must be related to those mechanisms characteristic of the alkyl ester type reactions, the present discussion will deal with those mechanisms that are commonly applicable to alkyl ester solvolyses. In solvolyses the solvent is generally present in very large excess compared with the substrate under consideration, and therefore its concentration does not appear in the solvolytic kinetic expression (pseudo first order). However, the lyate ion of the solvent can be present in quantities comparable to that of the alkyl halide, and thus does appear giving rise to the empirical expression

$$-\frac{d[RX]}{dt} = k_1[RX] + k_2[RX][SO^-] \qquad (8)$$

where SOH represents the solvent.

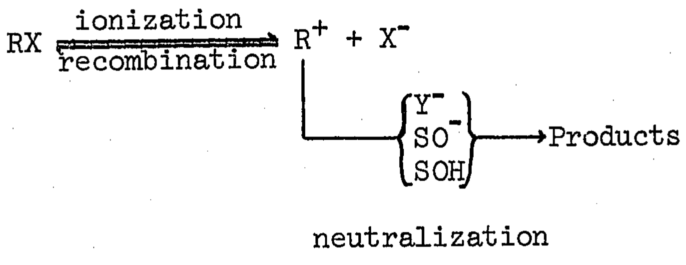
Olson and Halford,[60] Taylor,[61-63] and Ogg,[64] proposed a direct displacement reaction by the solvent. Bateman, Hughes and Ingold pointed out that direct displacement by the solvent requires the amounts of products to be proportional to the respective rate constants for reaction with the components and to the activities of the components when mixed solvents are used.[65] This was not found to be the case in the solvolysis of t-butyl chloride in aqueous ethanol and methanol.[65] Similar results were found in the ethanolysis of benzhydryl chloride.[65] In effect, addition of water was found to enhance the rate of alcoholysis.

Results such as this led to the conclusion that some substrates undergo preliminary ionization to give a carbonium ion and the halide anion; the rate determining step being the ionization, not the subsequent attack of the solvent. This was first proposed by Ward.[66] Ingold later utilized an ionization mechanism to explain the hydrolysis of benzyl chloride.[67] This was followed by an extensive development by Hughes and Ingold of what they called the S_N1 and S_N2 mechanisms.[68]

S_N1

The S_N1 mechanism consists of three processes--ionization, recombination and neutralization. The ionization step, being the only endothermic one in this reaction, is rate determining. Evidence in support of the heterolysis has been obtained by observing the formation of stable carbonium ion complexes of triarylmethyl halides.[41b] Further, it was found that in the solvolysis of arylmethyl halides strongly electron attracting substituents decrease the rate while electron donating substituents enhance it in accord with the ionization hypothesis.[41b] In 1939, Ogg showed that ionization is energetically unfavorable for the primary methyl bromide system since it would require energy in excess of 50 kcal./mole.[64] Later calculations by Evans[69] and Franklin[70] demonstrated that the required energies for secondary and tertiary systems are, however, readily available for reactions in solution.

The recombination reaction results from the ability of the carbonium ion to combine with any nucleophile present in its vicinity. Recombination is simply the reaction of the carbonium ion with the "parent" anion to regenerate the substrate thereby decreasing the observed reaction rate. Considerations of this process have led to such concepts as internal and solvent separated ion pairs.[71]



$$RX \underset{\text{recombination}}{\overset{\text{ionization}}{\rightleftharpoons}} R^+ + X^- \qquad R^+ \xrightarrow[\text{neutralization}]{} \left\{\begin{matrix} Y^- \\ SO^- \\ SOH \end{matrix}\right\} \longrightarrow \text{Products} \qquad (9)$$

The neutralization or product forming step is generally a complex one owing to the variety of neutralizing agents. Reaction with the parent anion results in regeneration of the substrate (*vide supra*). Added anions, or those present due to ionization of the solvent, can also participate in neutralization. If these products can further solvolyze the kinetics become quite complex. It is also possible for the carbonium ion to react with a hydroxylic solvent molecule to generate the corresponding oxonium ion which will lose a proton leaving the alcohol or ether behind. Ogston has defined the competition factor of a nucleophile as the ratio k_Y/k_o where k_Y and k_o are the rate constants for reaction of the carbonium ion with the nucleophile Y and with water respectively.[72] However, these competition factors are dependent upon the nature of the carbonium ion. This results since the less stable a carbonium ion the less selective it will be in its reactivity toward nucleophiles.

Aside from neutralization by addition to nucleophiles, the carbonium ion can produce products by elimination of a beta proton, if they are present, to generate an olefin. It is evident that if the ionization hypothesis is correct the ratio of elimination products to displacement products must be independent of the nature of the leaving group in the substrate. This is in fact found to be the case.[54a]

S_N2

The S_N2 mechanism is simply a one step displacement reaction by an available nucleophilic reagent. Tertiary systems generally solvolyze by the S_N1 mechanism while primary systems generally undergo S_N2 reactions.

Secondary systems are subject to both types of decomposition depending upon the given set of conditions. It is necessary to point out that these two mechanisms are limiting cases, and it is an academic question whether the true limiting cases are ever observed. It is evident that borderline cases do exist, i.e. reactions which cannot be classified as limiting S_N1 or limiting S_N2. One example of such a species is the system of interest to the present study.

Solvent Effects

Dielectric Constant

The ionization hypothesis leads to considerations of the ionizing power of the solvent. Among the various measures of this quantity, the dielectric constant (D) has been most widely used along with various functions of this quantity--the Kirkwood equation perhaps being the most popular.[73] However, various studies have demonstrated that functions of the bulk dielectric constant are not good measures of the solvent's ionizing ability.[74,75]

Bateman, Hughes and Ingold showed that S_N1 hydrolyses which are slow in "moist" acetone (D = 25) are rapid in "moist" sulfur dioxide (D = 14) although both acetone and sulfur dioxide are non-hydroxylic.[74] Farianacci and Hammett found that for the solvolysis of benzhydryl chloride in ethanol-water mixtures the graph of log k vs. 1/D gives fairly good linearity up to 3 molar water, but fails completely for the three systems: ethanol-water, ethanol-nitrobenzene and ethanol-heptane mixtures.[75] In fact three distinct curves were obtained. Hudson and Saville pointed out that any relation between rate constants and solvation free energies requires the rate to be an increasing function of dielectric constant for reactions between neutral molecules, assuming the transition state structure to remain constant.[76] However, Fairclough and Hinshelwood gave several examples of unequal rates in isodielectric media.[77] From these studies, and others in mixed solvents, it has been demonstrated that the concept of a dielectric continuum is inadequate to describe the solvent effect on rate processes.

Empirical Parameters

In order to overcome the inadequacies of using bulk dielectric constants as a measure of the ionizing ability of the solvent many empirical parameters have been proposed. Grunwald and Winstein suggested the use of Y-values determined from the relative rates of *t*-butyl chloride solvolysis in various solvents,[78] and this was further advanced by Winstein, Grunwald and Jones.[79] Although this scheme served to correlate rates much better than did dielectric constant, it was found that more than one curve was frequently required for reactions in various binary solvent media.[54b]

Kosower has proposed that the energy (Z) of the solvent dependent, charge transfer absorption band of 1-methyl-4-carbomethoxpyridinium iodide be used as a measure of this property.[80] The reasoning behind this proposal lies in the fact that the dipole moment of the solute changes orientation during the excitation process. By the Frank-Condon principle the solvent molecules cannot reorient themselves to accommodate the molecular excited state, and therefore the electrostatic interaction between the solute and solvent immediately after the excitation cannot be optimum. The iodine exchange of methyl iodide, ethyl pyridinium iodide formation, and keto-enol equilibrium of ethyl acetoacetate are well correlated by this parameter.[81] A remarkable example of the usefulness of Z-values over dielectric constants is available in the solvolysis of t-butyldimethyl sulfonium iodide.[82]

Other solvent parameters which have been proposed are the Swain and Scott n and e parameters for measuring the nucleophilicity and electrophilicity, respectively,[83] the Swain and Dittmer b parameter which was used to correlate 124 reactions,[84] the Edwards E_n and H parameters for measuring the nucleophilicity and basicity, respectively,[85] and the Swain, Mosely and Brown d_1 and d_2 parameters[86] analagous to the Swain and Scott n and e parameters.

Specific Effects

The main problem with the use of bulk dielectric constant lies in the assumption that the solvent is a continuum. Specific effects such as dipole-dipole interaction and hydrogen bonding are neglected. Davis and LaMer[87] pointed out that a linear dependence of rate on dielectric constant can be observed even in the presence of a specific interaction; it is only necessary that the specific interaction change in a linear manner with dielectric constant.

The empirical parameters described above tend to overcome this difficulty by cancelling these specific effects provided that they are identical over the range of solvents considered. So long as only minor changes in solvent structure are involved this is probably a reasonable assumption. However, for large structural changes the specific nature of any interactions may vary in a manner such that cancellation does not occur. For example the change of solvent from ethanol to acetone undoubtedly involves changing from hydrogen bonding to dipole-dipole interaction.

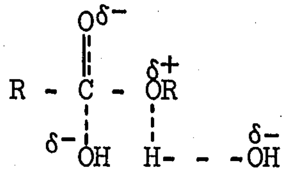
Binary Solvents. A cursory examination of the literature of the past four decades reveals that an overwhelming amount of work has been done in binary solvent systems. The reasons for this are rather obvious. In order for solvolysis to occur, the solvent must be capable of providing a lyate ion. The most common solvent capable of providing one is water, but unfortunately most of the substrates of interest have only limited solubility in this substance. Furthermore, solvolyses in water are often too fast to be convenient for study. To overcome both of these difficulties some miscible, organic liquid is added. However, it has been only during the past fifteen years that the specific effects of these solvent mixtures have been probed.

Work by Tommila, Tiilikainen and Voipio[88] and by Fainberg and Winstein[89] on mixed solvent systems give a good illustration of the fact that large changes in solvent-solute interaction can occur when only small changes are made in the solvent composition. Consideration of the free energy of activation (logk) alone can conceal such effects.[90] However, examination of the enthalpy and entropy of activation can reveal remarkable effects of solvent change.

Fairclough and Hinshelwood, using the reaction of methyl iodide with pyridine, were among the first workers to observe these effects.[91] The activation energy was found to decrease rapidly as acetone was added to benzene until the solvent contained 10% by weight of acetone after which it remained fairly constant. When alcohol was used instead of acetone a linear graph was obtained with positive slope. Nitrobenzene produced some surprising results. On addition of nitrobenzene to acetone the activation energy increased steadily until 90% nitrobenzene where it decreased abruptly. As nitrobenzene was added to isopropyl ether or to benzene a minimum was obtained in $\Delta H^{\ddagger}$ at 10% nitrobenzene, and a maximum occurred at 75%. The curves of logPZ were similar to those for the activation energy.

Tommila, _et_ _al_., studied the alkaline hydrolysis of ethyl acetate in various mixtures of water and organic solvents.[92] They observed that addition of methanol or ethylene glycol caused the rate to decrease, while small amounts of the other organic solvents caused a slight increase in the rate. Large amounts of organics always decreased the rate. In each case, except methanol and ethylene glycol, a minimum was found in $\Delta H^{\ddagger}$ at 0.06 to 0.1 mole fraction of organic component. This was attributed to a marked increase in the transition state solvation on addition of the organic solvent component.

Assuming the transition state to have the structure[93]



$$\begin{array}{ccccccc} & & O^{\delta-} & & & & \\ & & \| & & & & \\ R & - & C & - & \overset{\delta+}{O}R & & \\ & & \vdots & & \vdots & & \\ & & {}^{\delta-}OH & & H & - - - & \overset{\delta-}{O}H \end{array}$$

I

its external field is more powerful than the separated reactants, and will therefore orient more solvent molecules than the reactants together. Since both hydrophobic and hydrophilic groups are present in the transition state, suitable mixtures of water and organic solvents, having specific attraction for the respective groups, will solvate this entity to a greater extent than either pure component alone. This results in the activation energy being lower than in the pure solvents themselves, thereby giving rise to the observed minima.[92] Support for this interpretation has been found in the fact that as the temperature is raised the depth of the minimum for t-butanol-water mixtures decreases,[92] the transition state being less solvated at higher temperatures due to the thermal energy of the solvent molecules.

Saponification of alkyl salicylates showed similar behavior.[94] The methyl ester in methanol-water mixtures displayed a monotonic increase in ΔH^{*} with increasing methanol concentration. In aqueous ethanol the ethyl ester was found to have a minimum activation energy at 20% ethanol, while the i-propyl ester showed a larger minimum at the same composition of isopropanol.

Contrary to the behavior of ethyl acetate, ethyl formate shows no minimum in ethanol-water mixtures,[95] nor is one observed for the saponification of ethyl oxalate. These esters, for which minima do not appear, contain no hydrocarbon grouping in the acid part of the molecule. This has led Tommila to conclude that a necessary requirement for the occurrence of a minimum is the presence of a hydrocarbon substituent.[95] In such cases there is a hydrophobic attraction between the transition state and the organic component of the solvent. When the solvent composition is suitable the transition state solvation will be greater than in either pure solvent component, and the activation parameters will pass through a minimum at this composition. It was found that the acid hydrolysis of ethyl formate does pass through minimum values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$[95]--no explanation was offered.

In order to further investigate the requirement of a hydrophobic interaction, Tommila and Maltamo studied the saponification of methyl acetate.[96] Once again aqueous methanol displayed no extremum behavior, but aqueous acetone did give the minimum values. These workers concluded that the greater the hydrocarbon part of the organic solvent, the greater its attraction for the hydrophobic groups of the transition state, and the deeper the minima in the activation parameters.

Further evidence for the requirement of a hydrocarbon residue in the substrate lies in the difference in behavior of ethyl oxalate and ethyl malonate saponification. In aqueous ethanol and aqueous acetone no minima are observed for the former,[95] while the latter does give rise to minimum values of the activation parameters.[97] Since these substrates differ only in the presence of a methylene group, it was concluded that at least one such group is necessary in the acid end of the molecule.

In neutral solvolyses of alkyl halides the rate determining transition state involves partial charge separation and is more polar than the initial state. In acetone-water mixtures the transition state will tend to orient the more polar acetone molecules (μ= 2.89 Debye compared with that of 1.85 Debye for water[98a]) such that additon of acetone to water increases the total solvation of the transition state thus causing a decrease in $\Delta H^{\neq}$ and $\Delta S^{\neq}$.[99] This results in a minimum at 20% acetone.[99] However, in the basic hydrolysis of alkyl halides a dispersal of charge is involved in the transition state formation[41c] so that there is a decrease in the electrical field. It is therefore to be expected that the activation parameters will initially increase with added acetone. Such an effect has been observed for ethyl bromide which has a maximum at 18% acetone.[99] This was explained on the basis that as the acetone concentration increases the alkyl groups of the transition state will attract acetone molecules more and more whereas hydroxide solvation by water gradually weakens. Solvation of the alkyl halide also increases with increasing acetone concentration, but in dilute solutions each alkyl halide molecule surrounds itself with a maximum number of acetone molecules in very dilute acetone so that more acetone has only a slight effect.[99] Such an explanation assumes that the initial state solvation environment of the alkyl halide is saturated with acetone in highly aqueous solvents, whereas the transition state solvation environment does not become saturated with acetone until much higher acetone concentrations. Such a state of affairs could only exist if the water molecules are brought into the transition state by the hydroxide ion. In other words, the hydrocarbon part of the transition state must be solvated by the acetone molecules which initially surrounded the substrate, implying saturation of this environment by acetone in very dilute acetone solutions, or the transition state must exist for a long enough time to allow reorientation of the solvent molecules. An alternative explanation, which cannot be disproved, is that solvent reorientation accompanies, and perhaps causes, formation of the transition state--implying that the activation process is relatively long. This latter seems more plausible than solvent reorientation during the life-time of the transition state.

Activation enthalpy minima also have been observed for solvolyses of methyl benzenesulfonate,[100] *t*-butyl chloride,[101] *α*-phenethyl chloride,[102] isopropyl bromide[103] and benzyl chloride.[103] Hyne and Wonkka observed that the solvolysis of *t*-butyldimethylsulfonium iodide passes through an activation energy *maximum* in aqueous ethanol.[103]

In summary, the following trends might be noted. Alkaline carboxylic ester hydrolyses all give minimum values for the activation energy and logPZ (activation entropy) as the solvent composition is varied provided that the hydrocarbon residues of the ester and the organic solvent component are large enough to permit the occurence of hydrophobic bonding. Neutral solvolyses of uncharged species display minima in the activation parameters, while charged species appear to give maxima. The maximum values found for basic hydrolyses of alkyl halides do not agree with the carboxylic ester data, but agree with the charge dispersal reaction of sulfonium salts. The one non-aqueous example of ammonium salt formation gives a maximum in $\Delta H^{\ddagger}$.

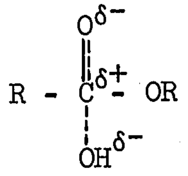
Solvent Sorting. In order to explain the activation parameter extremum behavior, Hyne invoked a model of selective solvation.[103] Such a concept was not entirely new, having been used by Tommila for solvolysis in aqueous acetone.[99] In fact much earlier work did involve solvent sorting interpretation. In 1927 Debye attempted a quantitative treatment of ionic solvation using the concept of solvent sorting.[104] Scatchard considered differences in solvent composition between the vicinity of the dissolved ion and the bulk solvent in aqueous ethanol.[105] Until the suggestion of solvent sorting by Tommila[99] almost no mention of it appears in rate studies.

Hyne's model[103] assumes that a polar species in a binary solvent is able to extract from the binary solvent a preferred solvation shell consisting of a greater proportion of the more polar component than exists in the bulk solvent. He assumes that in certain circumstances the selectivity can be such as to yield a solvation environment consisting entirely of the more polar solvent component. On this basis he demonstrates that reactions for which the transition state is more polar than the initial state should have an activation energy minimum, while for reactions in which the initial state is more polar a maximum should occur.

This model implies that the greater the polarity of the transition state the deeper should be the minimum in ionogenic reactions. This is indeed observed.[103,106]

Hyne's model further implies that changing the temperature should affect the depth of the minima since the higher the temperature the greater the kinetic energy of the system, and the more difficult the solvent sorting. Such a dependence was observed by Tommila[92] for ethyl acetate saponification (*vide supra*), and by Hyne, Wills and Wonkka[106] for benzyl chloride solvolysis. Additional studies on *p*-methylbenzyl chloride in various aqueous-organic binary solvents[107] have verified Tommila's findings[92] that the depth of the extremum is strongly dependent upon the nature of the organic solvent component.

This model accounts for the minima observed in neutral alkyl halide solvolyses and the maxima in the neutral *t*-butyldimethylsulfonium iodide solvolysis and alkaline alkyl halide solvolyses. However, in order to account for the carboxylic ester saponification minima, the transition state must have a total charge greater than unity. Such a structure could exist if the carboxylic carbon atom has some positive charge density in the transition state.



$$R - \underset{\underset{OH^{\delta-}}{\vdots}}{\overset{\overset{O^{\delta-}}{\|}}{C}}{}^{\delta+} - OR$$

II

Recently, Arnett and co-workers have measured the heats of solution of various reactive and non-reactive species in binary solvents.[108,109] They have found that the heats of solution also pass through extremum values at about the same solvent composition as the activation energies. They do not behave in the monotonic manner proposed by Hyne.[103] For *t*-butyl chloride the observed dependence of solution enthalpy in ethanol-water mixtures on compostion exactly compensates for the activation energy dependence.[108] This implies that the heat of solution of the transition state is constant through the aqueous region of the binary solvent range. On the basis of Hyne's model this in turn implies that the transition state is solvated only by water over the solvent composition range in question although Arnett and co-workers[108,109] have not stated that this implication necessarily follows from their observations.

Whalley has studied the acid catalyzed hydrolyses of methyl acetate and ethylene oxide, and found no minimum occurring in the constant volume activation energy.[110] He therefore concluded that the extrema observed for the constant pressure parameters are trivial, and are not related to the reaction mechanism. It would seem that such a statement opens the question as to whether the immediate solvent environment should be considered as part of the reacting species. Evidently, without a precise definition many an argument based solely on semantics could arise.

Supporting Evidence. Additional evidence for solvent sorting does appear in the literature for non-solvolytic reactions. Olson and Voge[111] observed that a small addition of water to acetone changes the activation energy for bromide catalyzed racemization of <u>l</u>-bromosuccinic acid by 1000 cal./mole while further addition has a much smaller effect. This was assumed to be due to a statistical distribution of water molecules largely in favor of the bromide ion--the hydrated bromide ion being a weaker nucleophile.

Swain's "push-pull" mechanism[112] is based upon the assumption of a very high degree of solvent sorting. He observed that in the presence of both phenol and methanol the reaction of trityl halides in benzene was faster than when only one was present. This he attributed to preferential solvation of the leaving anion by a phenol molecule, and nucleophilic attack at the central carbon atom by methanol.

Benzyl Solvolyses

From the above review, it would appear that further studies relating to the activation parameter behavior in binary solvents would be most profitably pursued in either carboxylic ester saponification or benzyl halide solvolyses in neutral media. For reasons which will be presented later (Chapter 3) the benzyl systems appear to be more profitable. Before such a study is undertaken, a review of the knowledge concerning the mechanism of benzyl "ester" solvolyses is appropriate.

The earliest quantitative studies of which the present author is aware are those of Olivier and co-workers. In 1922 Olivier found that 2.2 molar sulfuric acid has no effect on the hydrolysis rate of benzyl chloride.[113] Olivier and Berger found that benzyl acetate is not affected by water over a period of four days at 40°C., but in the presence of 0.0244 molar sulfuric acid about 50% hydrolysis occurs.[114] This, together with the previous findings of Olivier,[113] led these authors to conclude that in general the rate of hydrolysis of ester derivatives of strong acids, especially the mineral acids, are not affected by the presence of hydrogen ions.

Olivier demonstrated that the influence of a substituent present in the benzene ring on the reactivity of the side chain halogen parallels the effect on the reactivity of the hydrogen atom of the benzene ring,[115] and ascribed such influences to the theory of "alternate induced polarities". This apparently is a pictorial description of bond dipoles permitting the prediction of the effect of a substituent on the reacting center as it affects changes in electron density at that center due to inductive effects.[116] This parallelism led Ingold to suggest that benzyl chloride solvolyzes by an ionization mechanism,[67] since those substituents which facilitate the reaction should facilitate the ejection of a negative ion from the side chain.

In 1934 Olivier and Weber undertook an extensive study of the solvolyses of benzyl chloride, benzylidene chloride and benzotrichloride along with their ring substituted derivatives.[117] They found that the unsubstituted forms of the latter two compounds are not affected by either hydrogen or hydroxide ions; benzyl chloride, however, is catalyzed by hydroxide ions, although to a lesser extent than carboxylate esters. This was explained by assuming that introduction of a second or third chlorine into the side chain produces a barrier to the approach of the hydroxide ion. The substituent studies led these authors to conclude that as well as the inductive effect a resonance effect exists between the substituent and the reaction center, and the latter predominates whenever the two effects are opposed.[117]

Bennett and Jones found that the rates of solvolyses of m-halogenated benzyl chlorides in 50% acetone are generally independent of the substituent, whereas the ortho and para isomers show a strong dependency on the substituent,[118] the rates decreasing in the order F>>Cl>Br>I.

Roberts and Hammett studied the reaction of benzyl chloride with mercury salts in aqueous dioxane.[119] They noted that when a high concentration of benzyl chloride is used a yellow transient color is produced which they concluded was indicative of the presence of the unstable benzyl cation as an intermediate in the reaction.

Beste and Hammett studied the reaction of benzyl chloride with water, hydroxide and acetate ions in 61% dioxane.[120] They found that the first order solvolysis rate constant decreases some 20% over a ten-fold increase in initial alkyl halide concentration. It was also found that addition of benzyl alcohol or chloride ions decreased the specific rate although to a lesser extent than the alkyl halide itself. They concluded that the reaction simulates a true unimolecular reaction because the increase in concentration of the reaction products, as the reaction proceeds, and the subsequent retarding effect, compensates for the decrease in benzyl chloride concentration which tends to increase specific rate. Similar effects were observed for the displacement reaction with hydroxide[120] where the second order rate constant decreases by 14% when the benzyl chloride concentration is doubled. The acetate displacement reaction was found to decrease by 13% for a 100% increase in substrate concentration. It was concluded that this behavior cannot be accounted for by changes in the activity coefficient of the substrate alone.[120] The simplest interpretation which occurred to these authors was that of ionization to give the benzyl cation which could then react with water to form the alcohol, chloride ions to reform the substrate or the other anions to form products.[120] It should be noted that benzyl acetate was found to solvolyze under these conditions with a negligible relative rate, $k_{\phi CH_2OAc}/k_{\phi CH_2Cl} = 0.0288$.

Lucas and Hammett observed that hydrolysis of benzyl nitrate is accompanied by first order decomposition to benzaldehyde and nitrous acid in aqueous dioxane.[121] These reactions are also accompanied by a second order reaction with hydroxide ion leading to the same products. The solvolysis reaction predominates in neutral or acidic media. Benzyl nitrate solvolysis has a ΔH^* value larger than that for benzyl chloride by about 4 kcal./mole, whereas that for the hydroxide displacement is 5 kcal./mole larger than for the chloride. However, t-butyl nitrate and t-butyl chloride have the same activation energies.[121] Lucas and Hammett concluded that the t-butyl compounds both undergo S_N1 solvolyses, whereas the benzyl nitrate may solvolyze via displacement by a water molecule.

Miller and Bernstein studied the reactions of some substituted benzyl fluorides with sodium ethoxide.[122] The order of reactivity of the substituents implied a predominant S_N2 mechanism favored by electron withdrawal. Use of hydroxide did not follow the inductive order, but followed that of Olivier and Weber for the reaction of substituted benzyl chlorides with hydroxide in aqueous acetone.[117] Miller and Bernstein concluded that both S_N1 and S_N2 mechanisms are operative for the fluorides. It was also found that the benzyl fluoride hydrolyses are acid catalyzed,[122] whereas the benzyl chlorides are not.[113] This was attributed to hydrogen bond formation between the fluorine atom and the hydronium ion, other halides being less capable of forming hydrogen bonds.[122] The greater the electron density about the fluorine atom, the greater should be its acceptor properties and the greater the catalysis. This is in fact observed.[122]

Winstein, Grunwald and Jones observed that benzyl tosylate and benzyl chloride both gave curved logk vs. Y plots.[79] Since both primary and tertiary systems which undergo only one or the other mechanism give linear relationships whereas secondary systems do not, they concluded that benzyl chloride solvolyzes by two separate processes, S_N1 and S_N2. Swain and Langsdorf found similar curvature for the Hammett plots of benzyl chloride solvolyses,[123] and concluded that rho for this reaction is a function of sigma because p-methoxy not only stabilizes a transition state with a high positive charge, but also increases the capacity of the alkyl group for a positive charge. Therefore a higher degree of bond breaking relative to bond formation is favored and rho is more negative. A strongly electron attracting group, on the other hand, should increase the alkyl group capacity for negative charge and favor bond making; therefore a more positive rho. Since this effect is basically mesomeric n origin, meta substituted benzyl chlorides should give less curvature which as observed.[123]

Kochi and Hammond[124] found a linear Kirkwood relation[73] for enzyl tosylate solvolysis (*vide supra*), but also found curvature for he Hammett plot, *p*-methoxy and *p*-methyl being the worst points. Since hese are also the worst points in the benzyl chloride case,[123] the same actors probably apply to both solvolyses. These authors concluded that ince rho is more negative for the tosylates than for the chlorides omitting the two aforementioned substituents), the tosylates undergo ore bond breaking, and there is a large formal charge on the alkyl roup in the tosylate transition state. The deviation of the *p*-methoxy nd *p*-methyl groups may be due to a mesomeric effect.

Charlton and Hughes observed that a methyl group in the para or rtho position of benzyl chloride have about the same accelerating ffect.[125] Since introduction of a second *o*-methyl group accelerates he rate by the same order of magnitude as the first, it was concluded hat there is no steric effect and hence no change in the S_N1 mechanism.

Bensley and Kohnstam studied the solvolysis of benzyl chloride in 50% aqueous acetone and 50% aqueous ethanol.[126] The negative values found for $\Delta C_p^{\ddagger}$ were attributed to increased solvation associated with the development of electric charge at the transition state. A *p*-methyl or *α*-chloro group was found to enhance the rate by increasing the activation entropy, while electron releasing substituents accelerated S_N1 solvolyses by reducing $\Delta H^{\ddagger}$. Therefore, these authors concluded that this reaction is probably not S_N1. The ratio of heat capacity of activation to the entropy of activation was found to be independent of the substrate for the S_N1 reactions of benzylidene chloride and benzotrichloride.[127] This is because the relative degree of solvation in the two states is the most important factor in determining the magnitude of these two activation parameters, therefore the ratio would depend solely upon solvent and temperature for S_N1 reactions. The decrease found for this ratio on going from benzylidene chloride to benzyl chloride was taken to mean that the latter does not solvolyze via the S_N1 mechanism, but involves some co-valent attachment to a solvent molecule.

Robertson and Scott[128] have criticized Bensley and Kohnstam's criterion for reaction mechanism.[126,127] Since $\Delta S^{\ddagger} = \Delta S^{\ddagger}_{o} + \Delta C^{\ddagger}_{p}\ln T$, and since $\Delta S^{\ddagger}_{o}$ is positive while $\Delta C^{\ddagger}_{p}$ is negative for all the compounds studied, $\Delta S^{\ddagger}$ must equal zero when $T = \exp(-\Delta S^{\ddagger}_{o}/\Delta C^{\ddagger}_{p})$. On either side of this temperature the ratio $\Delta C^{\ddagger}_{p}/\Delta S^{\ddagger}$ will have different signs. Therefore the physical significance of this ratio is difficult to envisage. Allyl bromide and iodide undergo a sign change in the activation entropy with temperature such that the heat capacity to entropy ratio must change sign. Consequently it is difficult to interpret the sign and the magnitude of this ratio. The heat capacity of activation for benzyl chloride and the allyl halides are all negative, and similar in magnitude to the heat capacities for weak acid ionizations. Therefore, the transition state can be either a unimolecular heterolytic bond cleavage or an S_N2 attack by a water molecule.

The evidence in favor of S_N1 solvolysis of benzyl chloride was summarized by Bensley and Kohnstam[126] as being a constancy of rate increase on successive ortho methylation,[125] alteration of the rate by para substituents by values expected for S_N1 reactions[118] and the mass law retarding effect of added chloride ion.[57] The behavior of benzyl chloride was concluded to be consistent with an increasing tendency to react unimolecularly as the ionizing power of the solvent is increased.[126] This argument derives support from the increasing value of $k_{50\%\ \text{ethanol}}/k_{50\%\ \text{acetone}}$ in the order p-nitro $<$ H $<$ p-methyl. Since the ionized structure has more contribution to the transition state hybrid, the solvolytic behavior may approach that of a unimolecular process since the effect of changing experimental conditions on the stability of the ionized structure will be an important factor in determining the rate.

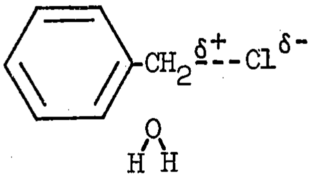
In studying the product ratio from benzyl chloride solvolysis in aqueous ethanol, Kohnstam and Robinson[129] found that it does not adhere to the Olson-Halford equation.[60] This was found to be the case for S_N1 solvolyses,[65] but the S_N2 solvolysis of n-butyl bromide does give the Olson-Halford predicted results.[130] Unimolecular solvolysis could explain the benzyl chloride behavior, but the previous work by Bensley and Kohnstam[127] showed that a solvent molecule participates in the transition state. Kohnstam and Robinson concluded that this behavior could be explained by solvent sorting such that the vicinity of the substrate is richer in water than in ethanol.[129]

Tommila, et al., have reviewed the literature of benzyl chloride solvolysis.[131] They concluded that the neutral solvolysis mechanism involves co-valent participation by the solvent to an extent dependent increase on successive ortho methylation,[125] alteration of the rate by para substituents by values expected for S_N1 reactions[118] and the mass law retarding effect of added chloride ion.[57] The behavior of benzyl chloride was concluded to be consistent with an increasing tendency to react unimolecularly as the ionizing power of the solvent is increased.[126] This argument derives support from the increasing value of $k_{50\%\ \text{ethanol}}/k_{50\%\ \text{acetone}}$ in the order p-nitro < H < p-methyl. Since the ionized structure has more contribution to the transition state hybrid, the solvolytic behavior may approach that of a unimolecular process since the effect of changing experimental conditions on the stability of the ionized structure will be an important factor in determining the rate.

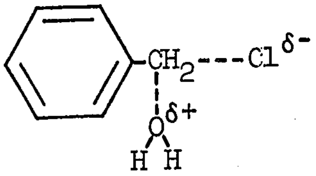
In studying the product ratio from benzyl chloride solvolysis in aqueous ethanol, Kohnstam and Robinson[129] found that it does not adhere to the Olson-Halford equation.[60] This was found to be the case for S_N1 solvolyses,[65] but the S_N2 solvolysis of n-butyl bromide does give the Olson-Halford predicted results.[130] Unimolecular solvolysis could explain the benzyl chloride behavior, but the previous work by Bensley and Kohnstam[127] showed that a solvent molecule participates in the transition state. Kohnstam and Robinson concluded that this behavior could be explained by solvent sorting such that the vicinity of the substrate is richer in water than in ethanol.[129]

Tommila, et al., have reviewed the literature of benzyl chloride solvolysis.[131] They concluded that the neutral solvolysis mechanism involves co-valent participation by the solvent to an extent dependent upon the nature of substituents and the nature of the solvent. In hydrolysis the p-nitro derivative appears to be very near the classical S_N2 mechanism with considerable O-C and C-Cl co-valent bonding and small charge separation. However, the transition state of the p-methyl derivative must have large fractional charges on the carbon and chlorine atoms and very little O-C bond formation--very near the classical S_N1 limit. The unsubstituted compound shows mechanistic properties very similar to the p-methyl derivative.

In summary it may be concluded that the classification of the solvolysis of benzyl chloride itself as S_N1 or S_N2 cannot be made. However, it can be concluded that the transition state is more polar than the initial state and has a stronger electrical field. This would be the case in either the limiting S_N1 (structure III) or S_N2 (structure IV) mechanisms, and must therefore be the case for any mechanism in between. Consequently this system is useful from the viewpoint of studying solvation phenomena associated with reacting systems. The accessibility of the rates of benzyl chloride solvolysis in various solvents over convenient ranges of temperature and pressure serves to accent its utility as a tool in this type of study.



III



IV

CHAPTER 3

PROPOSAL

Since activation volumes invariably reflect solvation changes in ionic reactions (Chapter 1), it would seem that they might shed more light on the phenomenon causing the extrema discussed in Chapter 2. It is therefore proposed that the pressure dependence of a solvolysis reaction be studied as a function of both pressure and solvent composition in binary solvent media. Since small changes in the activation volume with solvent composition change are to be expected, a precise method must be used for obtaining the rate constants in order to minimize the uncertainties in the activation volumes. An in situ conductimetric method meets this requirement.[132] Since alkaline hydrolyses involve exchange of ions in solution, changes in electrical resistance would be small. Also, reactions of this type generally have small magnitudes for the activation volume (Chapter 1), so that any dependence on solvent composition may not be observable. Therefore, a neutral solvolytic reaction would probably give more meaningful results. Of the systems available, benzyl chloride and *p*-methylbenzyl chloride have been subjected to the most scrutiny as regards activation parameter extrema.[106,107,133] The latter has been studied in a large number of solvent systems,[107] and therefore would seem the logical choice. However, the data are available at 30°C., and at the time this study was undertaken thermostating equipment operable at this temperature was not available.

Therefore benzyl chloride at 50.25°C. was the system chosen.

Two of the obvious solvent systems to be studied, from the preceding chapter, are those of aqueous ethanol and aqueous methanol. The values of the activation energy for the former are available,[106] while the latter is interesting in view of Tommila's findings that no extrema occur in this system.[92,96] It is therefore proposed that these solvent systems be exploited. In order to test the hydrophobic bonding hypothesis suggested by Tommila,[92,96] it is proposed that higher alcohols be used as the co-solvent with water. Such a choice would minimize changes in the nature of specific interactions, although the strength of such interactions would undoubtedly be affected. Therefore, it is proposed that i-propanol and t-butanol be used. The choice of these alcohols rather than the normal isomers is dictated by the low solubility of n-butanol in water,[98b] and is recommended by the deep minimum observed for ΔH^{*} for p-methylbenzyl chloride solvolysis in aqueous t-butanol.[107]

In order to compare the various activation parameter dependencies, it is necessary to have them all available. Since the ethanol-water system is the only one for which benzyl chloride solvolysis was studied as a function of temperature, it is necessary to measure the temperature dependence of the solvolytic rate in the various solvent systems mentioned. It is therefore proposed that the atmospheric rate constants for these systems be measured at 40.00° and 60.50°C. so that the enthalpy and entropy of activation can be determined as a function of solvent composition.

Since discussion of the reason for the solvent dependence of $\Delta V^{\ddagger}$ must involve the individual contributions of the initial and transition states, it would be helpful to know the behavior of the individual states. Therefore, it is proposed that the partial molal volume of benzyl chloride in each of the solvents to be studied be measured. Such determinations can be made using the dilatometric technique of Shinoda and Hildebrand[134] after modifying it for reactive species (see Chapter 7). The partial molal volume of the transition state is therefore given by

$$\bar{V}_t = \Delta V^{\ddagger} + \bar{V}_g. \qquad (10)$$

Since Whalley has observed that the constant volume activation energy is a simple function of solvent composition for the acid catalyzed hydrolyses of methyl acetate and ethylene oxide,[135] it is of interest to determine whether the same dependence is found in the neutral hydrolyses. Whalley has used eq. 11 to calculate the constant volume

$$\Delta U_v^{\ddagger} = \Delta H_p^{\ddagger} - T\frac{\alpha}{\kappa}\Delta V^{\ddagger} \qquad (11)$$

parameter, rather than the more rigorous relation

$$\Delta U_v^{\ddagger} = \Delta H_p^{\ddagger} - T\left(\frac{\bar{\alpha}_t}{\bar{\kappa}_t}\bar{V}_t - \frac{\bar{\alpha}_g}{\bar{\kappa}_g}\bar{V}_g\right). \qquad (12)$$

Eq. 11 assumes that the partial molal ratios $\bar{\alpha}/\bar{\kappa}$ of the two states are identical to that of the bulk solvent, a highly questionable assumption in view of the lack of such information. However, it is proposed that the values for α and κ of the solvents used in this study be measured in order to evaluate eq. 11, and determine whether a simple relation is also found for the neutral solvolysis. The values of the partial molal α could be determined by measuring the partial molal volume of benzyl chloride in each solvent (vide supra) at two different temperatures. However, since the partial molal κ's cannot be evaluated, such measurements seem impractical at this time.

In summary, the activation volume, enthalpy and entropy for benzyl chloride solvolysis in aqueous methanol, ethanol, i-propanol and t-butanol are to be determined from the temperature and pressure dependence of the rate constant. The partial molal volume of benzyl chloride is to be determined in each of the solvent systems. The thermal expansivity, α, and the isothermal compressibility, κ, of each of the solvents is to be determined, and used to evaluate the activation energy at constant volume for benzyl chloride solvolysis.

PART II

KINETIC MEASUREMENTS

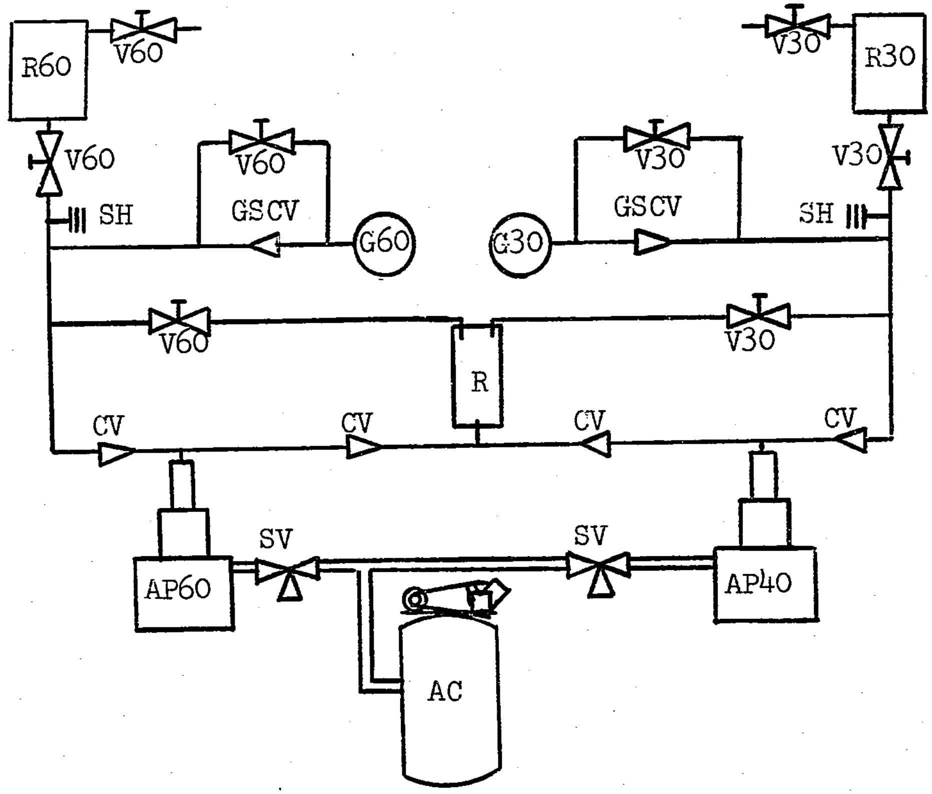
CHAPTER 4

EXPERIMENTAL I. KINETICS

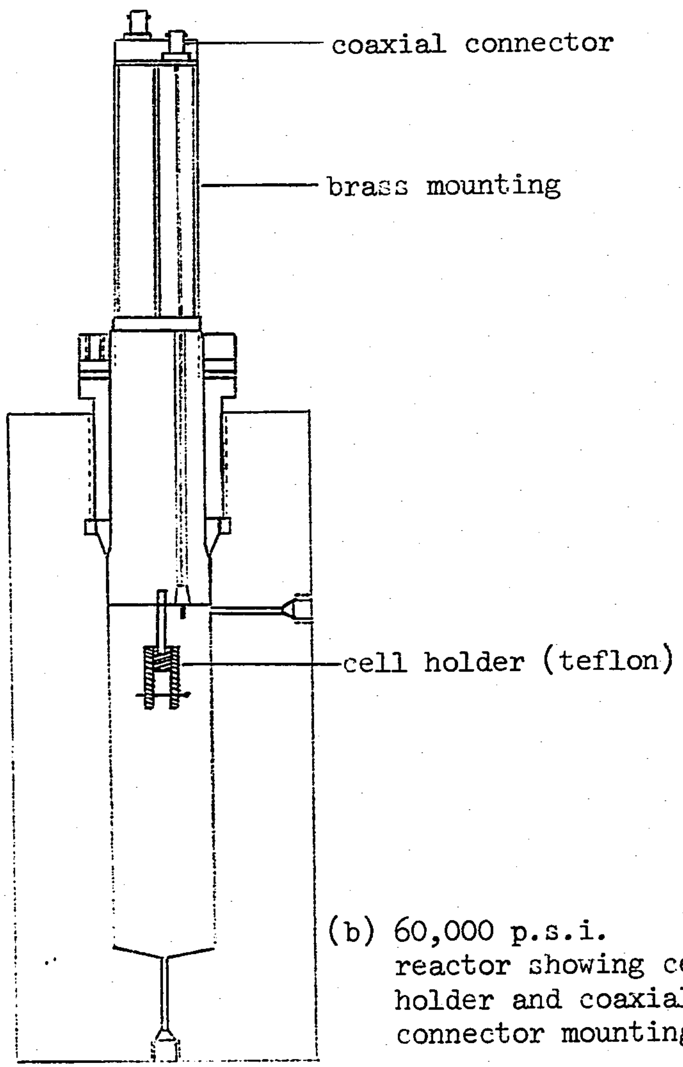
The High Pressure Apparatus

A schematic diagram of the hydrostatic systems is presented in Fig. 1(a). The high pressure vessels (Fig. 1 (b)) are modified versions of the AEM series manufactured by Autoclave Engineers, Inc. (Erie, Pennsylvania). They are each equipped with four Covar leads which pass through the cover, and which are insulated from the bomb by porcelain. A brass mounting fitted to the outside of each cover holds the BNC series coaxial connectors (Amphenol-Borg Electronics Corp.; Chicago, Illinois) which are connected to the Covar leads. The connecting wires are insulated with fiber glass spaghetti.

Pressurization of the fluid in the reactors was accomplished by means of air-hydraulic intensifier type pumps. That for the 60,000 p.s.i.g. system was manufactured by Autoclave Engineers, Inc., and that for the 30,000 p.s.i.g. system was American Instrument Co.'s (Silver Springs, Maryland) 40,000 p.s.i.g. model. The air was supplied by an Ingersoll-Rand (New York, N.Y.) Type-30 compressor operating between 125 and 150 p.s.i.g. The pressurizing liquid was Blackhawk LX-21 hydraulic fluid (Blackhawk Manufacturing Co.; Milwaukee, Wisconsin). Pressure measurement was accomplished by means of 16 in. dial Bourdon tube gauges manufactured by Heise-Bourdon Tube Company (Newtown, New Jersey). The 61,000 p.s.i.g. gauge was calibrated in units of 50 p.s.i.g., while the 30,000 p.s.i.g. gauge was calibrated in units of 20 p.s.i.g.



(a) Schematic diagram of the hydrostatic system: AC, compressor; AP40, air driven 40,000 p.s.i. pump; AP60, air driven 60,000 p.s.i. pump; CV, check valve; G30, 30,000 p.s.i. guage; G60, 60,000 p.s.i. guage; GSCV, guage surge check valve; R, reservoir; R30, 30,000 p.s.i. reactor; R60, 60,000 p.s.i. reactor; SH, safety head; SV, selenoid valve; V30, 30,000 p.s.i. valve; V60, 60,000 p.s.i. valve

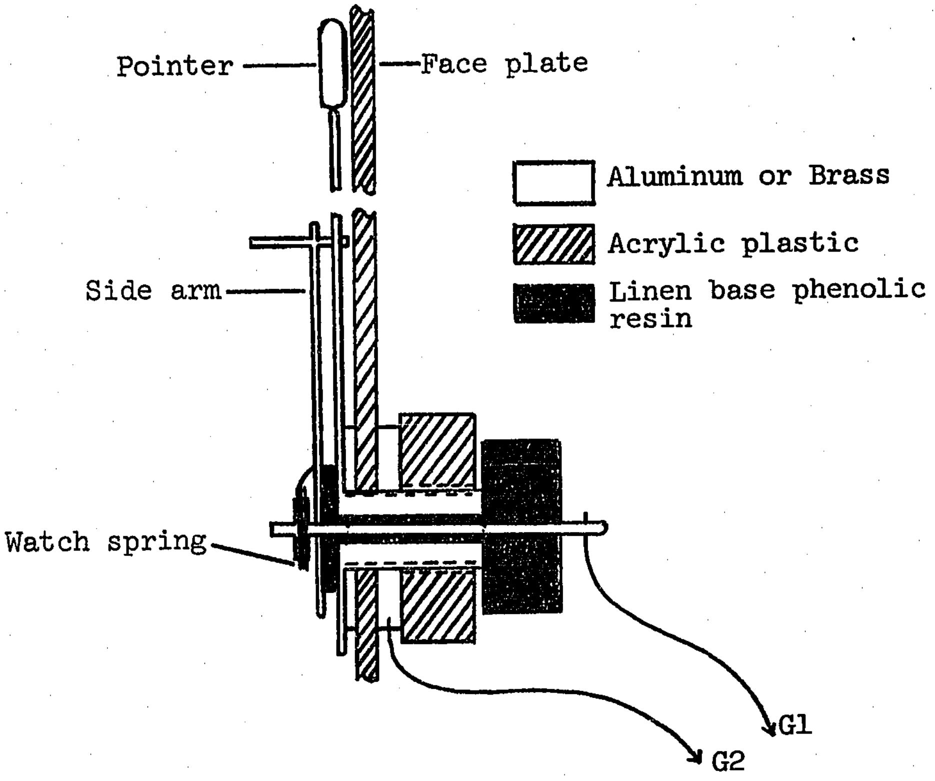


(b) 60,000 p.s.i. reactor showing cell holder and coaxial connector mounting

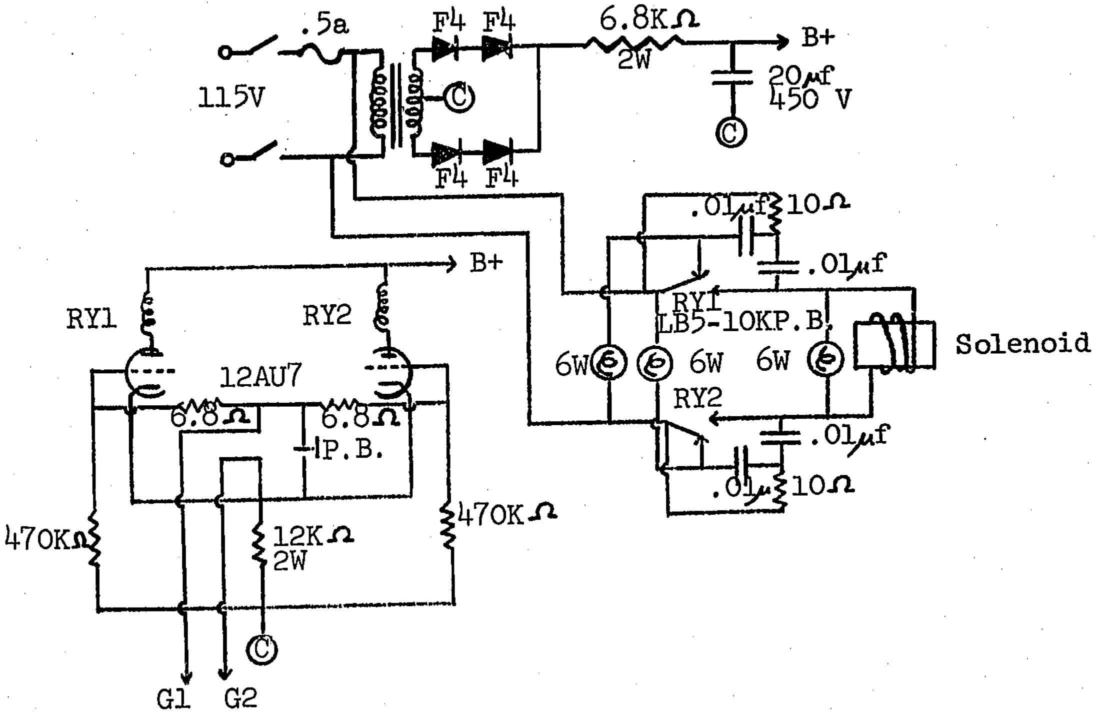
Fig. 1. The hydrostatic apparatus

Automatic pressure control was accomplished by the use of specially designed switching devices (Fig. 2 (a)) located in the face plates of the gauges. The main pointer of the switch was preset to the desired gauge pressure, and the pump activated. When this pressure was reached, the gauge needle lifted the auxiliary side arm of the switch away from the main pointer causing a break in the control circuit. This deactivated a relay system (Fig. 2 (b)) resulting in the closure of a normally closed selenoid valve (Skinner Electric Valve Div.; New Britain, Connecticut) located in the air supply line. When the pressure fell contact between the auxiliary side arm and the main pointer was remade, activating the relay system, causing opening of the solenoid valve, and resulting in commencement of pressurization.

It should be noted that a delicate balance of the watch spring tension in the switching device was necessary to avoid distortion of the gauge needle while furnishing positive contact between the side arm and pointer. This method enabled the pressure to be controlled to better than ±200 p.s.i.g. over the entire range above atmospheric. While this pressure fluctuation may appear large it represents only a maximum 4% pressure change at 5,000 p.s.i.g. The sensitivity of measured rates to pressure is such that any resultant effect on rate is within the experimental errors claimed for the rates particulary in view of the fact that these pressure fluctuations are averaged out over the course of the reaction time studied. It was found helpful to coat the contact points of the switch with silver solder to insure good electrical contact.



(a) Gauge switch



(b) Relay circuit

Fig. 2. Pressure regulating system

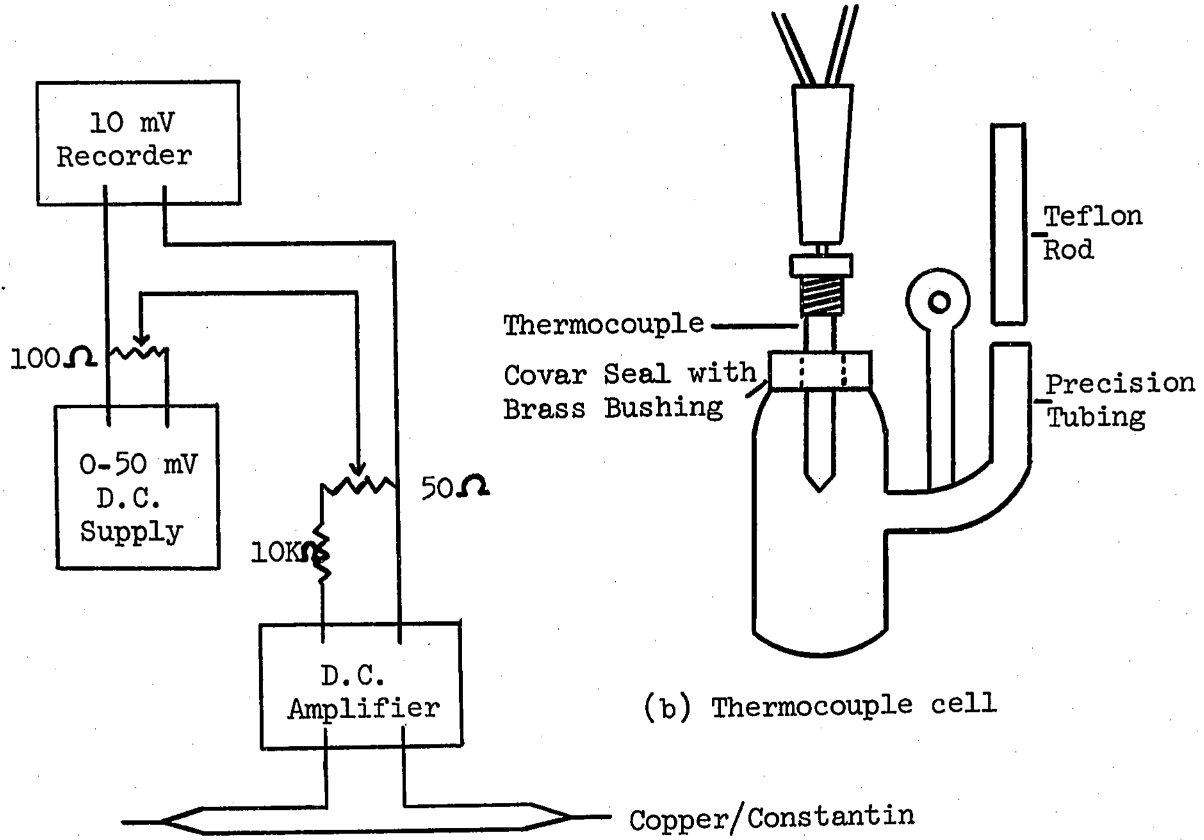
Thermostats

The thermostats for both the high pressure kinetics and the kinetics at atmospheric pressure were of the same basic design, but differed in size. The hydrostatic vessels were bolted to support plates which were suspended by means of chain hoists in 55 gallon oil thermostats (Voltesso 35 Transformer Oil; Imperial Oil Ltd.). Two vertical guide rods mounted in the thermostats passed through holes in the support plates, and prevented swaying of the bombs. Each 55 gal. drum was wrapped with asbestos paper and a 50 ohm non-inductively wound coil of nichrome wire. The entire apparatus was placed inside a wooden box, and the annular space filled with vermiculite or fiber glass insulation. The nichrome coil was used to heat the thermostat to within ten degrees of the desired temperature. Final heating was accomplished by a 250 watt infra-red heating lamp, immersed in the oil, which was controlled by a thyratron relay system activated by a mercury in glass thermoregulator. Efficient stirring of the oil was accomplished by an Eberbach immersion pump (Universal Electric Co.; Owosso, Michigan) and a 4 in. diameter propellor type stirrer. The temperature was measured with a six degree Beckmann thermometer which had been standardized against a platinum resistance thermometer (Leeds & Northrup; Philadelphia, Pennsylvania). In an air conditioned room at 22°C. ambient control to within 0.005°C. was obtainable. The thermostats for the atmospheric studies were of identical design, but ranged from 5 to 25 gallons in size.

Temperature Equilibration

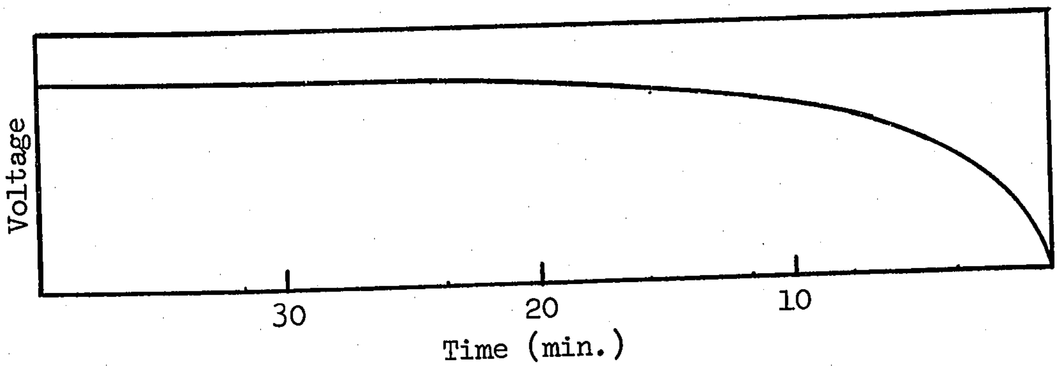
In order to determine the time interval required for the reaction mixture to come to thermal equilibrium inside the hydrostatic chamber two studies were conducted. The apparatus depicted in Fig. 3 was used to measure the temperature directly. A thermocouple cell (Fig. 3(b)) of somewhat greater capacity than the conductivity cells used (see below) was filled with water at 0°C. This was placed into the hydrostatic vessel, the thermocouple leads being soldered to the bomb leads. A matched thermocouple in an ice-water mixture was used as a reference, and the voltage difference between the two thermocouples was recorded as a function of time. The zero was set with both thermocouples in an ice-water mixture, and the gain was adjusted with the "hot" thermocouple in the thermostating fluid. A 90% deflection of the recorder chart was obtained. After the vessel was lowered into the thermostat, the "hot" thermocouple was connected to the recording apparatus (Fig. 3(a)). It was found that after 25 to 35 minutes the temperature of the water in the thermocouple cell was equal to that of the thermostat, 50.25°C., within 0.2°C.(Fig. 3(c)). Initial pressurization of the apparatus did not appear to alter the time interval for temperature equilibration.

The second study involved the use of electrical conductivity. A conductivity cell of the type described below was filled with an aqueous solution of 5×10^{-4} molar potassium chloride at 0°C., and placed into the pressure vessel. After lowering into the thermostat, the electrical resistance of the solution was measured at one minute intervals. It was found that after 30 minutes the change in resistance between readings was



(a) Circuit schematic

(b) Thermocouple cell



(c) Emf vs. time record

Fig. 3. Thermal equilibration determination

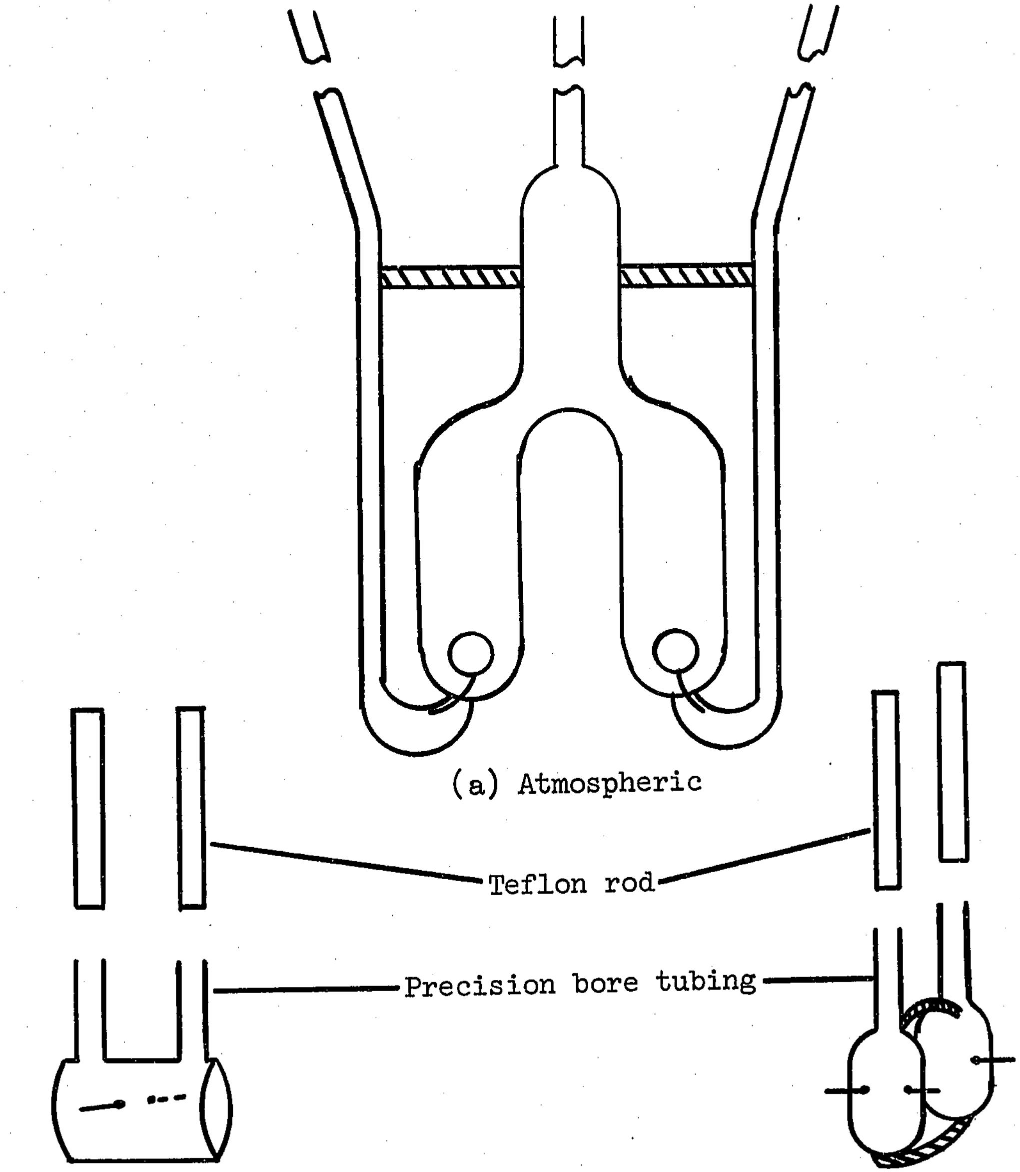
only two or three ohms, indicating that the cell contents were very close to thermal equilibrium. As the initial drop in resistance of a typical kinetic run was 1000 ohms or greater, the effect on conductance of the slight deviation from thermal equilibrium could be ignored.

Conductivity Apparatus

Cells

Three types of conductivity cell were used in this study. For determining the atmospheric pressure rate constants at 40.05°C. and 60.50°C. the cell shown in Fig. 4(a) was used. These had a capacity of about 50 ml. The side arms were filled with mercury permitting the cells to be connected to the conductivity bridge by dipping one end of the bridge connecting wire into the mercury side arms. After filling the inner compartment the cells were heated in a water bath to the approximate thermostat temperature, and then sealed and wiped dry prior to insertion into the thermostat.

The high pressure conductivity cells (Fig. 4(b) and (c)) were used for all rate measurements at 50.25°C. The single compartment cells had a capacity of 15 ml., and were used for the faster rates requiring resistance measurements every minute or less. The double compartment cells were used for determining the duplicate rate constants simultaneously when the rate was slow enough to permit. Each compartment had a capacity of about 8 ml. After filling, the 0.25 in. diameter plugs were inserted into the precision bore glass tubing, care being taken



(a) Atmospheric

(b) Single compartment high pressure

(c) Double compartment high pressure

Fig. 4. Conductivity cells

not to entrap air bubbles. The cell electrodes were then connected to the bomb leads with 20 gauge braided copper wire insulated with fiber glass spaghetti. All connections were soldered to prevent their separation. Buchanan and Hamann[6] have used mercury to seal their conductivity cells and to transmit the pressure. The use of teflon pistons was preferred in view of the findings of Wall and Gill[16] that below concentrations of 0.1 N. electrolyte mercury contaminates the solution. Leakage past the pistons did not produce any problem, indeed when decompressed very slowly none of the pressurizing fluid was observed inside the cell indicating that no fluid enters during compression or during the course of the conductivity measurements.

The main problem which arose in the use of these cells was fracturing of the glass to platinum seals. This was more of a problem above 20,000 p.s.i.g. than at the lower pressures. Inconvenient as it was, this behavior was tolerated, and the cells simply replaced at necessary intervals. These cells were usually constructed in batches of six at a time, and it was frustratingly found that either a batch was adequate or completely unusable. The reason for this was never determined. Various types of graded seals were tried, but proved to be unsatisfactory.

Bridge

The A. C. conductivity bridge was of conventional design, but specially constructed by Mr. T. Clement of this department from high precision components. A sensitivity of one ohm in eighty thousand was attainable. When the resistance of the cell did not fall within the range of the bridge (0 to 111,111 ohms) a precision 100 Kohm resistor (±0.1%) was placed in parallel with the cell. Wills has shown experimentally that such a procedure has no effect on the extracted rate constants.[136] All connections between the cells and the bridge were made with metal sheathed coaxial cable.

In order to determine the effect that the inherent pressure fluctuation would have on the measured conductivity, an aqueous solution of 10^{-3} molar hydrochloric acid was placed in a conductivity cell. The electrical resistance of the cell was measured at 10,000 p.s.i.g. intervals between atmospheric pressure and 30,000 p.s.i.g. It was found that the maximum sensitivity of the conductance to pressure was at atmospheric pressure where the variation was 0.0008% per p.s.i.g. (30°C.). Thus, for the 200 p.s.i.g. fluctuation inherent in the pressure regulating system described previously, a maximum error of 0.2% could be expected. It might be noted that for relatively long runs the pressure fluctuation was very slow, and this 0.2% represents an absolute maximum. The kinetic results indicate that this source of error was negligible.

The Kinetic Method

The mixtures of alcohol and water were prepared by weight to ±0.0002 mole fraction. Solutions of approximately 5×10^{-4} molar alkyl halide in the desired solvents were prepared by weight, and filtered into a vial equipped with a stopcock and standard taper joint. The vial was then closed with a rubber septum, and the solutions degassed by twice freezing, evacuating to a pressure of about 10^{-3} mm. Hg and thawing.

The evacuated vials were stored in an ice-water bath until needed. If the rubber septum had been punctured previously, a piece of masking tape was placed over it to seal the pin hole. The solutions were generally used within 24 to 48 hours for the 40° and 60° runs; storage times were longer for the 50° runs. This was because the entire solution was used for the duplicate runs at atmospheric pressure, but only 20 ml. was necessary for the high pressure runs. In any event, the solutions were never kept longer than approximately one quarter-life at 0°C. Although this period was never actually determined, the initial resistances of the kinetic runs showed that no significant solvolysis had occurred during storage.

The degassing was necessary to prevent formation of air bubbles on the electrodes of the cell. It was found in the preliminary studies that discontinuous decreases in resistance occurred frequently. It was further found that when the filled cell was heated to a temperature in excess of ambient, a profusion of air bubbles formed on the inner surface. Degassing the samples resulted in the cessation of resistance discontinuities. It would appear obvious that if bubble formation were a problem, the rate determinations at higher pressures would exhibit little or no discontinuities. This in fact was observed, but degassing the samples did appear to give better results even at the higher pressures.

Different times were required to obtain thermal equilibration of the cells at atmospheric pressure (cell not in a high pressure vessel) compared with cells inside the reactor. Accordingly different techniques were employed for the two types of study.

For the atmospheric rates at 40° and 60° the following method was employed. The storage vial was thoroughly agitated to assure homogeneity. It was then warmed under tap water, with agitation, to approximately room temperature or slightly warmer. The vial was wiped, and the vacuum released. The solution was then poured into the conductivity cells whose side arms had previously been filled with mercury. The cells were sealed except for a small opening, and they were heated in a water bath to the approximate temperature of the thermostat then sealed. After being wiped they were placed in the appropriate thermostat. This method prevented the development of two problems. Sealing the cells after preheating them to the desired temperature assured that no pressure build-up occurred. Although the amount of pressure would certainly have no measurable effect on the rate, it could be great enough to crack the platinum to glass seals. Secondly, preheating the cells insured that disturbance of the thermostat equilibrium would be a minimum. Since the thermostats held from six to twelve cells each, there usually were some cells already in the thermostat. This technique helped to keep these cells undisturbed while others were being introduced into the bath.

A minimum of fifteen minutes was allowed for thermal equilibration. Twenty resistance measurements were taken over a period of time approximating one half-life of the reaction. After about two half-lives had elapsed a second set of measurements was made at the same intervals as the first. It should be noted that, for convenience, the time intervals between consecutive measurements of the set of twenty were constant. Each rate constant was determined in duplicate during simultaneous runs in different cells. If the half-life of the reaction was such as to require measurements every minute or less, non-simultaneous duplicate determinations were conducted.

As previously stated the rates determined in the hydrostatic vessels utilized a different technique. The rate determinations at atmospheric pressure and 50.25°C. (the temperature at which the high pressure rate constants were measured) were also determined inside the high pressure vessel in order to insure consistency in the 50.25°C. results at all pressures. However, the results obtained, on comparison with those at atmospheric pressure and 40.05° and 60.50°C., indicate that this precaution was unnecessary. Time therefore could have been saved by determining all of the atmospheric pressure kinetics in the sealed conductivity cells outside the high pressure reactor.

New high pressure conductivity cells were initially cleaned with hot concentrated nitric acid and distilled water after the method of Murr and Shiner.[137] They were then kept filled with double distilled water (see below). Prior to a kinetic run each cell was aged for 12 hours at the pressure and temperature to be used. An ageing solution of 5×10^{-4} molar hydrochloric acid in the solvent to be used for the kinetic run was used. The cell was then removed from the high pressure vessel, emptied and rinsed thrice with acetone and thrice with double distilled water.

After thorough agitation, the vacuum in the vial containing the reaction mixture was released, and the desired amount of solution extracted through the rubber septum into a syringe. The aged reaction cell was rinsed twice with the solution, and then filled to the top of the precision tubing. The teflon pistons were inserted displacing some of the solution. The method minimized the entrapment of air bubbles. The cell was then placed into the hydrostatic vessel which was lowered into the thermostat and connected to the pressurizing system. The vessel was brought up to the desired pressure, and sufficient time was alloted for thermal equilibrium to occur (30 minutes for those runs having half-lives of less than two hours, and 60 minutes for the longer runs). Resistance measurements were then taken in the same manner as for the atmospheric kinetics.

Materials Preparation

Single distilled water was passed through Illco-Way deionizing resin. It was then distilled in a pyrex apparatus from which atmospheric carbon dioxide and water vapor were excluded, and stored in polyethylene containers.

Standard hydrochloric acid was prepared by the method of Hulett and Bonner.[138] Concentrated hydrochloric acid, 240 ml., was mixed with distilled water, 160 ml. The mixture was distilled through a glass helix packed fractionating column at 660.0 mm. Hg. The first fractions were discarded, and the main distillate was collected to give a solution of 20.47% (wt.) HCl.[138]

Fisher certified reagent potassium chloride was used without further purification.

The methanol used was Fisher certified reagent grade. It was dried over magnesium turnings by the method of Lund and Bjerrum.[139] Methanol, 100 ml., was added to 5 g. magnesium turnings along with a small crystal of iodine. The mixture was refluxed overnight. An additional 1 liter of the alcohol was added, and the refluxing resumed for another 12 hours. The alcohol was then distilled through a glass helix packed fractionating column, the first 100 ml. being discarded.

Ethanol was Reliance Chemicals absolute ethanol. It was dried and distilled in the same manner as the methanol.

Isopropanol was Eastman white label reagent. The alcohol, 100 ml., was refluxed with anhydrous calcium metal, 5 g. After the isopropoxide was completely formed, 1 liter additional alcohol was added, and the mixture refluxed overnight. It was then distilled through a glass helix column, the first 100 ml. being discarded.

_t_-Butanol was Fisher certified reagent grade. It was dried over anhydrous potassium carbonate and distilled.

Recovered alcohol water mixtures were distilled to concentrate the alcohol. The distillate was dried over calcium oxide for several days and distilled. The distillates were then treated by the above procedures.

Eastman white label _t_-butyl chloride was used without further purification.

Eastman white label benzyl chloride was distilled at 23.5 mm. Hg, and the middle portion was collected at 78.5 - 80.0°C. It was periodically distilled in small quantities at 10^{-3} mm. Hg as needed.

CHAPTER 5

RESULTS I. KINETICS

Rates

As previously mentioned (Chapter 4) the progress of the benzyl chloride solvolysis was followed by conductimetric monitoring of the hydrochloric acid produced. The rate expression for the pseudo first order reaction is

$$-\frac{d[\phi CH_2Cl]}{dt} = k[\phi CH_2Cl]. \qquad (13)$$

The rate of disappearance of benzyl chloride equals the rate of production of HCl so that the concentration of substrate at any time t is equal to its initial concentration less the concentration of acid at time t. Therefore

$$-\frac{d([\phi CH_2Cl]_o - [HCl])}{dt} = k([\phi CH_2Cl]_o - [HCl]) \qquad (14)$$

or

$$\frac{d[HCl]}{dt} = k([\phi CH_2Cl]_o - [HCl]). \qquad (15)$$

On integrating eq. 15 we obtain eq. 16. The concentration of acid at

$$[HCl] = [\phi CH_2Cl]_o(1 - e^{-kt}) \qquad (16)$$

any time t is obtained from the electrical conductivity, Λ_t, by eq. 17. Substituting this into

$$\frac{[HCl]}{[HCl]_\infty} = \frac{\Lambda_\infty - \Lambda_t}{\Lambda_\infty - \Lambda_o} \qquad (17)$$

eq. 16 gives

$$[HCl]_\infty\left(\frac{\Lambda_\infty - \Lambda_t}{\Lambda_\infty - \Lambda_o}\right) = [\phi CH_2Cl]_o(1 - e^{-kt}). \qquad (18)$$

Since one mole of hydrochloric acid is produced for every mole of benzyl chloride decomposed, $[\phi CH_2Cl]_o = [HCl]_\infty$. Rearranging eq. 18 therefore gives eq. 19

$$\Lambda_t = \Lambda_\infty - (\Lambda_\infty - \Lambda_o)(1 - e^{-kt}) \qquad (19)$$

If Λ_t at some time t is subtracted from the value at some time $t+\Delta t$ we obtain eq. 20. Taking Naperian logarithms

$$\Lambda_{t+\Delta t} - \Lambda_t = -(\Lambda_\infty - \Lambda_o)(e^{-kt})(1 - e^{-k\Delta t}) \qquad (20)$$

gives eq. 21.

$$\ln(\Lambda_{t+\Delta t} - \Lambda_t) = -kt + \ln\{(\Lambda_o - \Lambda_\infty)(1 - e^{-k\Delta t})\} \tag{21}$$

If a set of conductance measurements is taken at times t_1, t_2, t_3,... and another set at the times $t_1+\Delta t$, $t_2+\Delta t$, $t_3+\Delta t$,... such that Δt is a constant interval, then the second term on the right hand side of eq. 21 will be independent of time. A plot of $\ln(\Lambda_{t+\Delta t} - \Lambda_t)$ vs. t is therefore linear with slope of -k. This method was originally proposed by Guggenheim[140] who demonstrated that the best results are obtained when Δt is approximately two half-lives of the reaction. A typical set of data for this analysis is presented in Table I and Fig. 5 ($1/R = \Lambda \times$ const.).

The use of a shunt across the cell to lower the effective resistance (p. 62) has been shown experimentally to have no effect on the results.[136] That this was to be expected can be demonstrated in the following manner. If the shunt resistance is R_s and that of the cell is R_c, then the measured resistance, R_B, is

$$\frac{1}{R_B} = \frac{1}{R_c} + \frac{1}{R_s}. \tag{22}$$

Subtracting the value of $1/R_B$ at time t from the value at time $t+\Delta t$ gives eq. 23 which is equivalent to

$$\frac{1}{R_{B_{t+\Delta t}}} - \frac{1}{R_{B_t}} = \frac{1}{R_{c_{t+\Delta t}}} + \frac{1}{R_s} - \frac{1}{R_{c_t}} - \frac{1}{R_s} \tag{23}$$

TABLE I

Conductimetric Rate Determination No. 288

Substrate: Benzyl chloride, 3.9×10^{-4} moles/liter

Date: 28 Jan. 1965 Solvent: $X_{i\text{-Propanol}}$ 0.10004

Temp.: 50.25°C. Pressure: 20,000 p.s.i.g.

Time (min.)	R_1 (ohms)	R_2 (ohms)	$10^6 \times \Delta(1/R)$ (ohms)	$\ln(\Delta(1/R))$
0	72620	27289	22.874	-10.685
15	65865	27088	21.734	-10.737
30	61196	26867	20.879	-10.777
45	56223	26665	19.716	-10.834
60	52630	26493	18.745	-10.885
75	49426	26337	17.737	-10.940
90	46867	26192	16.843	-10.992
105	44678	26053	16.001	-11.043
120	42785	25924	15.202	-11.094
135	41225	25794	14.512	-11.141
150	39814	25689	13.810	-11.190
165	38451	25582	13.083	-11.244
180	37294	25486	12.423	-11.296
195	36246	25390	11.796	-11.348
210	35311	25291	11.220	-11.398
225	34401	25205	10.606	-11.454
240	33653	25126	10.084	-11.505
255	32956	25050	9.5767	-11.556
270	32314	24978	9.0889	-11.608
285	31737	24910	8.6356	-11.660

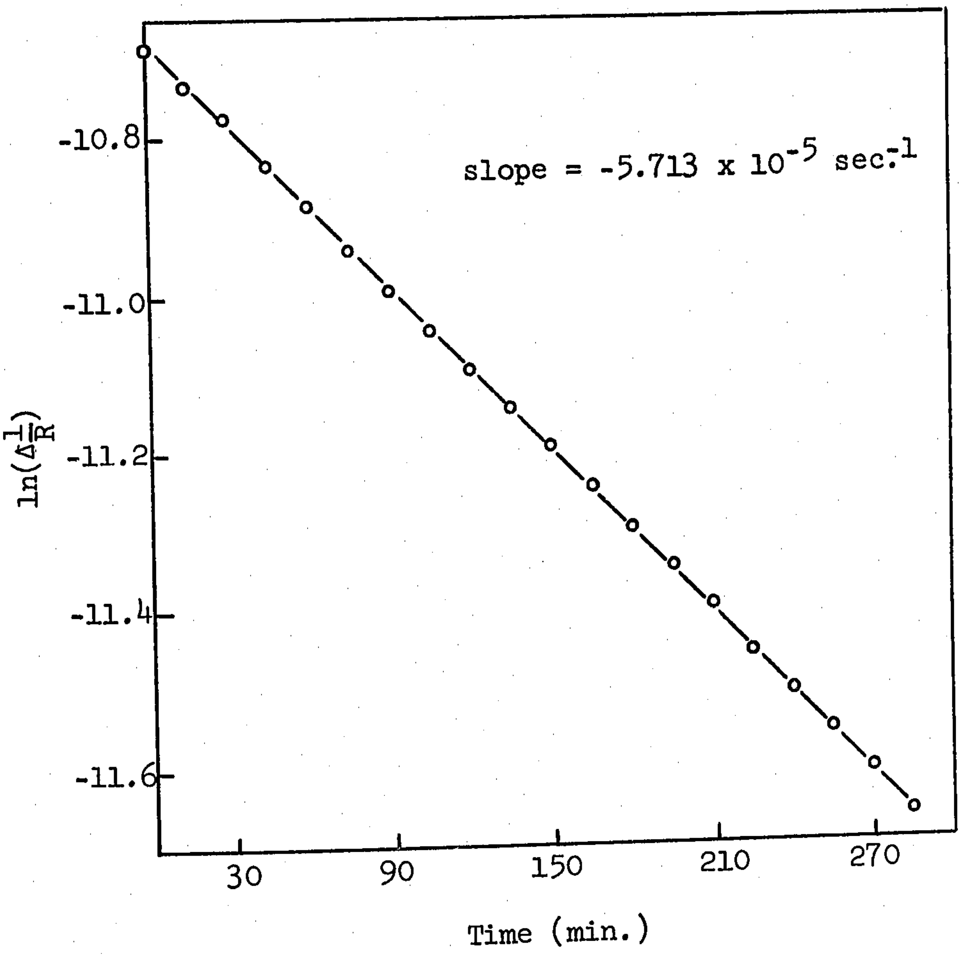


Fig. 5. Guggenheim conductimetric rate determination for the solvolysis of benzyl chloride in 0.10004 mole fraction i-propanol at 50.25°C. and 20,000 p.s.i.g.

eq. 24. Therefore, the use of the observed resistance when a shunt is

$$\frac{1}{R_{B_{t+\Delta t}}} - \frac{1}{R_{B_t}} = (\Lambda_{t+\Delta t} - \Lambda_t) \text{ x const.} \qquad (24)$$

placed across the cell does not alter the form of eq. 21 or the result obtained. It should be noted, however, that use of the shunt lowers the sensitivity of the measurements, and should not be used unless necessary (i.e. when the cell resistance is too great to allow balancing of the conductance bridge).

It may be pointed out that the second term on the right hand side of eq. 21 cannot be evaluated by the method used here. Since the reaction cells are allowed to attain thermal equilibrium prior to gathering of the resistance data, the true value of Λ_o is never obtained. In effect the time scale is displaced, and the initially observed value of the conductivity is equivalent to some non-zero time conductance. This however, has no effect on the extraction of the slope (i.e. the rate constant). If the true values of Λ_o and Λ_∞ were obtainable, then evaluation of the logarithmic term on the right hand side of eq. 21 would afford a verification of the rate constant obtained from the slope.

It may be noted that initial curvature of the Guggenheim graph (Fig. 5) was frequently encountered. Since such behavior was observed in both short runs and those having half-lives of several weeks, lack of thermal equilibrium cannot be the cause. The actual cause was not determined.

The conductance versus time data were analyzed by the method of least squares on an IBM-1620 computer using the Fortran program of Appendix II (p. 225). The slope of the linear plot was calculated rejecting points lying a distance of twice the average least squares deviation from the line (except for the initial point these were rarely encountered). Initial points were progressively rejected and the slope recalculated to eliminate any curvature. The data were plotted on 50 cm. graph paper to determine when the curvature ended. A minimum of nine points was used for each run.

t-Butyl Chloride

In order to check the apparatus and techniques used in this study, the rate of solvolysis of t-butyl chloride in 80% (v/v) aqueous ethanol was studied at 30.00°C. This system had been studied previously by Buchanan and Hamann.[6]

The results of this study for the first order rate constant, together with those interpolated from the data of Buchanan and Hamann, are presented in Table II. The errors reported for the present data are the average deviations of simultaneous, duplicate runs, whereas those for the interpolated data of Buchanan and Hamann are the 30% errors modestly claimed by Hamann.[141] The present results are well within the error range reported by the previous workers; of greater significance is the fact that the higher precision of the present rate determinations serves to enable the activation parameter to be evaluated with a considerable increase in confidence. The increase in confidence of the activation volume, and the smaller uncertainty, is necessary for studying the

TABLE II

Pressure Dependence of the Rate of Solvolysis of t-Butyl Chloride in 80% (v/v) Aqueous Ethanol at 30.00°C.

Pressure (p.s.i.g.)	10^5 x k (sec.$^{-1}$) This Work	10^5 x k (sec.$^{-1}$) Ref. 6
0	1.90 ± 0.03	1.7 ± 0.5
10,000	3.14 ± 0.07	2.7 ± 0.7
20,000	4.92 ± 0.05	4. ± 1.
30,000	6.7 ± 0.3	5. ± 2.
$\Delta V_o^{\ddagger}$ (ml./mole)	-22.2 ± 0.9	-21. ± 4.

variation of this parameter with solvent compostion, and is essential if the evaluation of the pressure dependence of this parameter is desired. Using the method outlined below, the value for the activation volume at atmospheric pressure, $\Delta V_0^{\ddagger}$, obtained from Buchanan and Hamann's data is -21 ± 4 ml./mole while that for the present work is -22.2 ± 0.9 ml./mole; in excellent agreement.

Benzyl Chloride

The first order rate constants for the solvolysis of benzyl chloride in aqueous methanol, ethanol, i-propanol and t-butanol are given in Tables III and IV. The former gives the values at 50.25°C. for various pressures above atmospheric, and the latter gives the values at atmospheric pressure and different temperatures. Most of these rate constants are the average of duplicate, simultaneous runs while some are the average of two to four non-simultaneous determinations. The average deviations reported in these tables are the measure of precision assumed throughout the subsequent discussions. The pressure dependence of the rate constant can be seen in Figs. 6 to 9, and its temperature dependence is shown in Figs. 10 to 13.

The accuracy of these rate constants may be inferred from a comparison of the data in Table IV with that of Hyne, Wills and Wonkka.[106] In water these authors found a value of 22.78×10^{-5} sec.$^{-1}$ at 50.30°C. and 60.00×10^{-5} sec.$^{-1}$ at 60.50°C. For 0.203 mole fraction ethanol the values reported are 1.885×10^{-5} at 50.30°C. and 4.762×10^{-5} sec.$^{-1}$ at 60.50°C. The agreement with this data is excellent in each instance

TABLE III

Rate Constants for the Solvolysis of Benzyl Chloride at 50.25°C. in Aqueous Alcohol as a Function of Pressure

Mole Fraction Alcohol	10^5 x k (sec.$^{-1}$) Pressure (p.s.i.g.) 5,000	10,000	20,000	40,000	60,000
			Methanol		
0.000	24.42 ± 0.02	30.0 ± 0.2	39.3 ± 0.3		
0.100		17.49 ± 0.04	23.1 ± 0.4	44. ± 1.	
0.200		10.7 ± 0.4	13.92 ± 0.01	23.09 ± 0.06	
0.300		5.9 ± 0.1	8.124 ± 0.009	14.01 ± 0.02	
0.400		3.31 ± 0.02	4.826 ± 0.003	8.773 ± 0.007	11.7 ± 0.4
0.500		2.00 ± 0.03	3.01 ± 0.01	5.40 ± 0.01	8.37 ± 0.04
			Ethanol		
0.100	8.47 ± 0.01	10.25 ± 0.02	13.68 ± 0.01	21. ± 2.	
0.200	2.47 ± 0.01	3.02 ± 0.07	4.64 ± 0.02	8.712 ± 0.004	12. ± 1.
0.300	1.06 ± 0.01	1.29 ± 0.01	2.04 ± 0.03	3.85 ± 0.02	6.4 ± 0.3
0.400		0.68 ± 0.03	1.041 ± 0.002	1.81 ± 0.02	2.6 ± 0.2
			i-Propanol		
0.100		3.71 ± 0.03	5.74 ± 0.03	10.96 ± 0.01	14.7 ± 0.1
0.200		0.77 ± 0.02	1.24 ± 0.01	2.20 ± 0.03	4.20 ± 0.01
0.300		0.387 ± 0.008	0.58 ± 0.01	0.91 ± 0.04	1.71 ± 0.05
0.400		0.187 ± 0.003	0.270 ± 0.009	0.46 ± 0.01	0.88 ± 0.06

TABLE III (con't)

Mole Fraction Alcohol	10^5 x k (sec.$^{-1}$) Pressure (p.s.i.g.) 5,000	10,000	20,000	40,000	60,000
			t-Butanol		
0.100		1.33 ± 0.06	2.35 ± 0.04	4.45 ± 0.02	7.79 ± 0.03
0.200		0.33 ± 0.01	0.50 ± 0.04	0.950 ± 0.003	1.252 ± 0.004
0.300		0.149 ± 0.003	0.17 ± 0.05	0.459 ± 0.002	0.692 ± 0.008

TABLE IV

Rate Constants for the Solvolysis of Benzyl Chloride at Atmospheric Pressure in Aqueous Alcohol as a Function of Temperature

Mole	10^5 x k (sec.$^{-1}$)		
Fraction	40.05°C.	50.25°C.	60.50°C.
		Methanol	
0.000	7.527 ± 0.002	23.1 ± 0.4	59.4 ± 0.5
0.100	4.74 ± 0.08	12.47 ± 0.04	34.6 ± 0.2
0.200	2.51 ± 0.02	7.045 ± 0.005	17.8 ± 0.4
0.300	1.41 ± 0.02	3.731 ± 0.008	9.8 ± 0.2
0.400	0.7803 ± 0.0001	2.035 ± 0.005	5.71 ± 0.03
0.500	0.441 ± 0.004	1.246 ± 0.002	
		Ethanol	
0.100	2.54 ± 0.03	6.83 ± 0.01	17.2 ± 0.1
0.200	0.677 ± 0.002	1.93 ± 0.01	4.71 ± 0.04
0.300	0.283 ± 0.001	0.80 ± 0.01	2.18 ± 0.01
0.400	0.159 ± 0.001	0.459 ± 0.007	1.273 ± 0.006
		i-Propanol	
0.050	3.51 ± 0.06	9.10 ± 0.03	22.58 ± 0.002
0.100	0.904 ± 0.007	2.094 ± 0.005	6.17 ± 0.03
0.200	0.158 ± 0.002	0.462 ± 0.001	1.30 ± 0.02
0.300	0.073 ± 0.002	0.2174 ± 0.0004	0.566 ± 0.008
0.400	0.0428 ± 0.0004	0.1288 ± 0.0001	0.362 ± 0.002
		t-Butanol	
0.050	1.630 ± 0.001	4.03 ± 0.01	9.78 ± 0.04
0.100	0.236 ± 0.002	0.679 ± 0.006	1.803 ± 0.008
0.200	0.0611 ± 0.0007	0.1868 ± 0.0002	0.577 ± 0.007
0.300	0.0299 ± 0.0002	0.0910 ± 0.0005	0.258 ± 0.003

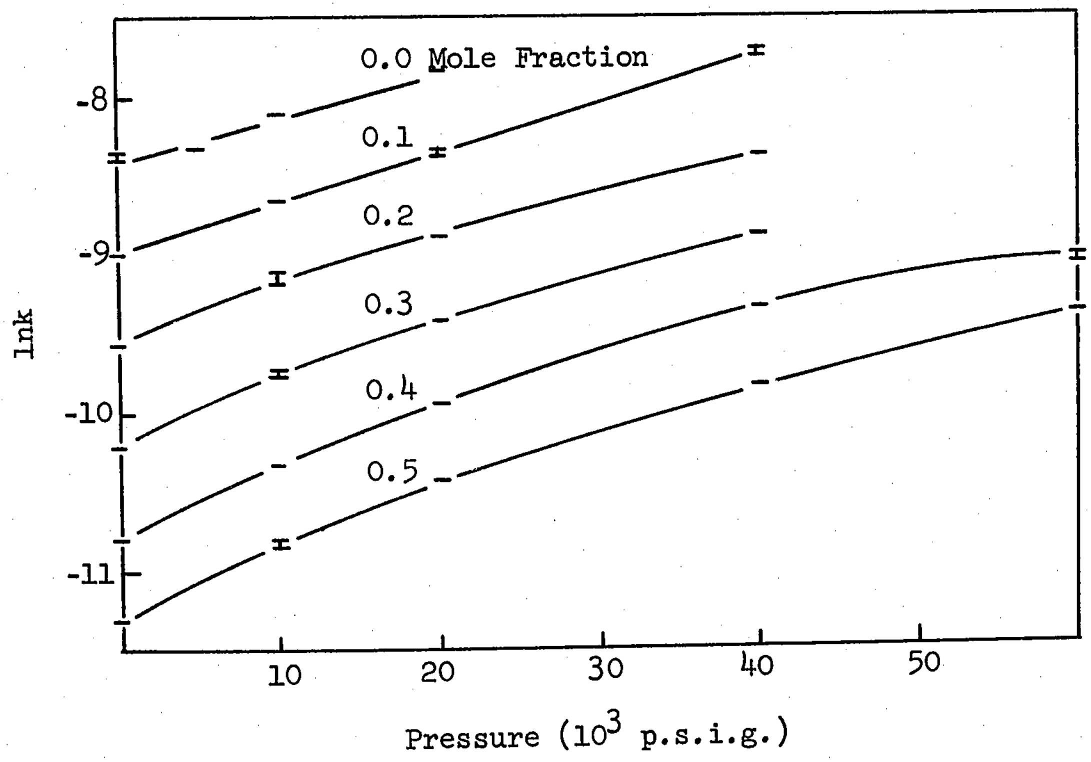


Fig. 6. Pressure dependence of the rate of solvolysis of benzyl chloride in aqueous methanol.

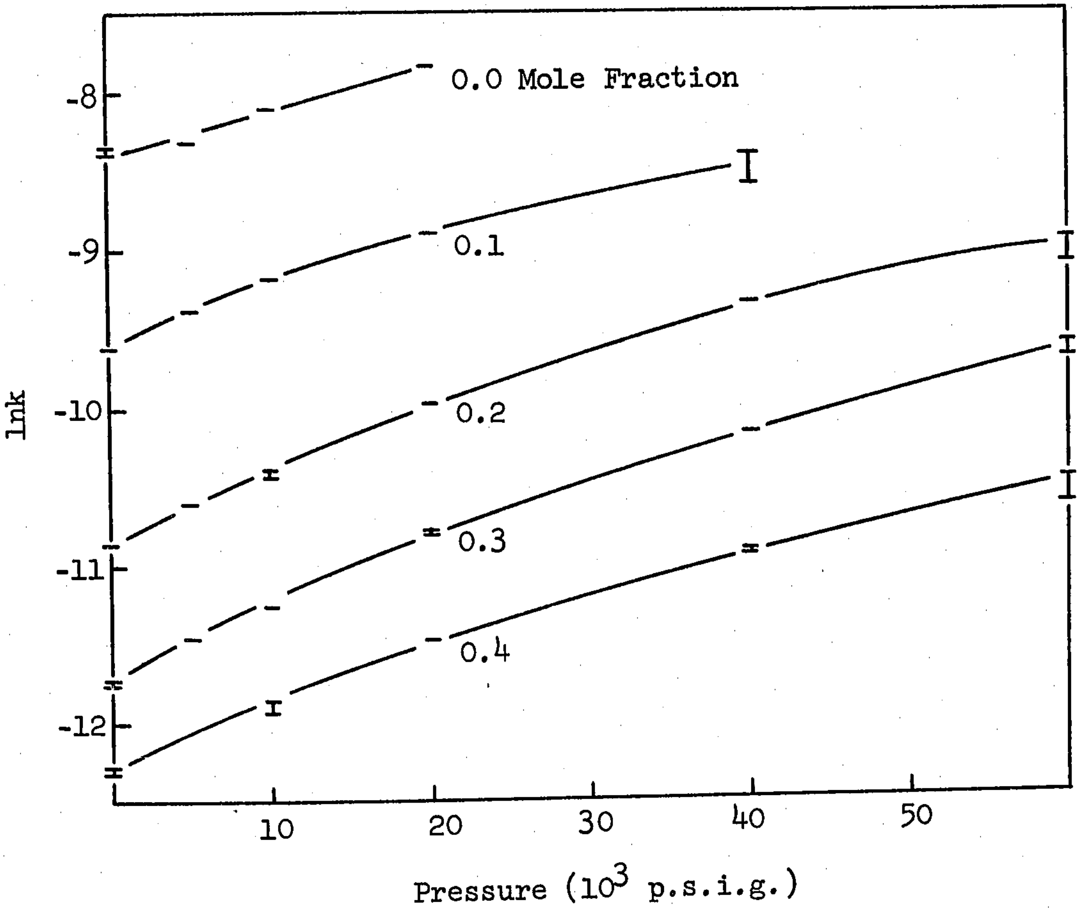


Fig. 7. Pressure dependence of the rate of solvolysis of benzyl chloride in aqueous ethanol.

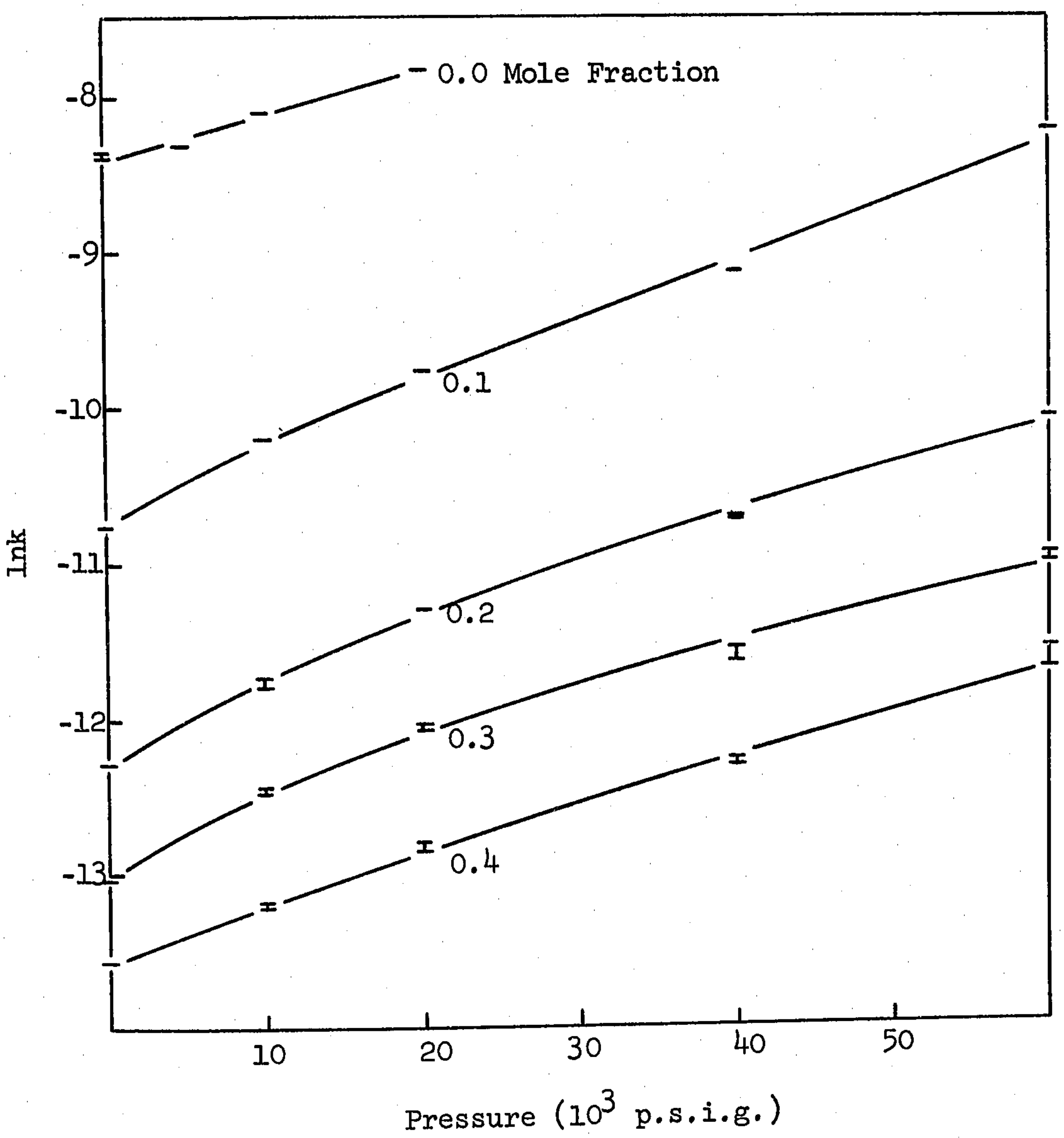


Fig. 8. Pressure dependence of the rate of solvolysis of benzyl chloride in aqueous i-propanol.

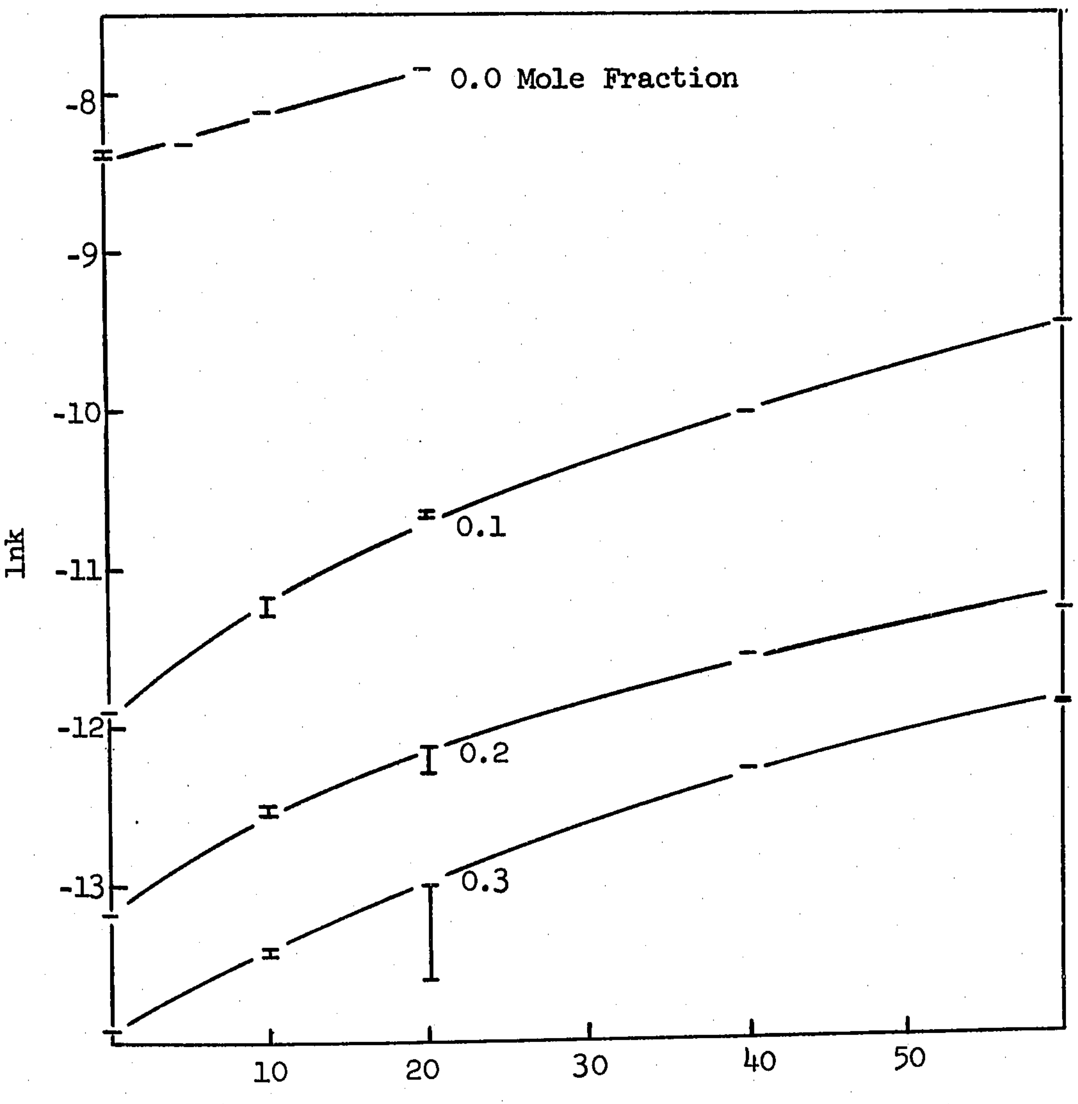


Fig. 9. Pressure dependence of the rate of solvolysis of benzyl chloride in aqueous t-butanol.

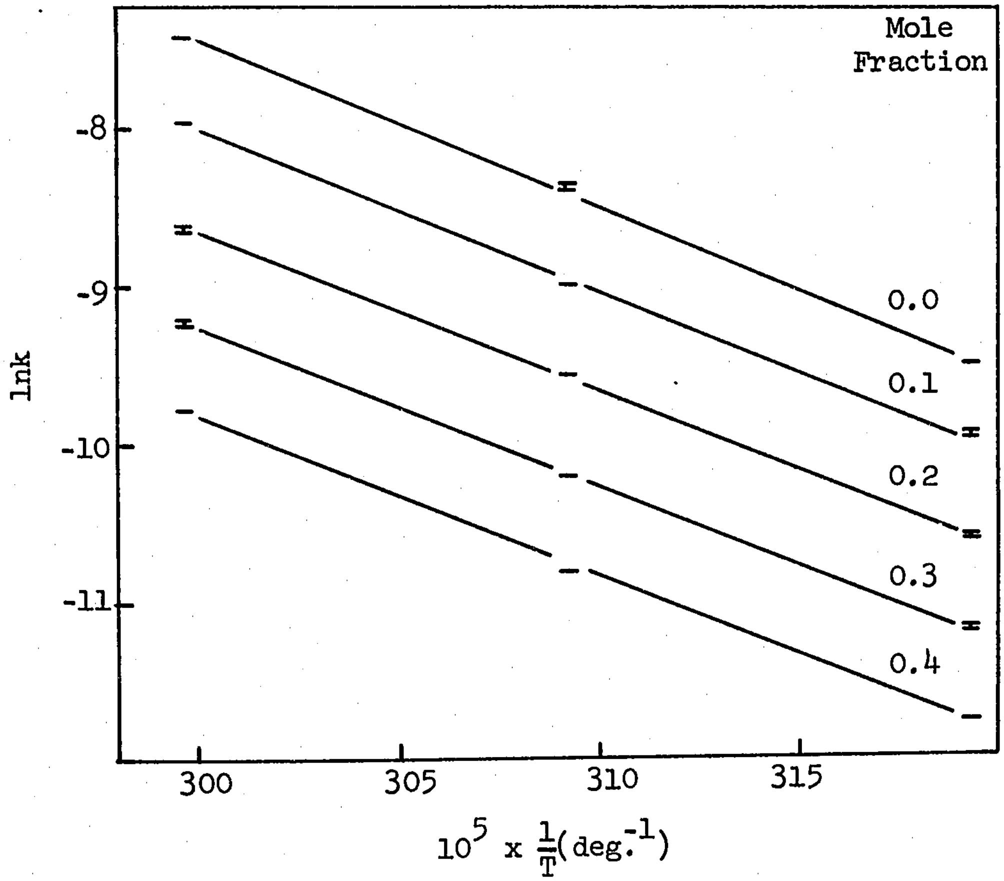


Fig. 10. Temperature dependence of the rate of solvolysis of benzyl chloride in aqueous methanol.

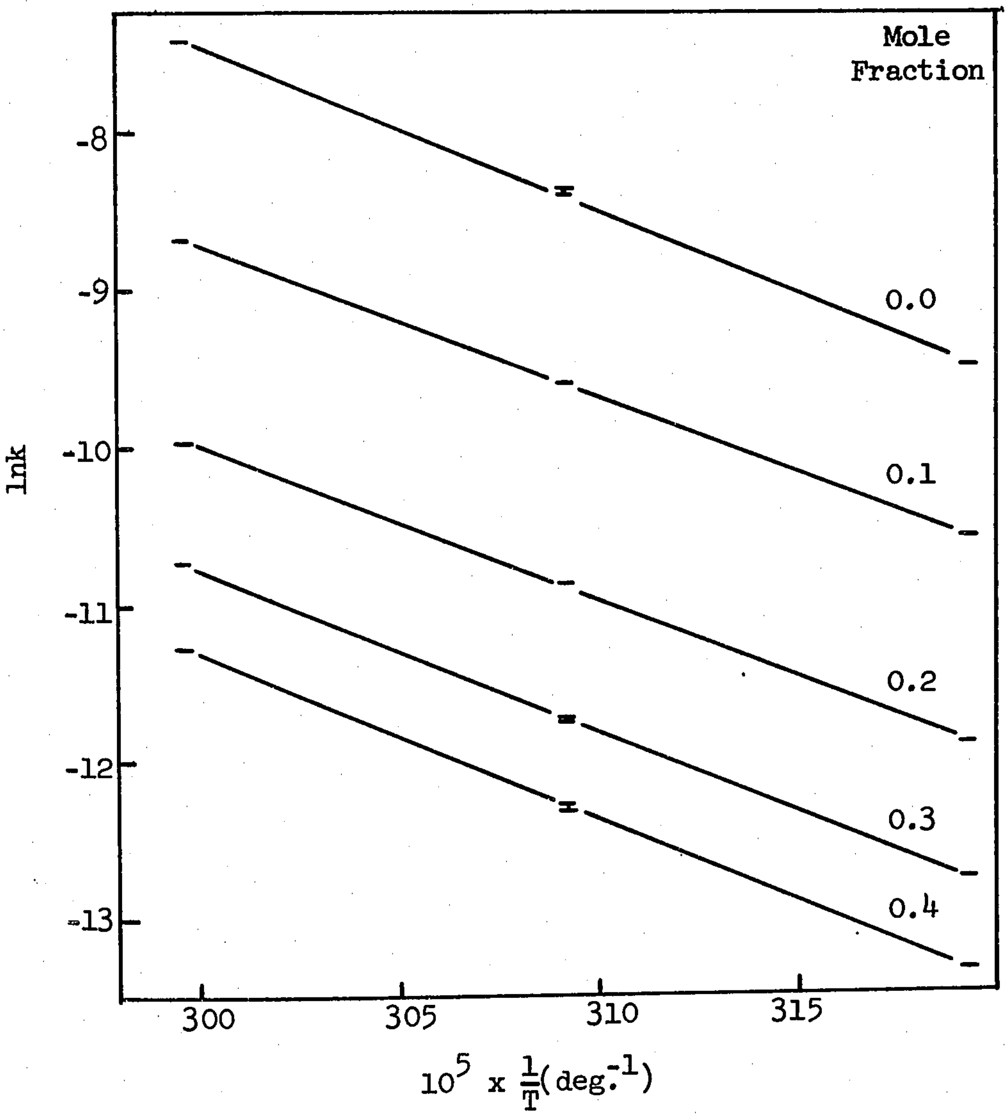


Fig. 11 Temperature dependence of the rate of solvolysis of benzyl chloride in aqueous ethanol.

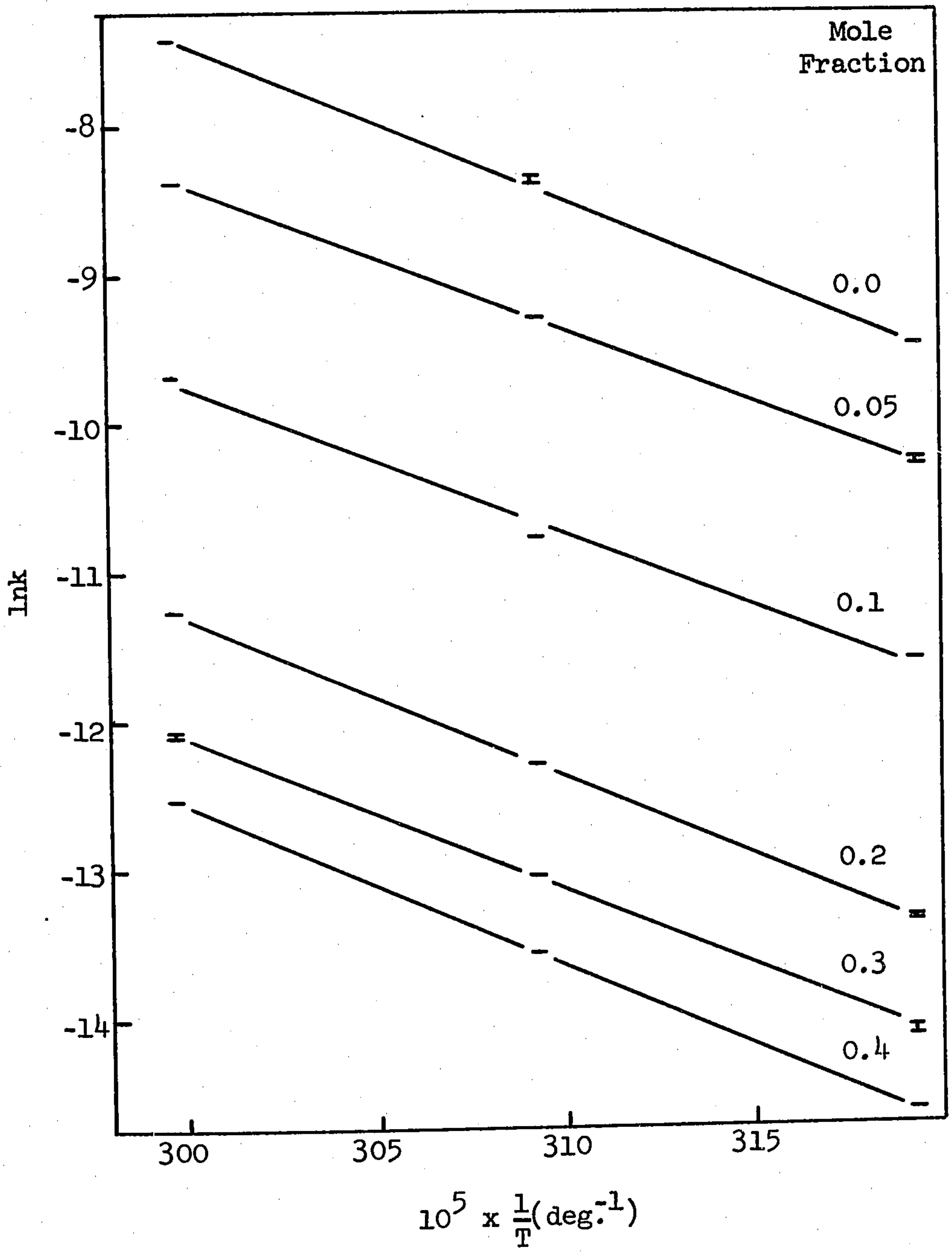


Fig. 12. Temperature dependence of the rate of solvolysis of benzyl chloride in aqueous i-propanol.

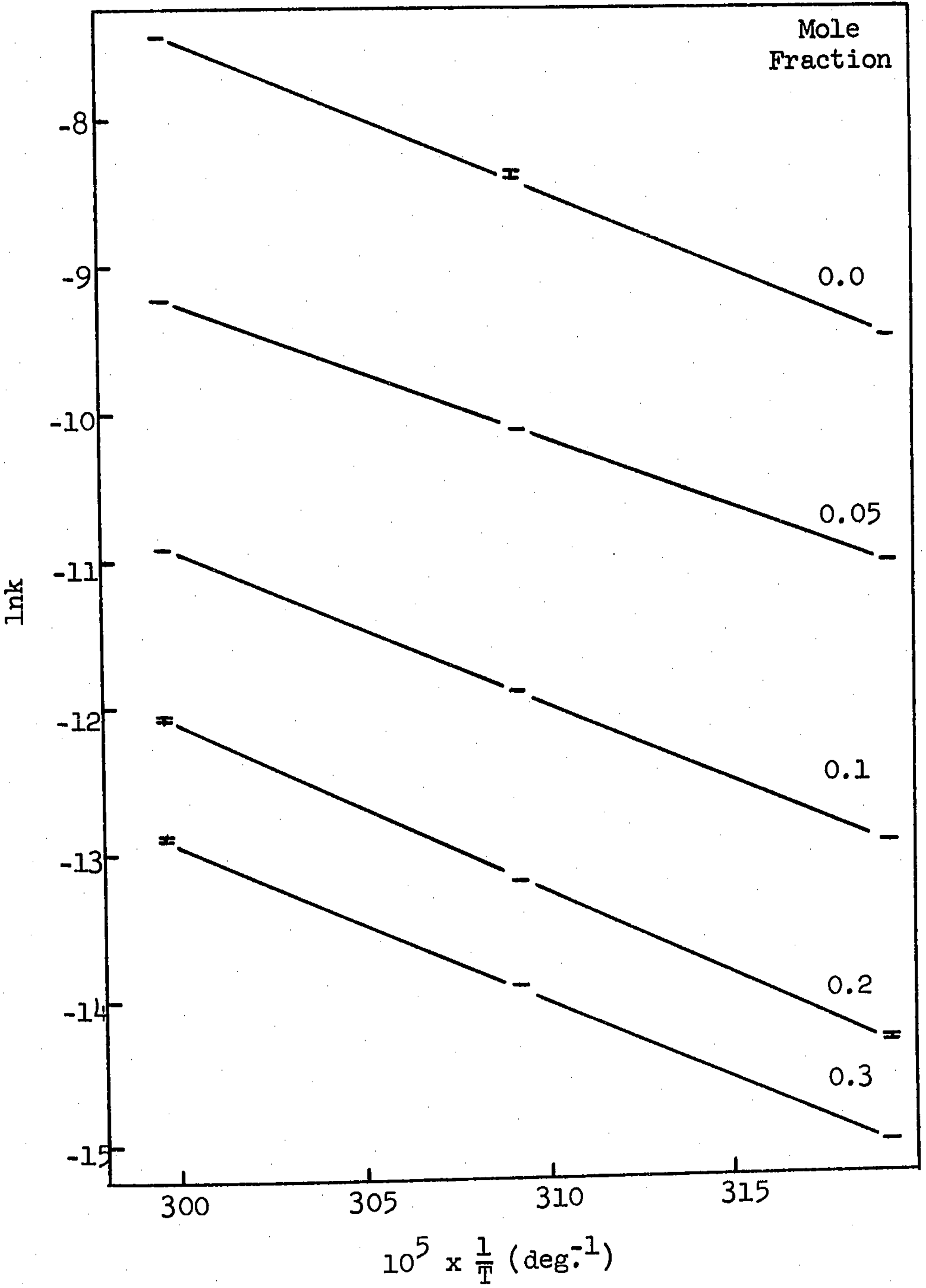


Fig. 13. Temperature dependence of the rate of solvolysis of benzyl chloride in aqueous t-butanol.

except that of 0.2 mole fraction ethanol at 50.30°C. However, the difference here is only 1.6%.

Activation Parameters

Volumes of Activation

In order to evaluate the volume of activation for a set of rate constants at various pressures using eq. 25, it is necessary to ascertain

$$\Delta V^{*} = - RT\left(\frac{\partial \ln k}{\partial p}\right)_T \qquad (25)$$

the functional dependence of lnk upon p. This functional dependence has been discussed at some length in the literature, but no unequivocal solution appears to have evolved.[a] This question will be treated in the following chapter.

It will suffice for the moment to indicate that of the analytical functions studied a second order polynomial (eq. 26) was found to best

$$\ln k = A + Bp + Cp^2 \qquad (26)$$

represent the data of Table III. Upon differentiation of eq. 26 with respect to pressure and identifying the coefficients with those of eq. 25 the activation volume at atmospheric pressure is given by eq. 27.

---

[a] The most common method involves a graphical estimation of the slope of lnk vs. p.

$$\Delta V_o^{\ast} = - RTB \qquad (27)$$

Similarily the pressure dependence of the activation volume is seen from eq. 25 to be

$$\left(\frac{\partial \Delta V^{\ast}}{\partial p}\right)_T = - RT\left(\frac{\partial^2 \ln k}{\partial p^2}\right)_T. \qquad (28)$$

Using the quadratic function (eq. 26) this pressure dependence is given by

$$\left(\frac{\partial \Delta V^{\ast}}{\partial p}\right)_T = - 2RTC. \qquad (29)$$

The parameters of eq. 26 were calculated from the rate data by the method of least squares on an IBM-1620 computer using the Fortran program of Appendix III (p. 229). (The values of these parameters are tabulated in Appendix III). The values of the activation volume for the solvolysis of benzyl chloride and the values for the pressure dependence of this parameter are given in Table V.

Enthalpies of Activation

According to the transition state theory, the temperature dependence of the rate constant is given by eq. 30. Hyne and Robertson[142] have shown that the temperature dependence of reaction rates is well

TABLE V

Activation Parameters for the Solvolysis of Benzyl Chloride at 50.25°C.

Mole Fraction Alcohol	$\Delta V_o^\neq$ (ml./mole)	$10^5 x(\partial \Delta V^\neq/\partial p)_T$ (ml./p.s.i. mole)	$\Delta H^\neq$ (kcal./mole)	$\Delta S^\neq$ (cal./deg. mole)
Methanol				
0.000	- 8. ± 1.	-20.0 ± 10.	20.3 ± 0.3	-12.5 ± 0.9
0.100	-12.13 ± 0.06	- 0.3 ± 0.5	19.54 ± 0.08	-16.1 ± 0.3
0.200	-15.6 ± 0.2	21. ± 2.	19.3 ± 0.3	-18. ± 1.
0.300	-17.9 ± 0.1	26. ± 1.	19.0 ± 0.3	-20.1 ± 0.8
0.400	-19.8 ± 0.5	28. ± 2.	20.1 ± 0.3	-18.2 ± 0.8
0.500	-18.8 ± 0.2	21.7 ± 0.4		
Ethanol				
0.100	-17. ± 1.	30. ± 9.	18.8 ± 0.1	-19.7 ± 0.4
0.200	-20.0 ± 0.9	27. ± 4.	19.1 ± 0.2	-21.3 ± 0.8
0.300	-19.5 ± 0.5	20. ± 2.	20.1 ± 0.2	-19.9 ± 0.7
0.400	-17.9 ± 0.9	22. ± 4.	20.5 ± 0.2	-19.8 ± 0.6
<u>i</u>-Propanol				
0.050			18.26 ± 0.02	-20.72 ± 0.06
0.100	-23.1 ± 0.2	35.0 ± 0.7	18.45 ± 0.07	-23.1 ± 0.2
0.200	-19.0 ± 0.1	16.8 ± 0.5	20.8 ± 0.3	-19. ± 1.
0.300	-18.1 ± 0.5	18. ± 1.	20.16 ± 0.07	-22.3 ± 0.2
0.400	-13.62 ± 0.04	5. ± 1.	21.0 ± 0.2	-20.6 ± 0.5
<u>t</u>-Butanol				
0.050			17.6 ± 0.2	-24.5 ± 0.7
0.100	-25.5 ± 0.1	33.52 ± 0.07	20.0 ± 0.2	-20.5 ± 0.5
0.200	-22.7 ± 0.8	35. ± 3.	22.2 ± 0.2	-16.4 ± 0.7
0.300	-17. ± 3.	11. ± 10.	21.2 ± 0.3	-20.7 ± 0.8

$$\ln k = \ln\frac{k_b T}{h} - \frac{\Delta H^{\ast}}{RT} + \frac{\Delta S^{\ast}}{R} \qquad (30)$$

expressed by the empirical relation

$$\ln k = \frac{A}{T} + B\ln T + C \qquad (31)$$

from which the activation parameters are given by

$$\Delta H^{\ast} = R(\,-A + BT - T) \qquad (32)$$

$$\Delta S^{\ast} = R(C - \ln\frac{k_b}{h} + B - 1) \qquad (33)$$

$$\Delta C_p^{\ast} = R(B - 1). \qquad (34)$$

In principle the parameters of eq. 31 can be found from three rate constants at three temperatures. Since this is precisely what is given in Table IV, it would appear that $\Delta C_p^{\ast}$ might also be obtained as an added dividend in this study. However, as Robertson has indicated,[143] a temperature range of approximately 50°C. is desired for the calculation of $\Delta C_p^{\ast}$, and the accurate determination of this parameter requires many more than three rate constants. Consequently, eq. 31 was not used here. Instead eq. 35 was used which is deriveable from eq. 30 for two rate

$$\Delta H^{\ast} = -R\left[\frac{\ln k_2 - \ln k_1 - \ln T_2 + \ln T_1}{\frac{1}{T_2} - \frac{1}{T_1}}\right] \qquad (35)$$

constants, k_2 and k_1, at temperatures T_2 and T_1 respectively.

The rate constants at 40.05°C. and 60.50°C. were used to calculate the activation enthalpy. The values obtained are shown in Table V and can be associated with the mean temperature of 50.25°C.

Comparison of the activation enthalpies with those previously reported shows excellent agreement. Robertson, Heppolette and Scott[144] reported a value of 20,388 cal./mole in water. If RT at 51.65°C. (646 cal./mole) is subtracted from the Arrhenius activation energies reported by Hyne, Wills and Wonkka[106] values of $\Delta H^{\ddagger}$ are obtained. These are in water 20,367 cal./mole and in 0.203 mole fraction ethanol 19,563 cal./mole.

Entropies of Activation

Having obtained the enthalpy of activation as in the previous section, the activation entropy can be calculated by means of eq. 30. This was done using the rate constant at 50.25°C. and atmospheric pressure. The values obtained are shown in Table V.

In summary, it should be indicated that a fairly extensive profile of the pseudo thermodynamic parameters for benzyl chloride solvolysis in aqueous methanol, ethanol, *i*-propanol and *t*-butanol is now available. Table V contains values for the volume change on activation, $\Delta V_0^{\ddagger}$, the pressure dependence of the activation volume, $(\partial \Delta V^{\ddagger}/\partial p)_T$, the enthalpy of activation, $\Delta H^{\ddagger}$, and the entropy of activation, $\Delta S^{\ddagger}$, all at 50.25°C.

Precision Estimates

As stated previously the precision of the rate constants was measured by the average deviation of the individual determinations from the mean. It was then necessary to estimate the precision of the derived parameters.

If the absolute errors of the rate constants were known, the maximum errors of the derived parameters could be readily obtained by differentiation of the appropriate functions.[145] It seemed, therefore, that the maximum deviation of the derived parameters could also be obtained in this manner, and this method indeed was used.

As an illustration of this procedure, consider the entropy of activation. Rewriting eq. 30 gives eq. 36. If the total derivative

$$\Delta S^{*} = R(\ln k - \ln\frac{k_bT}{h} + \frac{\Delta H^{*}}{RT}) \tag{36}$$

of this function is now taken eq. 37 is obtained. Thus, $d\Delta S^{*}$ can be evaluated by taking the average deviation of the rate constant for dk

$$d\Delta S^{*} = R(\frac{dk}{k} - \frac{dT}{T} + \frac{d\Delta H^{*}}{RT} - \frac{\Delta H^{*}dT}{RT^2}) \tag{37}$$

and the temperature fluctuation limit for dT--the signs being taken as positive in all cases. The value of $d\Delta H^{*}$ is obtainable by differentiating eq. 35 and using the same treatment.

In those instances where a least squares treatment was used to extract the derived parameter (e.g. volumes of activation), the appropriate least squares function was differentiated and evaluated in the manner described. The error limits quoted in Table V for the derived activation parameters are precision estimates obtained in this manner.

CHAPTER 6

PRESSURE DEPENDENCE OF REACTION RATES

The question of obtaining a volume of activation from a set of rate constants at various pressures is one which has not been unambiguously answered. As previously mentioned the relation between the activation volume and the pressure dependence of the rate constant is given by eq. 38. The difficulty lies in determining the functional

$$\Delta V^{*} = - RT\left(\frac{\partial \ln k}{\partial p}\right)_T \qquad (38)$$

dependence of lnk upon p so that the derivative of lnk with respect to p can be evaluated.

In this study the main interest was in the variation of ΔV^{*} for reactions in solution as the composition of the binary solvent medium is changed. Since small changes in ΔV^{*} were to be expected, it was important to obtain as reliable a set of activation volumes as the data permit. This led to a study of various functional dependencies of the rate constant on pressure.

Whalley has demonstrated that one set of experimental data can give rise to different values of the activation volume depending upon the form of the analysis used.[3] Thus, from Hamann's data for the reaction of ethyl iodide with pyridine[146] Whalley, using two graphical curves, obtained values of -17 and -34 ml./mole.[3] Another example is that of the analysis of the data for the dimerization of isoprene. Walling and Peisach determined the activation volume to be -24.3 ml./mole at 60°C. from which they concluded that a non-cyclic transition state is involved.[38] Benson and Berson,[39] using the same data as Walling and Peisach,[38] calculated the activation volume to be -36.5 ml./mole, and concluded that the original authors' inference was not justified.

Methods

An examination of the literature shows that three basic functions have been employed for expressing the change of rate constant with pressure. The first assumes that the dependence of the logarithmic rate constant on pressure is linear.[44] This treatment regards the activation volume as being pressure independent, and consequently neglects a possible additional parameter--the change in isothermal compressibility during the activation process. The second function is a power series in p, usually of second order,[147] allowing for the pressure dependence of the activation volume. Benson and Berson[39] have used a modified form of the Tait equation[18b] to calculate both the volume of activation and the change in compressibility on activation.

Whalley has plotted the average slope of any increment of the lnk vs. p curve against the average pressure of that increment.[3] Extrapolation to an average pressure of zero gives an intercept which can be taken as equaling $(\partial \ln k/\partial p)_{T,p=0}$.

Benzyl Chloride Solvolysis

In this study each of the above methods was considered in turn using the forms shown below. Eqs. 39 and 40 represent the linear

$$\ln k = A + Bp \tag{39}$$

$$\ln k = \ln k_o + Bp \tag{40}$$

$$\ln k = A + Bp + Cp^2 \tag{41}$$

$$\ln k = \ln k_o + Bp + Cp^2 \tag{42}$$

$$\ln(k/k_o)/p = A + Bp^{0.523} \tag{43}$$

$$\ln(k_{n+1}/k_n)/(p_{n+1} - p_n) = A + B(p_{n+1} + p_n)/2 \tag{44}$$

dependence. In the former the intercept as well as the slope is considered to be determined by all the rate constants, while in the latter the assumption is made that the measured atmospheric rate constant is exact and the function is forced to pass through this point. In the following this will be referred to as the "forced intercept treatment". Eqs. 41 and 42 represent the second order polynomial, and differ from each other by the forced intercept treatment. Eq. 43 is the Benson-Berson analysis.[39] The reader is referred to the original literature[39] for the relation of the parameters A and B to the physically significant functions. Eq. 44 is an incremental analysis of the type used by Whalley.[3] It is assumed here that the incremental function is linear in form. The subscripts n and n+1 refer to adjacent experimental data on the appropriate graph.

Using the data for the solvolysis of benzyl chloride in water and in aqueous alcohols (Tables III and IV pp. 77 and 79), the various parameters of eqs. 39 through 44 were calculated using the method of least squares on an IBM-1620 computer. The Fortran programs used can be found in Appendices V through VII (pp. 237 - 253) together with some representative data. The actual parameters of the various equations are also tabulated in these appendices.

The values of the activation volume for the benzyl chloride solvolysis thus derived can be found in Table VI. In every case the values given are for atmospheric pressure except for the linear functions for which only the average value for the pressure range studied can be obtained.

Results

As stated previously, the present study is concerned with the variation of ΔV^{*} with solvent composition. This dependence is shown in Figs. 14 through 17 for each of the functions. It is readily apparent that the general shapes of the curves in each figure are similar viz. they all show a minimum. Therefore, it can be concluded, from a qualitative viewpoint, that the different functions give similar results.

However, from a quantitative viewpoint there are striking differences. The depths of the minima vary from 5 to 8 ml./mole for the linear analysis between ethanol and t-butanol, but range from 24 to 34 ml./mole for the Benson-Berson analysis. In the case of methanol no minimum is observed if the linear function is used, while a minimum with a depth of 24 ml./mole is obtained for the Benson-Berson function.

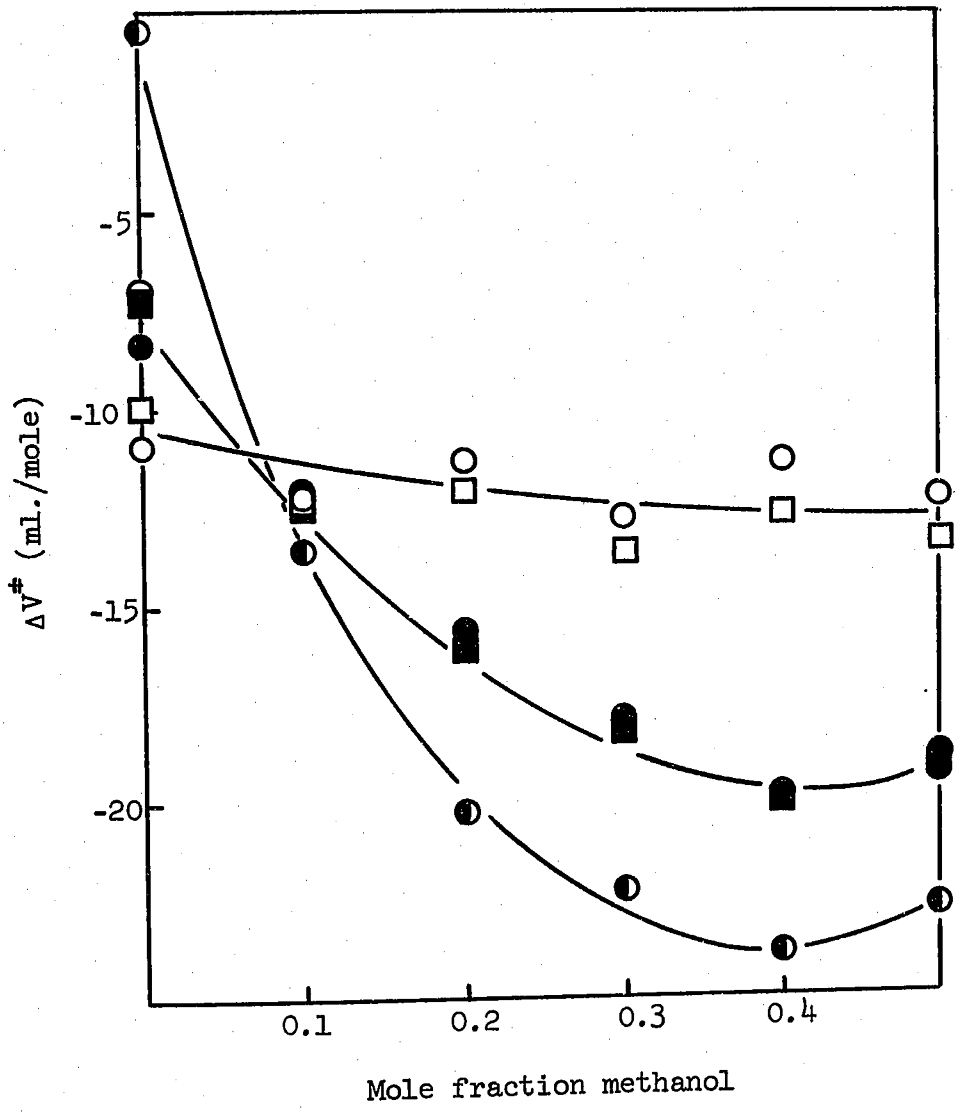


Fig. 14. Variation of $\Delta V^{\neq}$ for benzyl chloride solvolysis with solvent composition in aqueous methanol. ○linear, □linear forced intercept, ●quadratic, ■quadratic forced intercept, ◐Benson-Berson, ◒incremental.

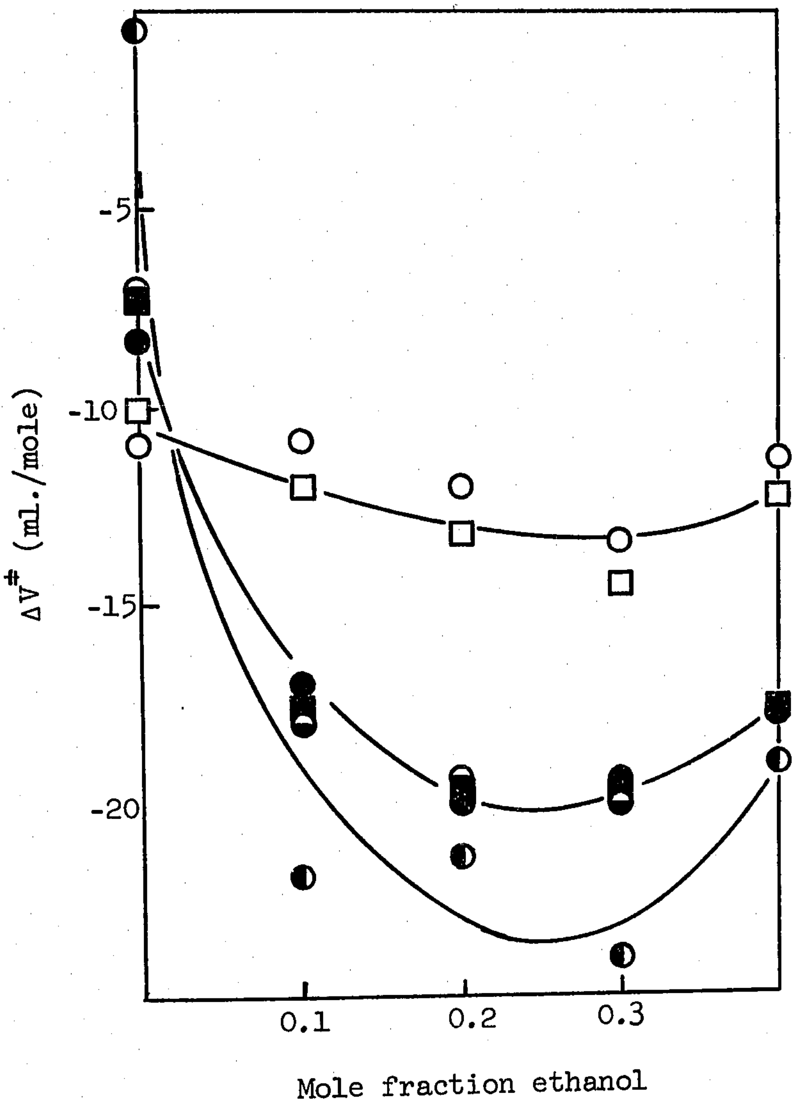


Fig. 15. Variation of $\Delta V^{\ddagger}$ for benzyl chloride solvolysis with solvent composition in aqueous ethanol. ○linear, □linear forced intercept, ●quadratic, ■quadratic forced intercept, ◐ Benson-Berson, ◓incremental.

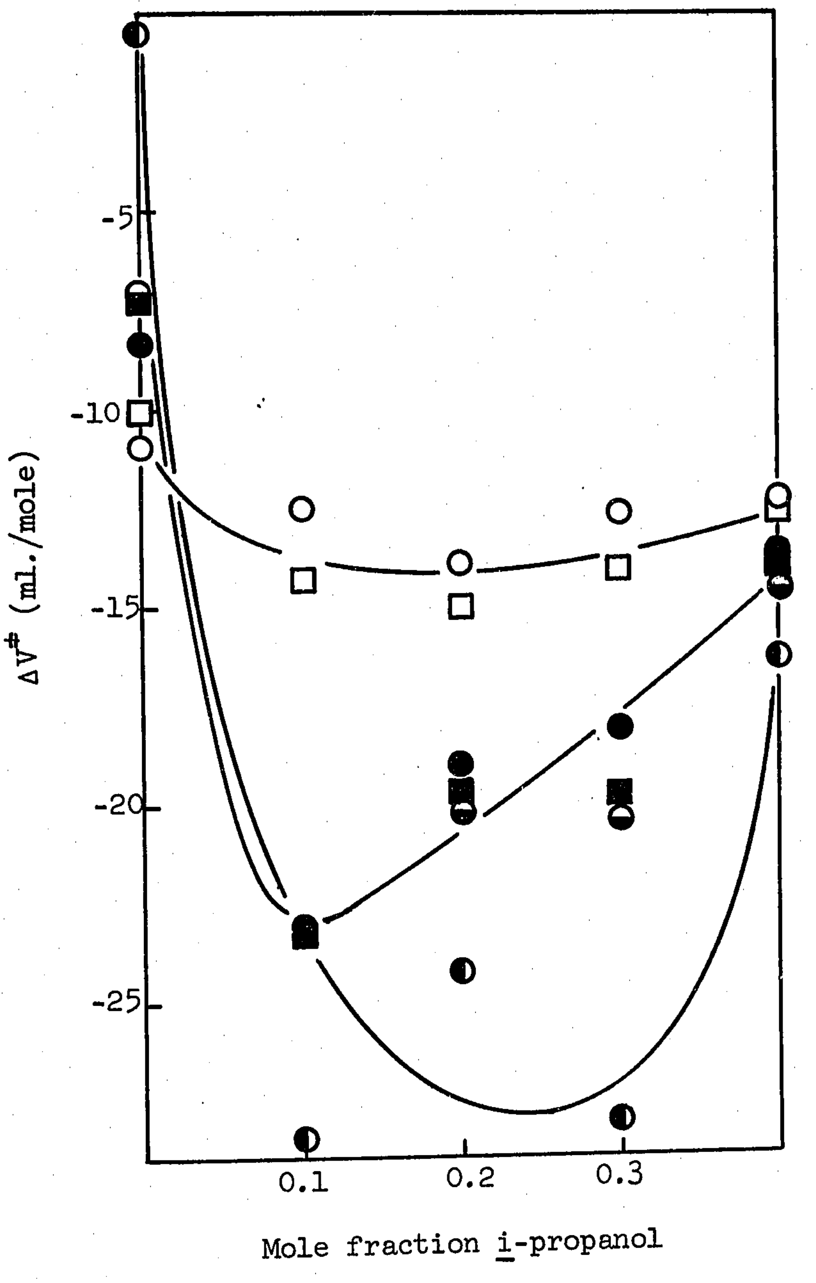


Fig. 16. Variation of $\Delta V^{\neq}$ for benzyl chloride solvolysis with solvent composition in aqueous i-propanol. ○ linear, □ linear forced intercept, ● quadratic, ■ quadratic forced intercept, ◐ Benson-Berson, ⊖ incremental.

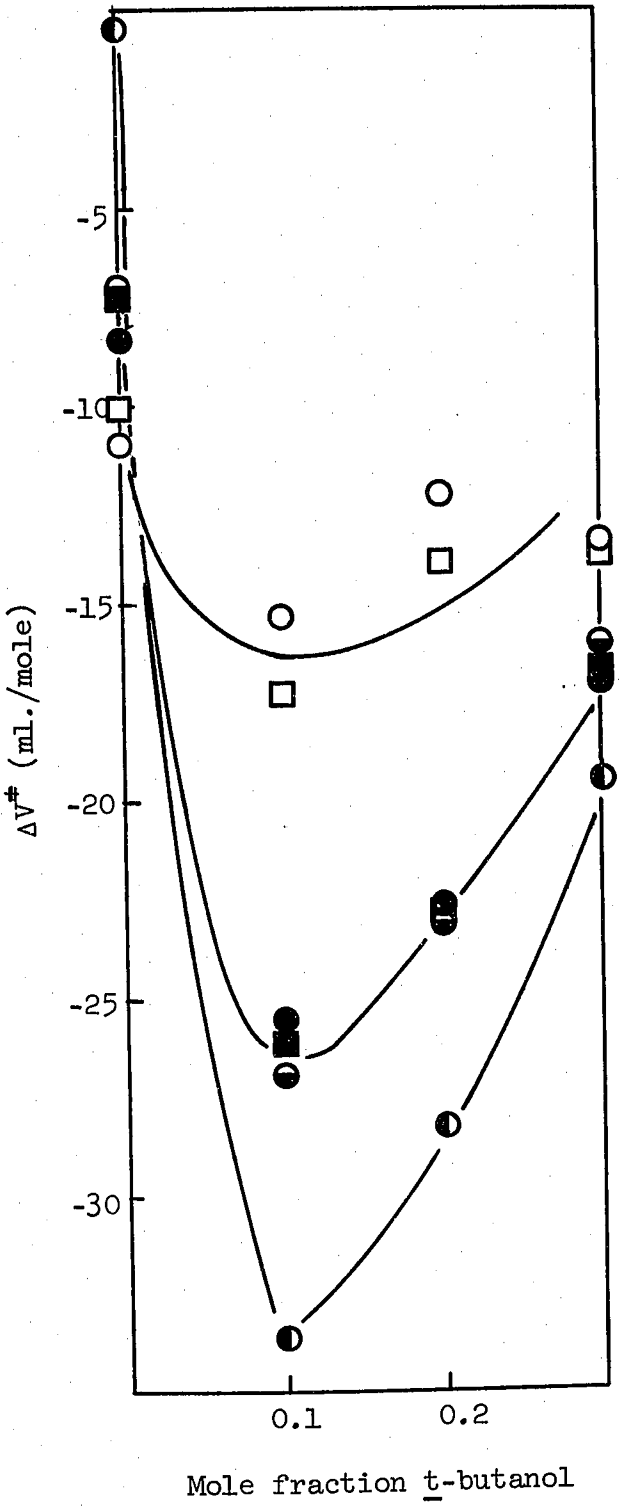


Fig. 17. Variation of $\Delta V^{\neq}$ for benzyl chloride solvolysis with solvent composition in aqueous *t*-butanol. ○linear, □linear forced intercept, ●quadratic, ■quadratic forced intercept, ◐ Benson-Berson, ⊖incremental.

TABLE VI

Volume of Activation for the Solvolysis of Benzyl Chloride at 50.25°C.

$\Delta V^{\ddagger}$ (ml./mole)

Method

Mole Fraction Alcohol	Linear	Linear Forced Intercept	Quadratic	Quadratic Forced Intercept	Benson-Berson	Incremental
	eq. 39	40	41	42	43	44
			Methanol			
0.000	-10.9	-10.0	- 8.3	- 7.2	- 0.4	- 7.0
0.100	-12.2	-12.3	-12.1	-12.4	-13.6	-12.4
0.200	-11.3	-12.1	-15.6	-16.1	-20.2	-16.1
0.300	-12.7	-13.6	-17.9	-18.2	-22.2	-18.3
0.400	-11.3	-12.7	-19.8	-19.9	-23.8	-19.9
0.500	-12.2	-13.4	-18.8	-19.1	-22.7	-19.2
			Ethanol			
0.100	-10.8	-12.0	-17.0	-17.6	-21.9	-18.0
0.200	-12.0	-13.2	-20.0	-19.7	-21.5	-19.4
0.300	-13.4	-14.5	-19.5	-20.0	-24.0	-20.0
0.400	-11.3	-12.3	-17.9	-17.7	-19.0	-17.7
			i-Propanol			
0.100	-12.5	-14.3	-23.1	-23.3	-28.5	-23.3
0.200	-13.9	-15.0	-19.0	-19.8	-24.2	-20.2
0.300	-12.6	-14.1	-18.1	-19.8	-28.1	-20.4
0.400	-12.2	-12.6	-13.6	-14.1	-16.3	-14.4

TABLE VI (con't)

ΔV^{*} (ml.mole)

Method

Mole Fraction Alcohol	Linear	Linear Forced Intercept	Quadratic	Quadratic Forced Intercept	Benson-Berson	Incremental
	eq. 39	40	41	42	43	44
			t-Butanol			
0.100	-15.3	-17.3	-25.5	-26.1	-33.6	-26.9
0.200	-12.2	-14.0	-22.7	-22.9	-28.2	-22.9
0.300	-13.4	-13.9	-16.9	-16.7	-19.5	-16.0

Though the exact position of the minima cannot be ascertained in the present study, it appears that the position is invariant with the function used. The one apparent exception is that of i-propanol (Fig. 16). The linear function shows a minimum near 0.2 mole fraction alcohol, while that for the quadratic and Whalley analyses is near 0.1 mole fraction. Due to the large amount of scatter in the Benson-Berson function the position cannot be determined.

Evidently, for the purpose of this study it is necessary to ascertain which analysis is the most reliable. Before undertaking this task, it will prove expedient to compare the linear and quadratic functions with their respective forced intercept treatments.

The results from the two quadratic functions can be seen to agree in each instance within 1 ml./mole (Table VI p. 103). The only two exceptions are water and 0.3 mole fraction i-propanol. The reason for these two discrepancies is not clear. The linear methods do not agree so well; the deviations being within 2 ml./mole. However, the agreement is still quite good. It is therefore apparent that only one each of the linear and quadratic treatments need be considered in the ensuing discussion.

Empirical Evaluation

Having obtained the constants of the functions (eqs. 39 to 44) it is a simple matter to calculate a value for lnk at each of the experimental pressures. Having this value the deviation can then be calculated according to eq. 45. For the Benson-Berson function

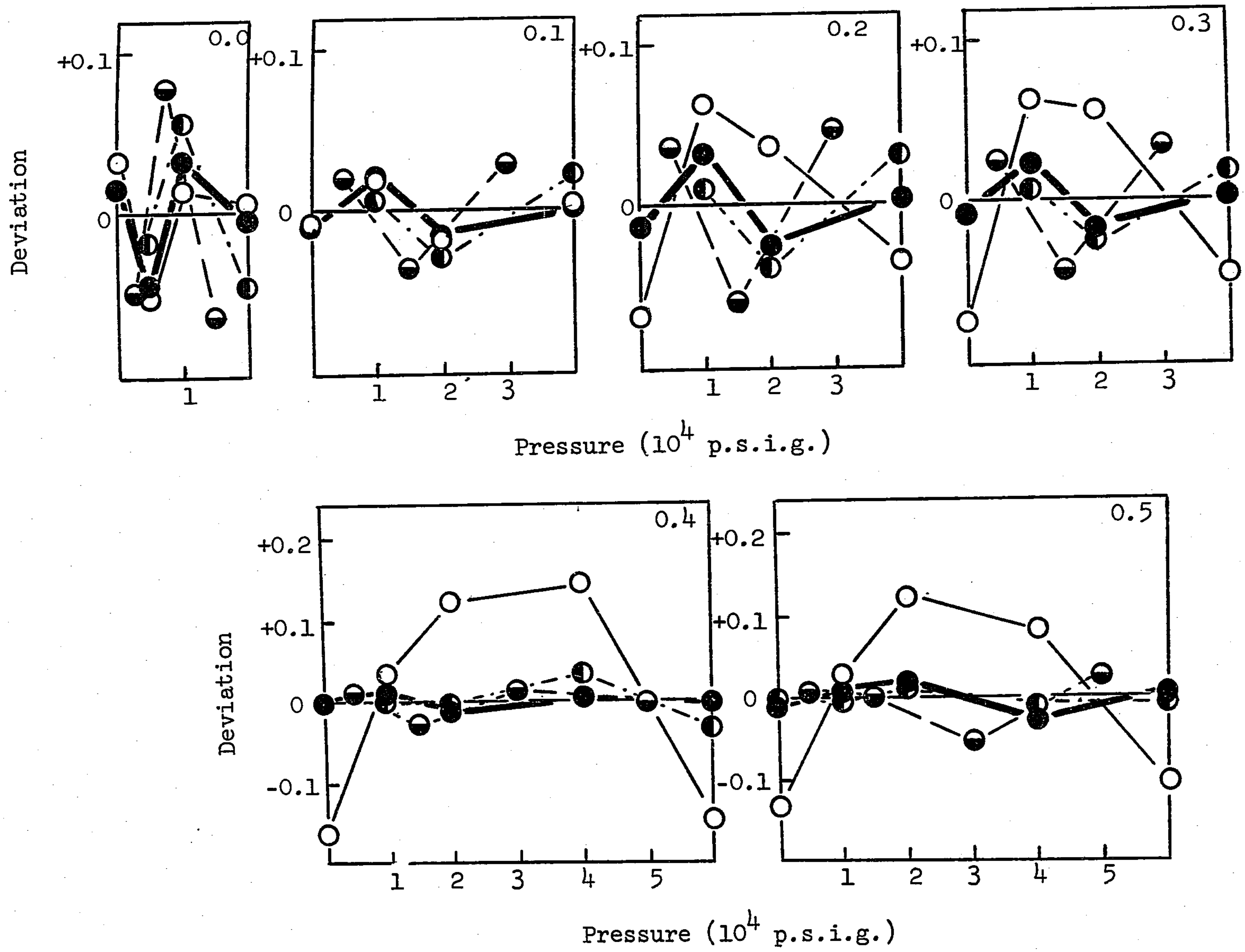


Fig. 18. Variation of the deviation of lnk with pressure for benzyl chloride solvolysis in aqueous methanol. ○linear, ●quadratic, ◐Benson-Berson, ⊖incremental.

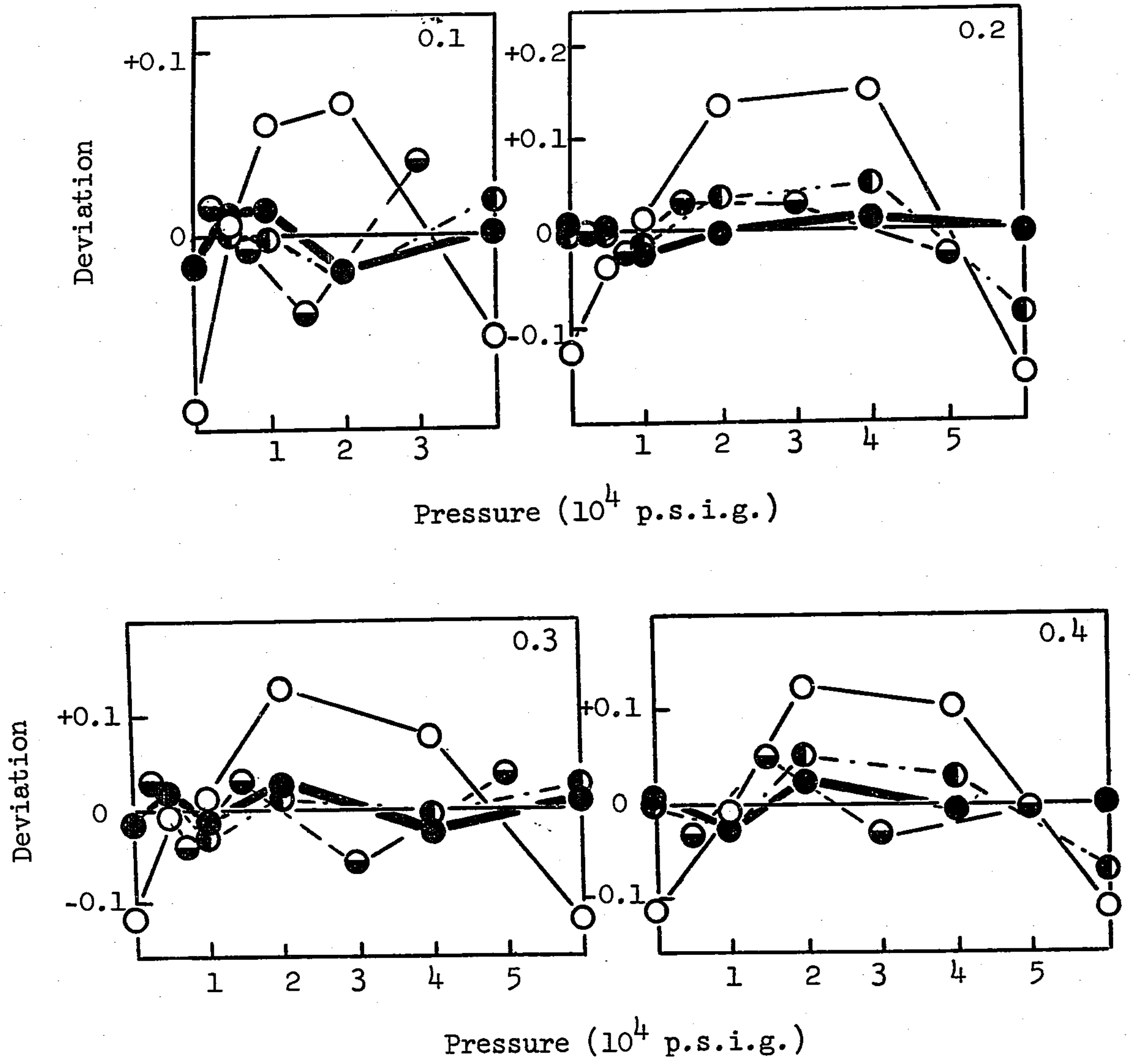


Fig. 19. Variation of the deviation of lnk with pressure for benzyl chloride solvolysis in aqueous ethanol. ○linear, ● quadratic, ◐Benson-Berson, ◒incremental.

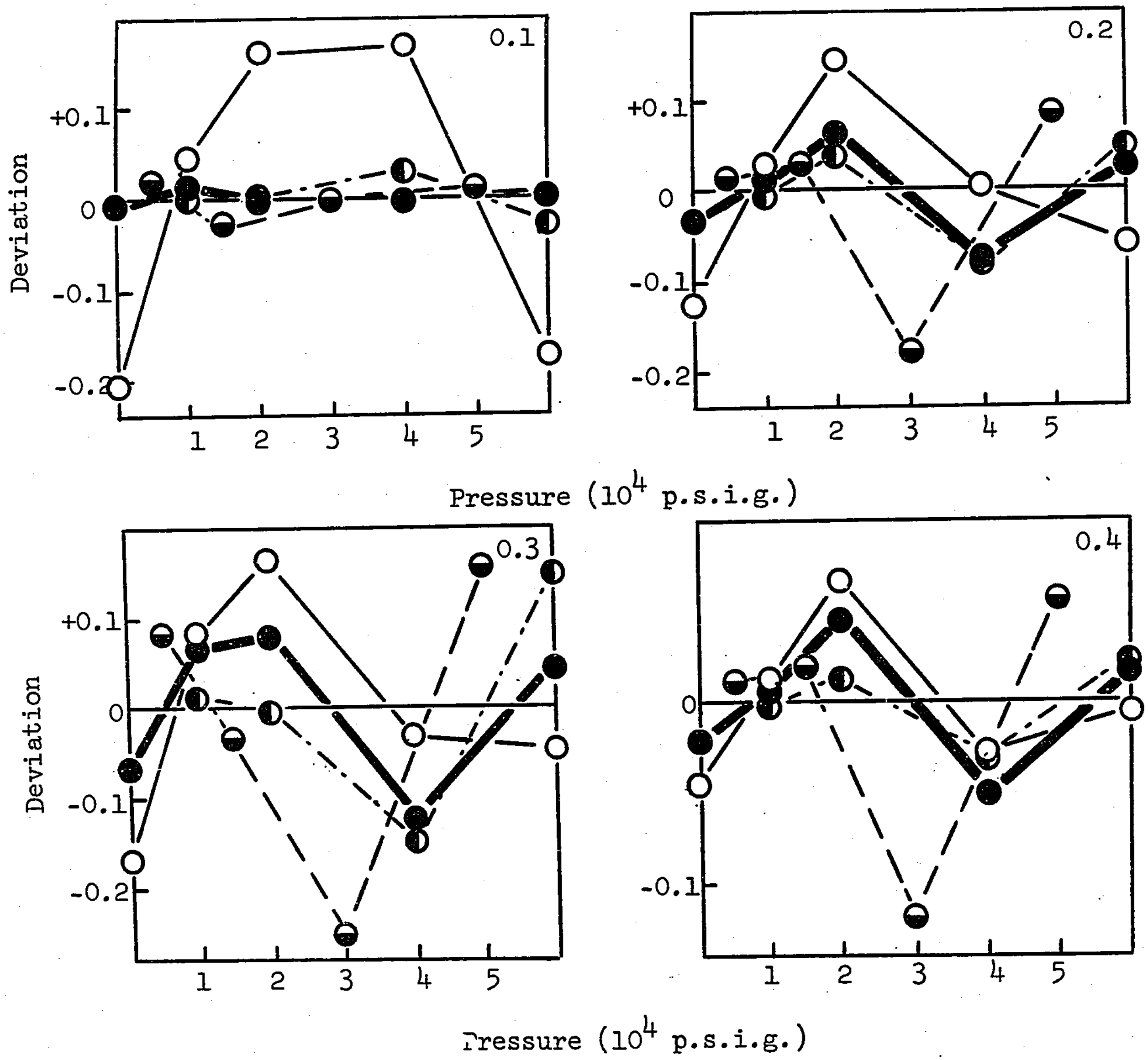


Fig. 20. Variation of the deviation of lnk with pressure for benzyl chloride solvolysis in aqueous i-propanol. ○linear, ●quadratic, ◐Benson-Berson, ◒incremental.

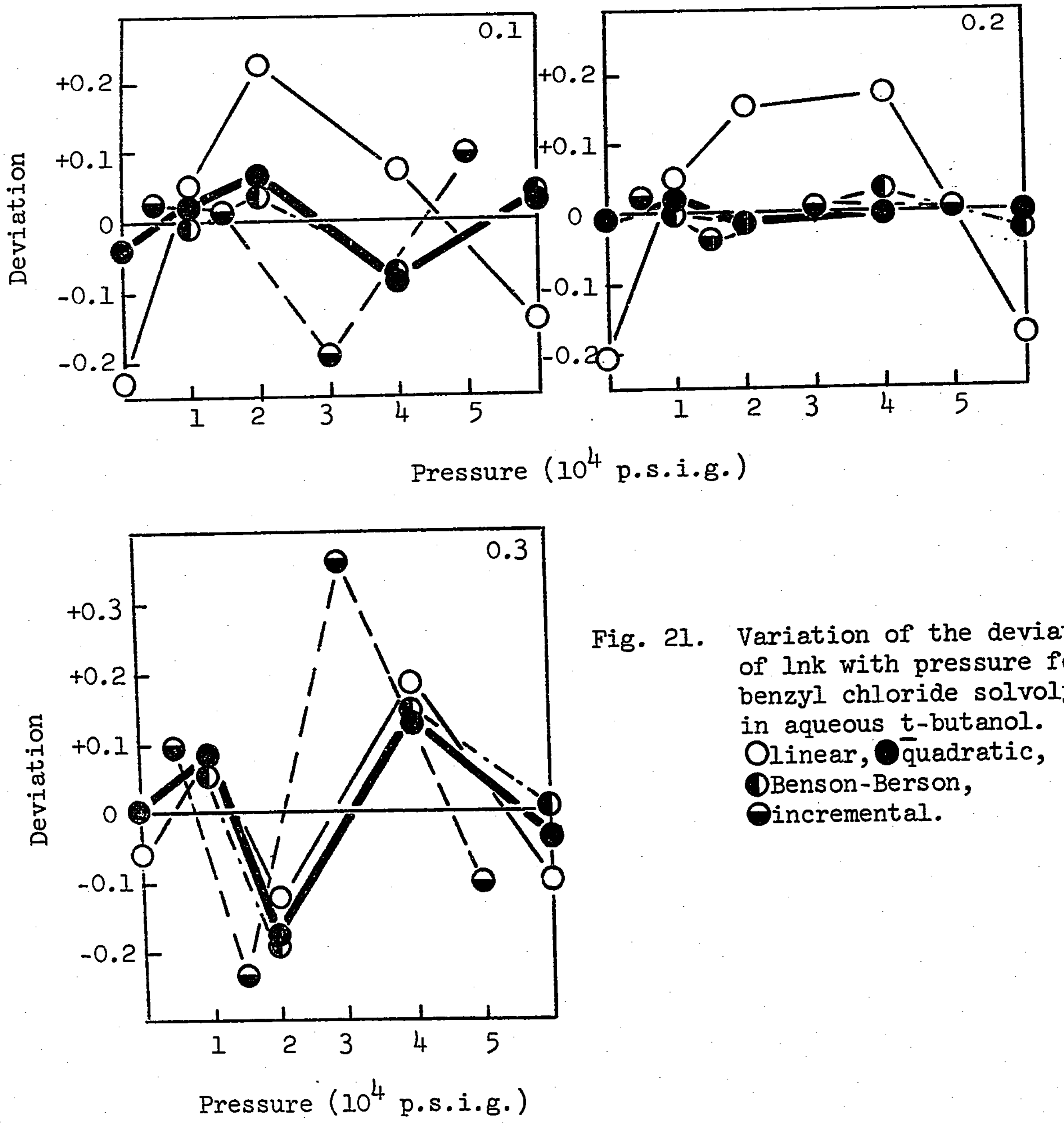


Fig. 21. Variation of the deviation of lnk with pressure for benzyl chloride solvolysis in aqueous t-butanol.
○linear, ●quadratic,
◐Benson-Berson,
◒incremental.

$$\text{deviation} = \ln k_{obs} - \ln k_{calc} \tag{45}$$

(eq. 43) the experimental value of $\ln k_o$ was used in these calculations. The Whalley method (eq. 44) has two unknowns, k_{n+1} and k_n, prohibiting the determination of $\ln k_{calc}$. Therefore only the value of $\ln(k_{n+1}/k_n)_{calc}$ can be evaluated and compared with the observed value. In this case the deviation is defined by eq. 46. The

$$\text{deviation} = \ln(k_{n+1}/k_n)_{obs} - \ln(k_n)_{calc} \tag{46}$$

deviations for the various analyses as a function of pressure are shown in Figs. 18 through 21. In order to avoid loss of clarity in these graphs only eq. 39 was used to represent the linear analysis, and eq. 41 was used for the quadratic analysis (i.e. the non-forced intercept treatments in each case).

The most noticeable feature in each of these figures is the systematic error present in the linear analysis. Only for water, 0.1 $X_{methanol}$, 0.3 $X_{\underline{i}\text{-propanol}}$ and 0.3 $X_{\underline{t}\text{-butanol}}$ does this function appear to give a random error. The fact that systematic errors appear when this function is used necessitates the conclusion that it is not a reliable representative function of the data presented here. The second order polynomial, the modified Tait equation, and the incremental analysis all appear to give random scatter about zero. The only exceptions appear to be the Benson-Berson treatment for 0.4 $X_{ethanol}$ and 0.3 $X_{\underline{i}\text{-propanol}}$, and the Whalley treatment for 0.2 $X_{ethanol}$, 0.1 $X_{\underline{i}\text{-propanol}}$, 0.3 $X_{\underline{i}\text{-propanol}}$ and 0.1 $X_{\underline{t}\text{-butanol}}$.

A further comparison of the various treatments is shown in Table VII where the standard deviations (as calculated by eq. 47) are recorded. In accord

$$\text{s.d.} = \sqrt{\frac{\Sigma(\text{deviation})^2}{n - 1}} \tag{47}$$

with the above conclusion, it can be seen that the standard deviations for the linear functions are generally the largest. It may also be noted that without exception the forced intercept treatment gives a larger standard deviation than the non-forced intercept method. This is not surprising since the forced intercept method removes one degree of freedom from the analysis. It is readily apparent that the quadratic function gives a smaller deviation than either the Benson-Berson or Whalley treatments. It can therefore be concluded that a second order polynomial is the most reliable function for the present data.

Physical Evaluation

Though it has been shown that the present data are best accommodated by a second order polynomial, there will undoubtedly be cases in which one of the other methods will be more appropriate. An analysis of the physical significance of each function would therefore be useful.

The first order polynomial ignores the fact that the transition

TABLE VII

Standard Deviations for Benzyl Chloride Solvolysis at 50.25°C.

	s.d.					
	Method					
Mole Fraction Alcohol	Linear	Linear Forced Intercept	Quadratic	Quadratic Forced Intercept	Benson-Berson	Incremental
	eq. 39	40	41	42	43	44
			Methanol			
0.000	0.0362	0.0529	0.0326	0.0416	0.0536	0.0779
0.100	0.0145	0.0187	0.0145	0.0187	0.0253	0.0351
0.200	0.0602	0.0952	0.0245	0.0311	0.0547	0.0583
0.300	0.0693	0.1087	0.0173	0.0224	0.0207	0.0421
0.400	0.1456	0.2144	0.0084	0.0095	0.0268	0.0182
0.500	0.1134	0.1710	0.0176	0.0215	0.0105	0.0362
			Ethanol			
0.100	0.0701	0.1131	0.0148	0.0195	0.0152	0.0339
0.200	0.1260	0.1748	0.0123	0.0155	0.0544	0.0251
0.300	0.0975	0.1477	0.0207	0.0259	0.0210	0.0449
0.400	0.1145	0.1617	0.0190	0.0228	0.0552	0.0405
			i-Propanol			
0.100	0.1808	0.2685	0.0030	0.0105	0.0241	0.0192
0.200	0.1025	0.1570	0.0551	0.0667	0.0579	0.1155
0.300	0.1286	0.2037	0.0895	0.1126	0.1243	0.1790
0.400	0.0434	0.0639	0.0365	0.0442	0.0440	0.0766

TABLE VII (con't)

	s.d.					
	Method					
Mole Fraction Alcohol	Linear	Linear Forced Intercept	Quadratic	Quadratic Forced Intercept	Benson-Berson	Incremental
	eq. 39	40	41	42	43	44
			t-Butanol			
0.100	0.1830	0.2817	0.0604	0.3943	0.0529	0.1250
0.200	0.1794	0.2532	0.0127	0.0158	0.0245	0.0267
0.300	0.1312	0.1585	0.1172	0.1354	0.1431	0.2600
83 points	0.1110	0.1524	0.0403	0.0949	0.0515	0.0783

state and substrate may have different isothermal compressibilities. Consequently, the inadequacy of this function in giving a good fit for the present data is not surprising.

The use of a second order polynomial recognizes that $(\partial \Delta V^{*}/\partial p)_T \neq 0$, but requires that $(\partial^2 \Delta V^{*}/\partial p^2)_T = 0$. The question arises as to whether the present data are precise enough to allow a meaningful calculation of the pressure dependence of the volume change on activation. As can be seen in Table V (p. 90) the data are good enough, giving deviations of less than 10×10^{-10} ml./p.s.i. mole in each instance.

It is true, of course, that $(\partial^2 \Delta V^{*}/\partial p^2)_T$ is not generally zero. The compressibility of a real substance is known to be pressure dependent,[148] so that $(\partial^2 V/\partial p^2)_T \neq 0$. It would be fortuitous indeed if two substances had the same value for this derivative, especially when the polarities of the two differed markedly. Since the polarity of the initial state in the present reaction is small when compared with the transition state in the reaction under consideration, it is not to be expected that the two states will have the same value for the second pressure differential of the volume. Hence the difference in the values of this derivative cannot be zero. However, from an examination of the graphs in Figs. 18 through 21 it can be seen that the present data are not precise enough to warrant the use of a higher order polynomial in order to evaluate this derivative. If the data were precise enough for such an evaluation, then the quadratic analysis would be expected to show a systematic error much the same as the linear treatment.

Unfortunately, it is not possible to obtain the value of the compressibility of activation, $\Delta\kappa^{\ddagger}$, from the quadratic analysis. The pressure dependence of the activation volume is related to the isothermal compressibilities of the two states by eq. 48. It is therefore necessary

$$\left(\frac{\partial \Delta V^{\ddagger}}{\partial p}\right)_T = \bar{\kappa}_g \bar{V}_o^g \exp(-\bar{\kappa}_g p) - \bar{\kappa}_t \bar{V}_o^t \exp(-\bar{\kappa}_t p) \qquad (48)$$

to determine the value of $\bar{\kappa}_g$ independently in order to obtain $\bar{\kappa}_t$. In the reaction studied here the substrate reacts with the solvent so that a static measurement of the partial molal compressibility in the appropriate solvents cannot be made.

A good fit of the Benson-Berson equation was perhaps not to be expected. Benson and Berson pointed out that the exact pressure dependence of the rate constant is due to both the change in volume and the change in activity coefficient during the activation process.[39] For ionic reactions in water, the authors demonstrated that the term due to the activity coefficients is negligible, but may become important in solvents of lower dielectric constant. For non-ionic reactions this term is zero, and the authors used the Tait equation[18b] to represent the compressibilities of both the initial and transition states of the reaction. This led to the development of eq. 43. Since this function was developed for non-ionic reactions, it would not be expected to be useable for the present data of an ionogenic reaction. However, the activity coefficient contribution can be shown to be negligible for the present reaction, by the following argument.

If the transition state is considered in the limit as a doubly charged ion, the Debye-Hückel limiting law[18c] can be used, after the method of Benson and Berson,[39] giving rise to eq. 49. In the reaction under consideration a 1:1 electrolyte, hydrochloric acid, is produced

$$\Delta V^{\ddagger}_{\gamma} = 1.5RTz^2_{t.s.}\mu^{1/2}A\left(\frac{\partial \ln D}{\partial p}\right)_T \qquad (49)$$

in a maximum concentration of 5×10^{-4} moles/liter (see Chapter 4). Using the values of 5.9×10^{-5} atm.$^{-1}$ and 0.51 lit.$^{1/2}$/mole$^{1/2}$ for $(\partial \ln D/\partial p)_T$ and A respectively for water at 25°C.,[39] the value of $\Delta V^{\ddagger}_{\gamma}$ is found to be 0.002 ml./mole. As an indication of the value of this contribution in the higher alcohol content solvents, pure ethanol can be considered as being representative. This value of A is 2.8 lit.$^{1/2}$/mole$^{1/2}$ while that for $(\partial \ln D/\partial p)_T$ is 9.2×10^{-5} atm.$^{-1}$ at 20°C.[149] This makes $\Delta V^{\ddagger}_{\gamma} = 0.03$ ml./mole. It is clear that the contribution due to the activity coefficients is completely negligible in the solvents considered in this study.

According to the Benson-Berson treatment, the volume of activation is[39]

$$\Delta V^{\ddagger}_{o} = -\frac{RTA}{1 - 0.008C} \qquad (50)$$

where A is the constant from eq. 43 and C is a parameter of the Tait equation. Since the Tait constant enters only as a small correction term in eq. 50, its value can vary widely from that reported by Benson and Berson and still show no significant effect on $\Delta V^{\ddagger}_{o}$. Consequently, the activation volumes calculated by eq. 43 should not be unreasonable. However, since the Tait equation parameters enter into the value of B of eq. 43 in a rather significant manner,[39] evaluation of $(\partial \Delta V^{\ddagger}/\partial p)_T$ by this method may have rather large errors.

The incremental slope analysis (eq. 44) is seen to give values for the activation volume which coincide identically with the second order polynomial (Figs. 14 through 18). This is because they both allow for the same pressure dependence of ΔV^{*}. That this is true can be shown in the following manner. The quantity on the left-hand side of eq. 44 is merely $\Delta \ln k/\Delta p$ which, in the limit of infinitesimal increments, is $(\partial \ln k/\partial p)_T$. In this limit the right-hand side of eq. 44 becomes A + Bp. Therefore,

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = A + Bp. \tag{51}$$

Integrating eq. 51 at constant temperature gives

$$\ln k = Ap + \frac{Bp^2}{2} + C \tag{52}$$

which is identical to eq. 41. Thus there is no evident advantage to using one of these methods over the other. However, the standard deviation of the quadratic function is smaller than that of the Benson-Berson analysis (Table VII). It may be noted further that eq. 41 is a strictly analytical function whereas eq. 44 becomes an analytical function only when the increments become infinitesimal. Therefore it is not surprising that the two functions do not give identical standard deviations. For these reasons, and because eq. 41 lends itself to a precision analysis of the type described in Chapter 5, the quadratic function is preferred to the incremental slope analysis.

Other Reactions

Having determined the relative reliability of various functional representations of the data for the pressure dependence of a unimolecular ionogenic reaction, it is interesting to consider the applicability of these functions to other types of reaction.[b]

Table VIII lists six reactions which were subjected to the analyses described above.

As can be seen in Table IX, the differences between the forced intercept treatment for the linear and quadratic functions and the non-forced treatments are small. The largest difference, 1.2 ml./mole, is in the quadratic function for t-butyldimethylsulfonium iodide solvolysis. Therefore, it is again apparent that only one of each type of polynomial need be considered.

Figures 22 through 27 demonstrate the variation of the deviation (eqs. 45 and 46) with pressure for each function (eqs. 39 - 44) and each reaction. It can be seen that of the six reactions considered, only two do not show a systematic error in the linear analysis. These are the

---

[b] This suggestion was originally proposed by Professor E. M. Arnett in a letter to Professor J. B. Hyne.

TABLE VIII

Reactions Used for the Pressure Dependence Analysis

Number	Reaction	Ref.
1	$BrCH_2COO^- + S_2O_3^=$ in H_2O at 24.5°C.	44
2	$CH_3CH_2Br + CH_3O^-$ in CH_3OH at 25°C.	150
3	$(CH_3)_3CS^+(CH_3)_2I^-$ in H_2O at 71°C.	46
4	$Co(NH_3)_5Br^{++} + OH^-$ in H_2O at 30.0°C.	44
5	Urea formation in H_2O at 60°C.	49
6	Isoprene dimerization at 60°C.	38

TABLE IX

Volumes of Activation for the Reactions of Table VIII

$\Delta V^{\neq}$ (ml./mole)

Method

Reaction[a]	Linear	Linear Forced Intercept	Quadratic	Quadratic Forced Intercept	Benson-Berson	Incremental
	eq. 39	40	41	42	43	44
1	- 4.8	- 4.7	- 4.7	- 4.8	- 3.5	- 4.6
2	- 1.5	- 2.1	- 3.3	- 4.2	- 7.5	- 5.6
3	+ 9.2	+ 9.6	+ 8.8	+10.0	+15.5	+ 9.6
4	+ 8.5	+ 8.7	+10.5	+10.5	+11.9	+10.4
5	+ 2.9	+ 3.9	+ 7.4	+ 8.1	+11.9	+ 8.7
6	-19.7	-21.7	-30.4	-29.1	-29.6	-27.6

[a] Numbers refer to reactions of Table VIII.

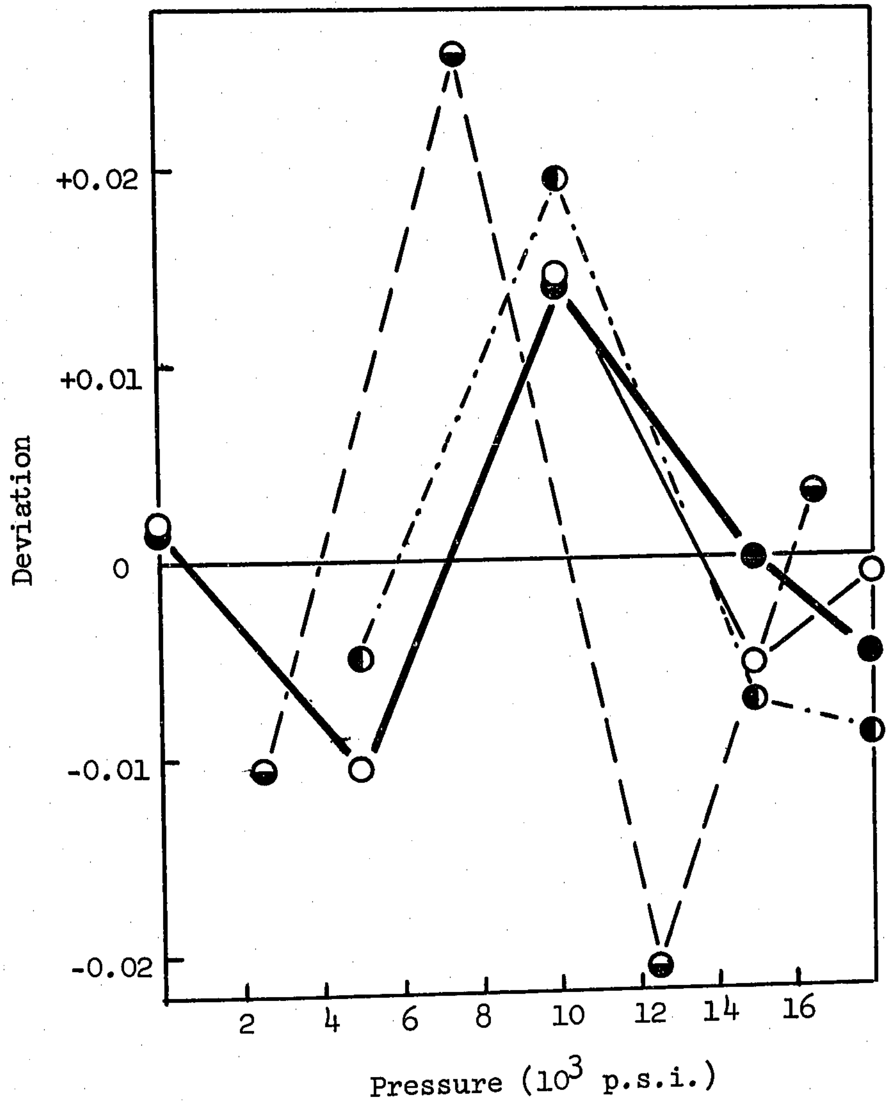


Fig. 22. Variation of the deviation of lnk with pressure for the reaction of bromoacetate with thiosulfate. ○linear, ● quadratic, ◐Benson-Berson, ⊖incremental

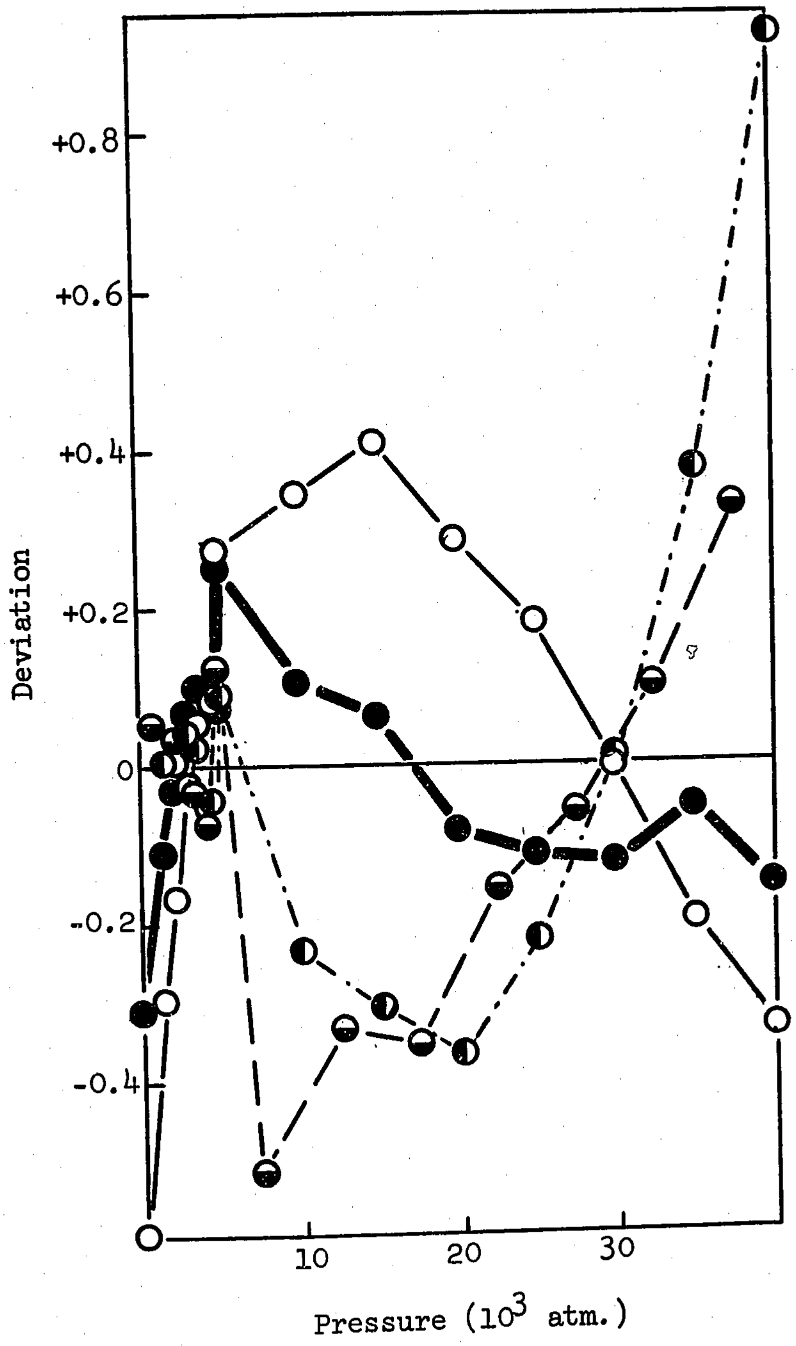


Fig. 23. Variation of the deviation of lnk with pressure for the reaction of ethyl bromide with methoxide. ○ linear, ● quadratic, ◐ Benson-Berson, ◒ incremental.

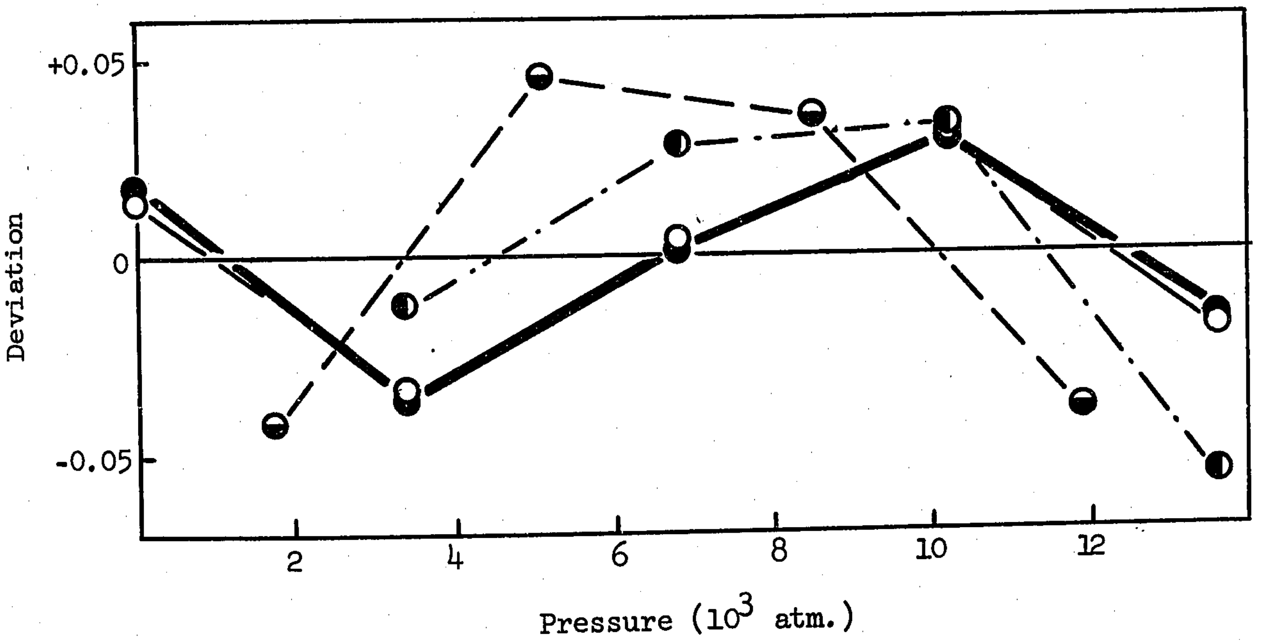


Fig. 24. Variation of the deviation of lnk with pressure for t-butyldimethylsulfonium iodide hydrolysis. ○linear, ●quadratic, ◐Benson-Berson, ⊖incremental.

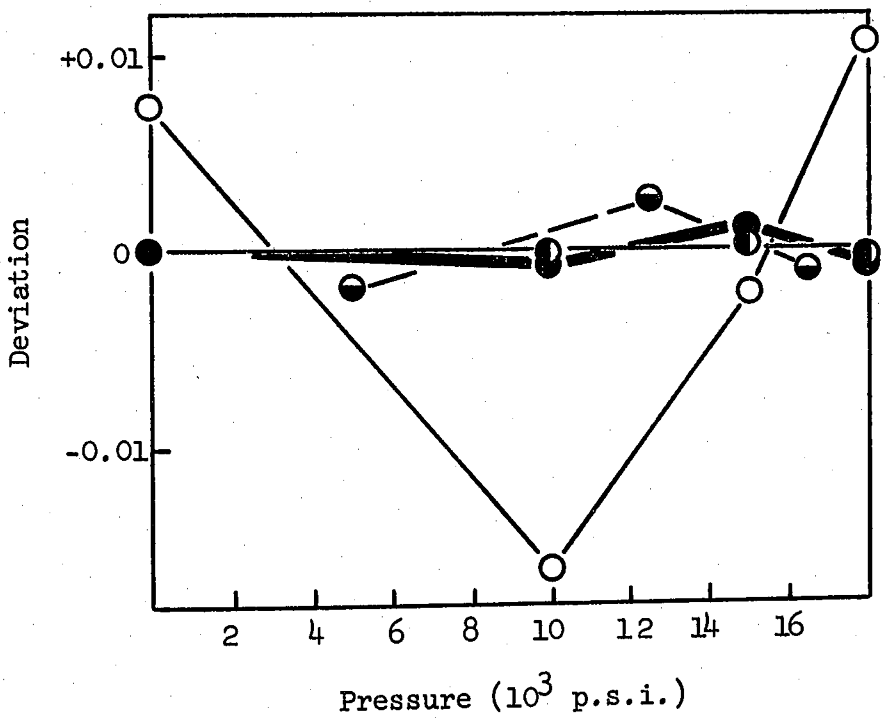


Fig. 25. Variation of the deviation of lnk with pressure for the reaction of bromopentammine cobaltic ion with hydroxide. ○ linear, ● quadratic, ◐ Benson-Berson, ◒ incremental.

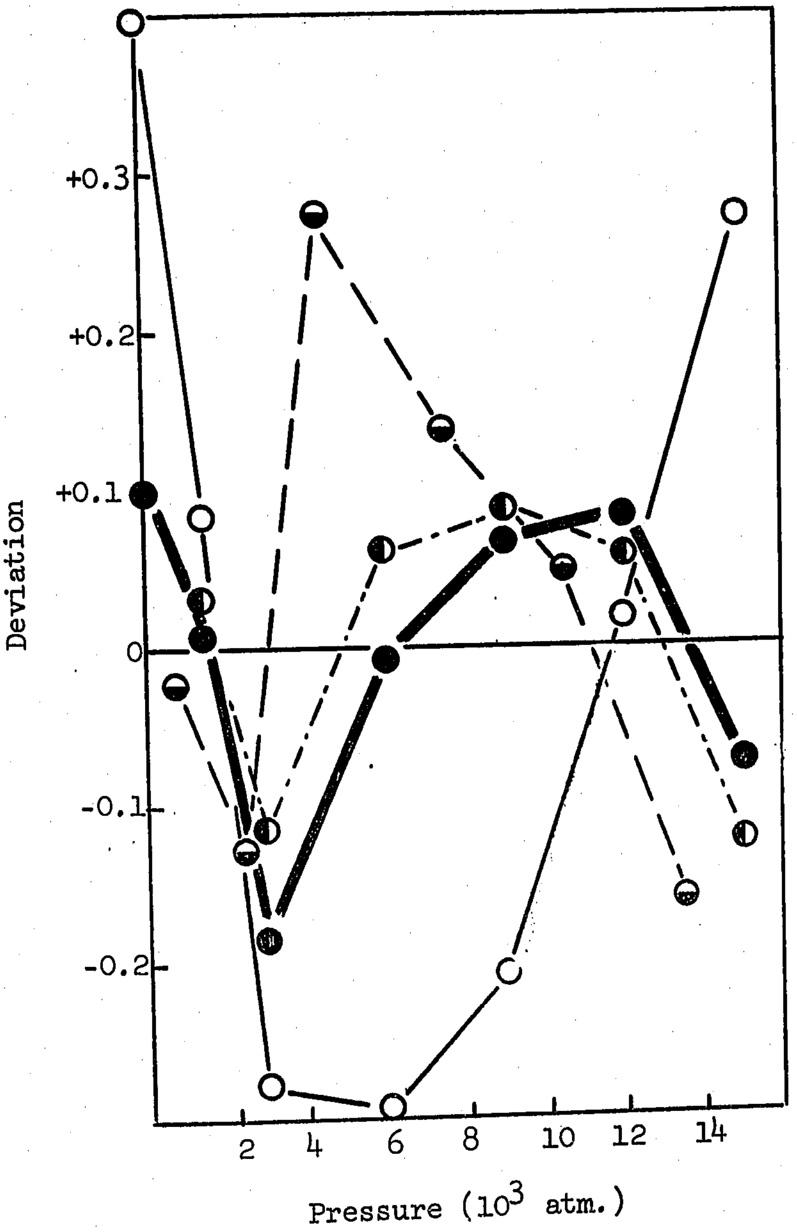


Fig. 26. Variation of the deviation of lnk with pressure for urea formation. ○linear, ● quadratic, ◐Benson-Berson, ◓incremental.

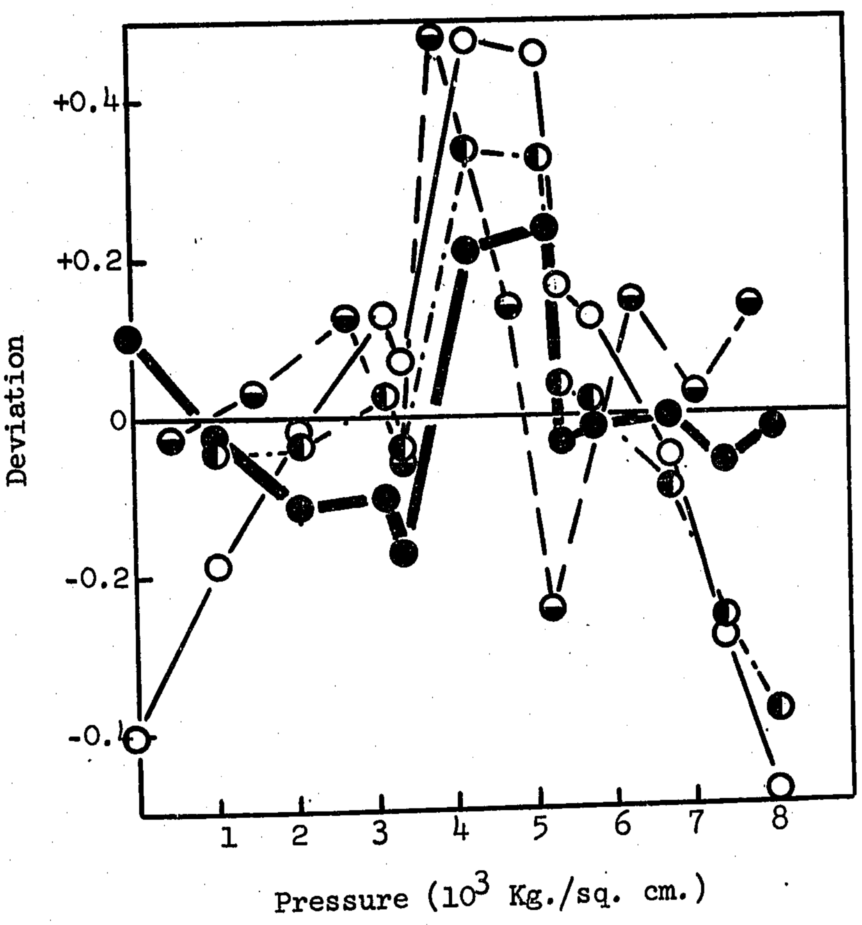


Fig. 27. Variation of the deviation of lnk with pressure for isoprene dimerization. ○ linear, ● quadratic, ◐ Benson-Berson, ⊖ incremental

reaction of thiosulfate with bromoacetate and the sulfonium salt solvolysis. Once again, however, the more quantitative aspects of the reliability of each function rests in the relative values of the standard deviations. These are presented in Table X. Since the various reactions are independent in contrast to the previous situation where one reaction was studied in various solvents, it is more convenient to consider each by itself.

Thiosulfate and Bromoacetate

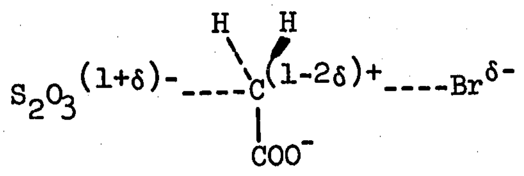
In this instance the quadratic and linear analyses give identical values for the standard deviation. Such a situation would be expected for a reaction whose pressure dependence of the logarithmic rate is truly linear. The fact that the linear analysis is observed to give a random scatter in the deviation (Fig. 22) also indicates that the pressure dependence is probably linear. This inference is supported by the quite small value of $(\partial \Delta V^{\neq}/\partial p)_T$, -1.7×10^{-5} ml./p.s.i. mole. This probably reflects the similarity in electrostriction of the solvent environment about the initial state ions and the ionic transition state. Since the transition state is composed of two negative ions, the total ionic charge of the transition state is probably no less than the sum of the initial state ions. It is even possible that the total ionic charge is somewhat greater than three units, even though the net charge cannot be greater. Such a situation might be represented by structure V where $\delta > 0.5$. It is

TABLE X

Standard Deviations for the Reactions of Table VIII

	s.d.					
	Method					
Reaction[a]	Linear	Linear Forced Intercept	Quadratic	Quadratic Forced Intercept	Benson-Berson	Incremental
	eq. 39	40	41	42	43	44
1	0.0089	0.0101	0.0090	0.0110	0.0130	0.0200
2	0.2923	0.5372	0.1455	0.2349	0.3336	0.2375
3	0.0259	0.0316	0.0257	0.0315	0.0418	0.0472
4	0.0120	0.0155	0.0009	0.0010	0.0005	0.0024
5	0.2719	0.4156	0.1006	0.1240	0.0940	0.1676
6	0.3043	0.3829	0.1239	0.1419	0.2125	0.1947

[a] Numbers refer to reactions of Table VIII.



V

interesting to note that in this example of a linear dependence, all of the analyses give approximately the same value for the activation volume, as well as consistently small values for the standard deviation.

Ethyl Bromide and Methoxide

The original study of this reaction by Hamann[150] was designed to demonstrate a viscosity inhibition of a bimolecular reaction in solution. Therefore, it is not surprising that the logarithmic rate constant pressure dependence is not linear. However, it is somewhat surprising that the Whalley and Benson-Berson analyses, which do take account of the pressure dependence of $\Delta V^{\ddagger}$, have such large standard deviations when compared with the quadratic analysis. For some reason, which is not readily apparent, the data are not well represented by these functions.

t-Butyldimethylsulfonium Iodide Solvolysis

Once again we have an example of a reaction which is well represented by a linear analysis. In fact Fig. 24 shows that the Benson-Berson and Whalley analyses give systematic errors. In support of the linearity, it is seen that the linear and quadratic standard deviations are identical, and $(\partial\Delta V^{*}/\partial p)_T = +62.1 \times 10^{-5}$ ml./atm. mole ($+4.2 \times 10^{-5}$ ml./p.s.i. mole); a rather small value. The linearity indicates that the ionic nature of the transition state is very similar to that of the salt itself. However, the large positive activation volume reflects a significant amount of stretching of the carbon-sulfur bond. If the positive volume change was due to desolvation of the solute during the activation process, the pressure dependence of the activation volume would be expected to be rather large--reflecting the difference in extent of solvent electrostriction. Unfortunately, the data do not indicate the charge distribution in the transition state, i.e. whether it remains on the sulfur atom or is distributed between the sulfur and carbon atoms equally.

Bromopentammine Cobaltic Ion and Hydroxide

Table X shows that the quadratic analysis is a much better fit than is the linear analysis. This is remarkably illustrated in Fig. 25 where the linear deviations are very much larger than the other three functions. It is surprising to note that the Benson-Berson analysis gives a standard deviation only half as large as the quadratic analysis. It would seem that the Benson-Berson analysis is suited to more severe conditions than imposed by the original authors.[39] One might conclude that the change in activity coefficient is negligible in this instance, but this is unlikely since there is partial neutralization during the activation process. This partial neutralization results in desolvation of the solute, as evidenced by the positive activation volume and by the fact that the pressure dependence of the activation volume is somewhat large, -23.0×10^{-5} ml./p.s.i. mole.

Urea Formation

Once again we find that the Benson-Berson analysis is no worse then the quadratic function, while the linear analysis is quite poor. Unfortunately there is a large difference in the activation volume obtained from the quadratic and Benson-Berson methods, and there is no way to distinguish between their reliability. The only useful mechanistic information obtained from these values is that the activation volume is positive indicating a desolvation of ions. Unfortunately, the mechanism of this reaction is still very much in doubt because of the equilibrium

$$NH_4^+ + NCO^- \rightleftharpoons NH_3 + NCOH. \qquad (53)$$

Thus, the positive activation volume can be due to either the fast equilibrium of eq. 53 followed by slow reaction of ammonia with NCOH, or the slow reaction of NH_4^+ with NCO^- to give the product directly.

Isoprene Dimerization

A great deal of attention has been given to the pressure dependence of this reaction as evidenced by the papers of Walling and

Peisach,[38] Benson and Berson[39] and rebuttals by both groups of workers. Benson and Berson disregarded the low pressure rate constants in analyzing the data for this reaction because of much scatter of the points.[39] They obtained an activation volume some 50% more negative than the original authors. In this study, all the rate constants were used, and it is seen that, except for the linear analysis, the activation volumes are all very similar (Table IX). A glance at Figure 27 indicates that if any of the points were to be omitted, those between 3500 and 5500 Kg./cm.^{2} should be the likely candidates. Nevertheless, Benson and Berson's criticism of the conclusions by Walling and Peisach appears to be unjustified by this study. In point of fact the quadratic analysis, which best represents the data (Table VIII), yields the value of -30.4 ml./mole for $\Delta V_0^{\ddagger}$, supporting the value of the activation volume obtained by the original authors, -24.3 ml./mole, at least as much as it supports the value obtained by Benson and Berson, -36.5 ml./mole.

In summary it can be concluded that the quadratic analysis is generally the best representation of the pressure dependence of a logarithmic rate constant--regardless of the reaction type. In those cases where a linear function was found to accommodate the data, the quadratic analysis gave good fits, and the results agreed well with those obtained from the linear analysis.

PART III

STATIC MEASUREMENTS

CHAPTER 7

EXPERIMENTAL II. STATIC

It was indicated in Chapter 3 that certain static measurements on the systems of interest to this study are necessary in order to interpret the behavior of the activation volumes. The methods by which these quantities (partial molal volumes, compressibilities and thermal expansivities) were determined are described in the following pages.

Partial Molal Volumes

Apparatus

A thermostat of similar design to those used for the kinetic runs was used (see Chapter 4). The nichrome coil heater was omitted since the size of the bath, about 3 gals., enabled the temperature to be maintained by the infra-red lamp alone. The front wall of the thermostat was made of plate glass to facilitate reading of the meniscus in the dilatometer. It was found that two propellor type stirrers, at different levels in the oil, were necessary in order to prevent fluctuation of the meniscus in the dilatometer due to temperature gradients.

A magnetic stirrer was modified by removing the controls from the casing, and placing them in the power cord some distance from the casing. The stirrer itself was encased in a Perspex box weighted with lead. The entire ensemble was placed on the bottom of the thermostat.

The dilatometers consisted of 100 ml. bulbs containing a magnetic stirring bar. These were each fitted with a 6 in. length of 0.7 mm. i.d. precision bore capillary. The capillaries were calibrated by weighing the amount of mercury they held, and by measuring the molal volume of water in water by the method described below for the partial molal volumes.

The microsyringe was a standard 25 µl. syringe fitted with a Chaney adapter and a 6 in., 27 gauge needle. The stop was set at 5 µl., and the volume delivered was determined by weighing the amount of water delivered on a micro balance. That the needle was uniform along its entire length was determined by repeatedly measuring its diameter at various positions.

Method

The method used was a modified technique of that reported by Shinoda and Hildebrand.[134] The dilatometer was filled by evacuating, and immersing the tip of the capillary in the solvent to be used. A short length of rubber tubing fitted over the capillary and equipped with a screw clamp was found to be helpful. The filled dilatometer was placed in the thermostat, the magnetic stirrer started, and several hours were allowed for thermal equilibration to occur. The meniscus was adjusted by means of a syringe equipped with a 6 in., 27 gauge needle.

The microsyringe was filled with benzyl chloride, or whatever solute which was being studied, and emptied to the stop of the Chaney adapter. The syringe needle was wiped, and then inserted into the capillary of the dilatometer. A special clamp was designed to maintain alignment of the microsyringe and the dilatometer capillary so that the point of the needle penetrated the bulb. It should be noted that in the method used here the constancy of the o.d. of the microsyringe needle is important since the evaluation of the volume change on solute dissolution depends on the validity of the assumption that the annular space between the needle and the capillary wall is regular. The constancy of the needle diameter was checked over the length immersed with a micrometer and was found to be 0.00496 ± 0.00004 mm., i.e. constant to 0.8%. Furthermore the satisfactory agreement between $\bar{V}_{H_2O}$ and $\bar{V}_{EtOH}$ in aqueous ethanol determined by this method and those reported by Mitchell and Wynne-Jones[153] (see Chapter 8) establishes that any error introduced by variation in needle diameter is not significant.

After several minutes, the level of the meniscus in the capillary was measured with a cathetometer to 0.01 mm., and the temperature of the air near the syringe was recorded. It should be noted that a polyethylene shield constructed around the thermostat reduced spurious air currents, helped to maintain a steady meniscus level, and prevented false air temperature readings.

The stop on the Chaney adapter was moved to the inject position, and the solute injected rapidly. Sufficient time was allotted for dissolution to occur (2 to 5 min.), and the meniscus level measured.

Compressibilities

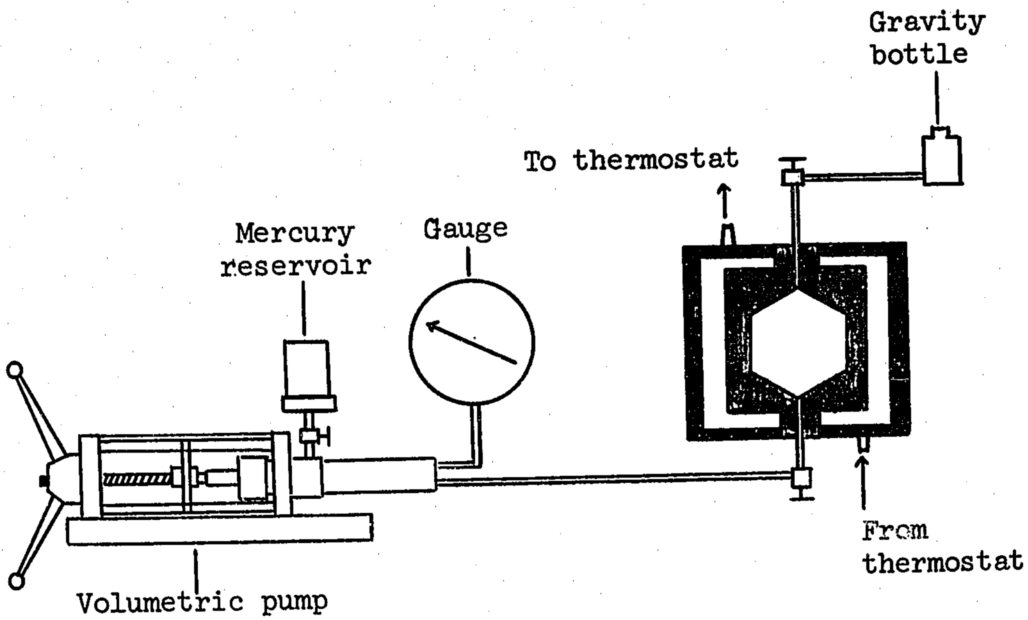


Fig. 28. Compressibility apparatus. (Rocking mechanism not shown.)

Apparatus

The apparatus used is depicted in Fig. 28. A Ruska Instrument Corp., Inc. (Houston, Texas) hand-operated volumetric pump was used. It had a total capacity of 100 cc. and could be read to 0.001 cc.

The pressure was measured with a 12 in. dial, 0 - 3,000 p.s.i.g. gauge manufactured by Heise-Bourdon Tube Co., Inc. (Newtown, Conn.).

The cell consisted of a 500 cc. vessel with openings at the top and bottom. This was jacketed, and the temperature was maintained by pumping the thermostating liquid through this jacket. The cell was equipped with a shaker.

Grateful acknowledgment is made to the staff of the Imperial Oil Research and Development Laboratories in Calgary for making this equipment available for our use.

Method

The cell, having been previously calibrated, was filled with mercury and pressurized to 3,000 p.s.i.g.; the thermostating temperature being 50.25°C. After thermal equilibrium had been attained, the pump reading was noted. The pressure was lowered, and the cell filled by introducing the sample through the top valve via the gravity bottle while mercury was withdrawn through the bottom. About 100 cc. of the liquid to be studied was used. The valve to the gravity bottle was closed, and the system pressurized to the reference pressure (3,000 p.s.i.g.). After thermal equilibrium had been attained, the pump reading was recorded. It should be noted that all valves were closed when the pump readings were taken since different amounts of opening of a valve could cause an appreciable change in the volume of the system. The pressure was lowered to the next step (2500 p.s.i.g.) in the cell, the bottom valve was closed, and the pump reading taken at the reference pressure. This procedure was continued every 500 p.s.i.g. down to 500 p.s.i.g., and a final measurement was made at 100 p.s.i.g.

Thermal Expansivities

Apparatus

Weld pycnometers of about 25 cc. were used to determine the densities of the various solvent mixtures as a function of temperature. The thermostats used were the same as used for the kinetic runs (Chapter 4).

Method

The pycnometers were calibrated at 40.05°C., 50.25°C. and 60.50°C. using water by the method described below. The density of water at each of these temperatures was taken from the International Critical Tables.[152a]

The solvent to be studied was placed in a ground glass stoppered Erlenmeyer flask and immersed in the thermostat. About 1 hr. was allowed for the liquid to come to temperature equilibrium in the 40.05°C. thermostat. The pycnometers, having been previously weighed, were filled with the liquid using a pipette, and covered--the plugs being left out. The pycnometers were then suspended in the thermostat to a point below the bottom of the ground glass joint of the cover, and allowed to equilibrate for about 15 min. At the end of this time, the covers were removed and the plugs inserted. The top of the plug was carefully wiped, the pycnometers covered and removed from the bath. They were then rinsed thoroughly with acetone and wiped dry. They were allowed to attain room temperature for a period of 1 hr., and weighed. The room temperature and barometric pressure were recorded. For the higher temperatures, the filled pycnometers from the 40.05°C. determinations were inserted into the 50.25°C. thermostat, and allowed to come to thermal equilibrium for one hour, and the above procedure followed. This was then repeated at 60.50°C.

CHAPTER 8

RESULTS II. STATIC

The calculations of the quantities measured in Chapter 7 are described below, and the tabulated results are presented.

Partial Molal Volumes

Since the solutions used in this study were very dilute (about 5×10^{-4} molar), they could be assumed to be infinitely dilute. Therefore, the apparent molal volume change can be taken as the partial molal volume of the solute at infinite dilution.

The observed volume change is equal to the change in height of the meniscus (as measured in Chapter 7), h, multiplied by the cross-section of the annular space between the capillary wall and the hypodermic needle. Having calibrated the capillary (vide supra), its radius, r_c, is known, and having determined the radius of the needle, r_n, with a micrometer, the cross-sectional area of the annular space is given by

$$A = \pi(r_c^2 - r_n^2). \tag{54}$$

Therefore the observed volume change on injecting the solute is

$$V_{obs} = \pi h(r_c^2 - r_n^2). \tag{55}$$

From the known volume delivered by the syringe (vide supra), and from the known density of the solute (benzyl chloride,[151] water[152a] and ethanol[152b]) at the room temperature, the weight (and therefore the number of moles, n) of the solute delivered to the solution can be calculated. If V_s if the volume delivered by the syringe, and d is the density of the solute at room temperature, then

$$n = \frac{V_s d}{M} \qquad (56)$$

where M is the molecular weight of the solute.

The apparent partial molal volume, which for all intents and purposes is equal to the partial molal volume of the solute, is then given by [134]

$$\bar{V} = \frac{V_{obs}}{n}. \qquad (57)$$

That the assumption of infinite dilution is a reasonable one can be seen in the results of Table XI. It is apparent that seven successive injections of the solute in the dilatometer gave similar results, within experimental error, and that no trend is apparent which would be indicative of solute-solute interactions.

In order to test the accuracy of this method, the partial molal volumes of water and ethanol were measured in the various aqueous ethanol solvents used in this study. The results of these measurements are given in Table XII and compare favorably with the results of

TABLE XI

Partial Molal Volume of Benzyl Chloride in 0.4 Mole Fraction Ethanol at 50.25°C.

Trial	$\bar{V}_{\phi CH_2Cl}$ (ml./mole)
1	117.81
2	117.00
3	116.59
4	117.00
5	117.97
6	117.08
7	117.32
Average	117.25 ± 0.38

TABLE XII

Partial Molal Volumes of Water and Ethanol in Aqueous Ethanol at 50.25°C.

Mole Fraction Ethanol	$\bar{V}_{H_2O}$ (ml./mole)	$\bar{V}_{EtOH}$ (ml./mole)
0.050	18.15 ± 0.08	54.9 ± 0.4
0.100	18.08 ± 0.08	55.6 ± 0.2
0.200	17.5 ± 0.1	57.6 ± 0.2
0.300	17.3 ± 0.1	59.19 ± 0.08
0.400	17.0 ± 0.1	61.3 ± 0.3

Mitchell and Wynne-Jones[153] as shown in Fig. 29.

The partial molal volume of benzyl chloride in each of the solvents pertinent to this study is given in Table XIII. Since the insolubility of benzyl chloride in water prevented the determination of the partial molal volume in this solvent, the value was determined by extrapolation of the $\bar{V}_{\phi CH_2Cl}$ vs. mole fraction alcohol curves.

Compressibilities

The volume determinations as measured by the volumetric pump, which was at room temperature and the reference pressure (3000 p.s.i.g.), must be corrected to the conditions of the compressibility cell. In order to accomplish this, the following cycle was employed.

$$\begin{tikzcd} V_{T_p,p_p} \arrow[r] \arrow[d, "1"] & V_{T_c,p_c} \\ V_{T_p,p=0} \arrow[r, "2"] & V_{T_c,p=0} \arrow[u, "3"'] \end{tikzcd} \qquad (58)$$

T_p and T_c represent the temperature of the pump and the compressibility cell respectively, p_p and p_c represent the corresponding pressures.

Knowing the isothermal compressibility of mercury at the temperature of the pump, $\kappa_{T_p}^{Hg}$, the correction for step 1 can be determined from eq. 59

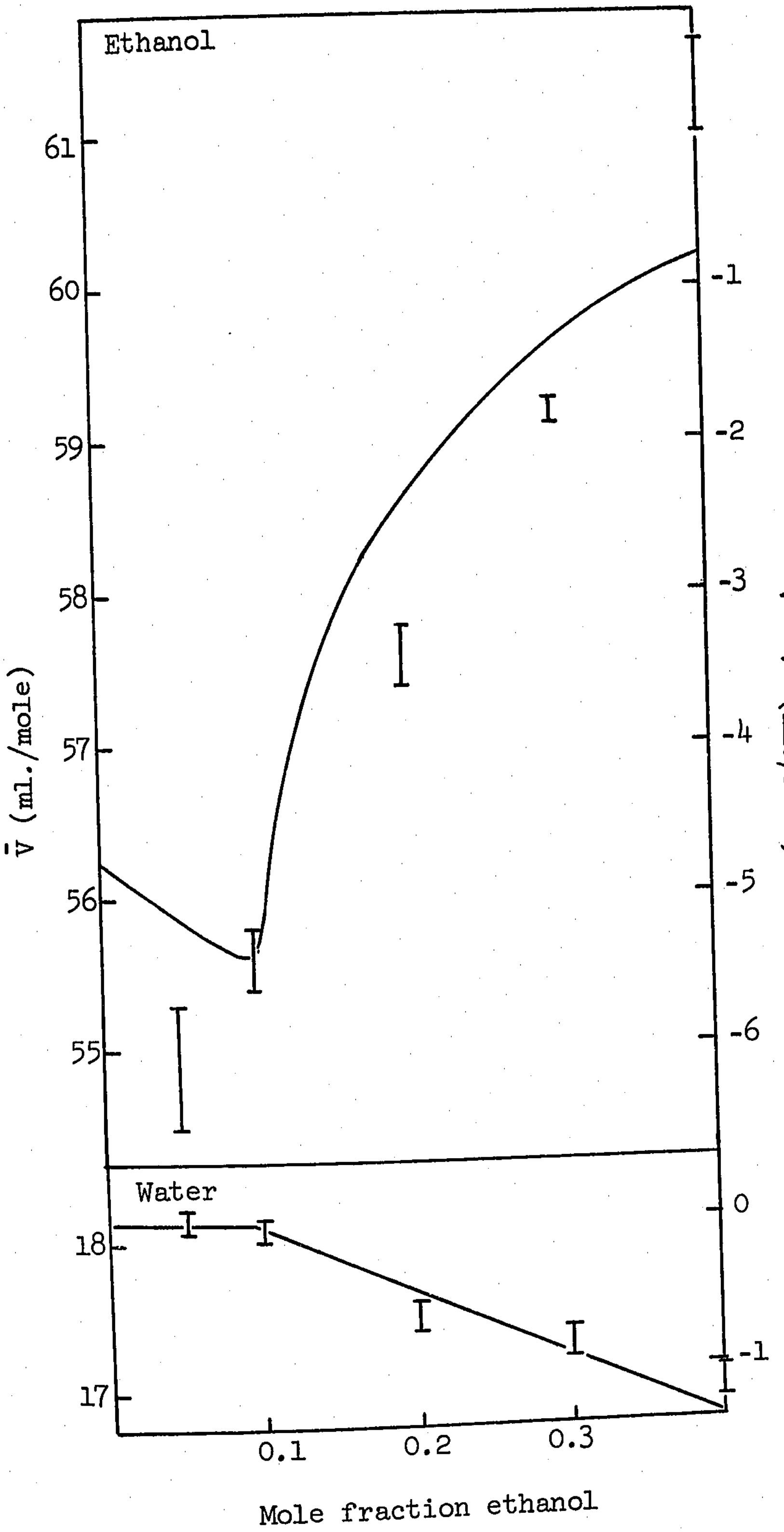


Fig. 29. Comparison of the partial molal volumes of ethanol and water (points) with the data of Mitchell and Wynne-Jones (curves) ref. 153.

TABLE XIII

Partial Molal Volume of Benzyl Chloride in Aqueous Alcohol Mixtures at 50.25°C.[a]

Mole Fraction Alcohol	$\bar{V}_{\phi CH_2Cl}$ (ml./mole) Methanol	Ethanol	i-Propanol	t-Butanol
0.010				115.2 ± 0.4
0.030				117.2 ± 0.3
0.050		115.95 ± 0.09	120.5 ± 0.3	126.2 ± 0.3
0.100	116.9 ± 0.2	117.5 ± 0.1	124.5 ± 0.4	129.1 ± 0.4
0.200	118.2 ± 0.3	123.1 ± 0.3	124.0 ± 0.3	123.0 ± 0.3
0.300	119.3 ± 0.3	119.9 ± 0.1	121.4 ± 0.3	118.8 ± 0.5
0.400	118.8 ± 0.3	117.3 ± 0.4	117.1 ± 0.2	116.5 ± 0.2
0.500	117.9 ± 0.4			

[a] Value in pure water as extrapolated from the data in this table is 115 ml./mole.

$$V_{T_p,p=0} = V_{T_p,p_p} \exp\left[-\kappa_{T_p}^{Hg}(0 - p_p)\right] \tag{59}$$

which is simplified to

$$V_{T_p,p=0} = V_{T_p,p_p} \exp(3000\kappa_{T_p}^{Hg}) \tag{60}$$

since the pump pressure is always the reference pressure of 3000 p.s.i.g.

The correction for step 2 is calculated by eq. 61 where α_{T_p,T_c}^{Hg}

$$V_{T_c,p=0} = V_{T_p,p=0} \exp\left[-\alpha_{T_p,T_c}^{Hg}(T_c - T_c)\right] \tag{61}$$

is the average value of the thermal expansivity of mercury between T_p and T_c.

The volume change for step 3 is calculated in a similar manner to step 1; the compressibility of mercury at the cell temperature being employed:

$$V_{T_c,p_c} = V_{T_c,p=0} \exp(-\kappa_{T_c}^{Hg} p_c) \tag{62}$$

Having determined the volume of mercury withdrawn from the cell at the reference pressure, the volume occupied by the liquid introduced into the cell is known. It then remains to determine the amount by which this volume of liquid expands as the cell pressure is reduced.

The cumulative amount of mercury withdrawn from the cell, as measured by the pump, as the pressure is reduced, is calculated by subtracting successive pump readings (with the cell at the successive pressures) from the pump reading with the cell at the maximum pressure. These values are corrected as above to the cell conditions at the appropriate pressure. This then gives $V_{c(p)}^{Hg(wd)}$.

As the pressure in the cell is reduced, the mercury which is left inside the cell expands, and this expansion must be taken into account. The volume of the mercury left in the cell at 3000 p.s.i.g., $V_{c(3000)}^{Hg}$, is equal to the volume of the cell at that pressure (from the original cell calibration) less the volume of liquid introduced into the cell. The volume by which the mercury in the cell expands as the pressure is reduced is then given by

$$V_{c(p)}^{Hg(ex)} = V_{c(3000)}^{Hg}\{\exp[-\kappa_{T_c}^{Hg}(p - 3000)] - 1\}. \tag{63}$$

The volume of the cell itself decreases, or expands negatively, as the cell pressure is decreased. This expansion is known from the original calibration of the cell, and is designated $V_{c(p)}^{ex}$.

The increase in the volume of the liquid being studied is therefore given by

$$V_{c(p)}^{Liq(ex)} = V_{c(p)}^{Hg(wd)} + V_{c(p)}^{ex} - V_{c(p)}^{Hg(ex)} . \tag{64}$$

The total volume of the liquid is then equal to the original volume introduced into the cell at 3000 p.s.i.g. plus $V_{c(p)}^{Liq(ex)}$. Knowing these volumes, the relative volume of the liquid at the various pressures can be determined, and the graph of $\ln V_{rel}$ vs. p will have a slope equal to $-\kappa_{T_c}^{Liq}$. This slope was determined by a least squares fit of the data to eq. 65 (Appendix VIII)

$$\ln V_{rel} = A + Bp + Cp^2 \tag{65}$$

from which

$$\kappa_{T_c}^{Liq} = -B. \tag{66}$$

The confidence limits of the compressibilities were determined by the method used for the activation volumes (Chapter 5). However, the values used for the errors in the volume and pressure measurements make this error a measure of the accuracy of the compressibility rather than a measure of the precision. As no duplicate samples were subjected to this determination, the precision measure is not available. It is to be noted that the compressibilities and thermal expansivities of mercury which were used were supplied by the Imperial Oil Research and Development Laboratories where this work was done. No literature citation for these values was available at the time.

The values for the compressibilities of the various solvents studied are shown in Table XIV and the relative values of the volumes are given in Table XV. It can be seen that agreement with the literature is only fair in that the compressibility of water calculated from the p-V

TABLE XIV

Physical Properties of the Solvents at 50.25°C.

Mole Fraction Alcohol	$10^6 \times \kappa$ (p.s.i.$^{-1}$)	$10^4 \times \alpha$ (deg.$^{-1}$)
	Methanol	
0.000	2.75 ± 0.08	4.59[a]
0.100	3.1 ± 0.3	5.7 ± 0.1
0.200	3.2 ± 0.2	7.4 ± 0.2
0.300	3.6 ± 0.1	8.05 ± 0.09
0.400	4.5 ± 0.5	8.93 ± 0.08
0.500	5.1 ± 0.7	9.9 ± 0.1
1.000		12.68 ± 0.09
	Ethanol	
0.100	2.84 ± 0.08	6.80 ± 0.07
0.200	3.7 ± 0.3	8.5 ± 0.1
0.300	4.4 ± 0.3	9.55 ± 0.07
0.400	5.2 ± 0.7	10.31 ± 0.02
1.000		11.1 ± 0.2
	i-Propanol	
0.050		5.9 ± 0.1
0.100	3.14 ± 0.03	8.1 ± 0.8
0.200	4.3 ± 0.5	9.1 ± 0.1
0.300	5.2 ± 0.7	9.79 ± 0.09
0.400	6.0 ± 0.1	10.8 ± 0.2
1.000		11.8 ± 0.2
	t-Butanol	
0.050		7.04 ± 0.05
0.100	3.7 ± 0.2	8.48 ± 0.07
0.200	4.8 ± 0.5	10.0 ± 0.1
0.300	5.8 ± 0.9	10.70 ± 0.06
1.000		14.2 ± 0.2

[a] Calculated from the data of ref. 152a

TABLE XV

Relative Volumes of the Solvents at 50.25°C.

Pressure (p.s.i.g.)	Mole Fraction Alcohol 0.000	0.100	0.200	0.300	0.400	0.500
			Methanol			
3000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
2500	1.00135	1.00118	1.00145	1.00163	1.00185	1.00209
2002	1.00277	1.00278	1.00290	1.00338	1.00388	1.00437
1507	1.00417	1.00424	1.00447	1.00519	1.00598	1.00671
1008	1.00571	1.00576	1.00615	1.00706	1.00810	0.00919
510	1.00694	1.00711	1.00754	1.00875	1.01013	1.01154
122	1.00809	1.00844	1.00890	1.01018	1.01199	1.01359
0	1.00841[a]	1.00879[a]	1.00927[a]	1.01063[a]	1.01250[a]	1.01421[a]
			Ethanol			
3000		1.00000	1.00000	1.00000	1.00000	
2500		1.00139	1.00169	1.00193	1.00211	
2002		1.00292	1.00340	1.00395	1.00434	
1507		1.00433	1.00506	1.00607	1.00678	
1008		1.00585	1.00698	1.00824	1.00929	
510		1.00719	1.00865	1.01028	1.01165	
122		1.00837	1.01013	1.01204	1.01371	
0		1.00870[a]	1.01057[a]	1.01256[a]	1.01434[a]	

TABLE XV (con't)

Pressure (p.s.i.g.)	Mole Fraction Alcohol 0.000	0.100	0.200	0.300	0.400	0.500
			i-Propanol			
3000		1.00000	1.00000	1.00000	1.00000	
2500		1.00157	1.00188	1.00215	1.00234	
2002		1.00309	1.00369	1.00439	1.00470	
1507		1.00471	1.00584	1.00689	1.00747	
1008		1.00643	1.00791	1.00939	1.01040	
510		1.00788	1.00986	1.01185	1.01310	
122		1.00913	1.01161	1.01381	1.01532	
0		1.00953[a]	1.01213[a]	1.01450[a]	1.01612[a]	
			t-Butanol			
3000		1.00000	1.00000	1.00000		
2500		1.00181	1.00222	1.00238		
2002		1.00340	1.00432	1.00475		
1507		1.00511	1.00657	1.00740		
1008		1.00702	1.00889	1.01018		
510		1.00871	1.01119	1.01298		
122		1.01019	1.01312	1.01510		
0		1.01062[a]	1.01368[a]	1.01587[a]		

[a] Extrapolated values.

data of reference 152a is 2.16 x 10^{-6} p.s.i.$^{-1}$ compared with the value found here of 2.75 x 10^{-6} p.s.i.$^{-1}$ However, for the purposes of this study, namely the calculation of constant volume activation parameters (Chapter 3 and 9), this difference is probably unimportant.

Thermal Expansivities

The weights of the empty and filled pycnometers were corrected to vacuum. For the empty pycnometers, eq. 67 was used [98c] which is

$$W_{vac} = W_{obs}\left(1 - \frac{d_{air}}{d_{pyr}} - \frac{d_{air}}{d_{wts}}\right) \tag{67}$$

simplified to

$$W_{vac} = W_{obs}\left(\frac{1 - 0.107 d_{air}}{1 - 0.448 d_{air}}\right) \tag{68}$$

where the density of pyrex, d_{pyr}, is taken to be 2.23 g./ml.[154] and that for the balance weights is taken as 9.3 g./ml.[155] For the filled pycnometers the following modification was made. Using the same principle as in eq. 67 we find for the filled pycnometers that

$$W_{vac} = W_{obs} + d_{air}\left(\frac{W_{pyr}}{d_{pyr}} + \frac{W_{liq}}{d_{liq}} - \frac{W_{obs}}{d_{wts}}\right) \tag{69}$$

or

$$W_{vac} = W_{obs}(1 - \frac{d_{air}}{d_{wts}}) + d_{air}(\frac{W_{pyr}}{d_{pyr}} + \frac{W_{liq}}{d_{liq}}). \tag{70}$$

But since $W_{liq} = W_{obs} - W_{pyr}$

$$W_{vac} = W_{obs}(1 - \frac{d_{air}}{d_{wts}} + \frac{d_{air}}{d_{liq}}) + W_{pyr}(\frac{d_{air}}{d_{pyr}} - \frac{d_{air}}{d_{liq}}). \tag{71}$$

Since the liquids of interest to this study have densities close to unity, and since the buoyancy corrections are small, the density of the liquid, d_{liq}, can be set equal to 1. Simplification then gives, for the filled pycnometers,

$$W_{vac} = W_{obs}(1 + 0.892d_{air}) - 0.552W_{pyr}d_{air}. \tag{72}$$

The density of air used in these calculations was determined from the barometric pressure, p_{bar}, and room temperature, t_{room}, using eq. 73 for dry air.[98d]

$$d_{air} = \frac{0.001293p_{bar}}{76(1 + 0.00367t_{room})} \tag{73}$$

The densities of the liquids were determined in triplicate using three pycnometers simultaneously. The values found, together with their average deviations, are given in Table XVI.

TABLE XVI

Densities of the Solvents at Atmospheric Pressure

Mole Fraction Alcohol	Density (g./ml.) 40.05°C.	50.25°C.	60.50°C.
	Methanol		
0.000	0.99225[a]	0.98796[a]	0.98298[a]
0.100	0.9638 ± 0.0002	0.95867 ± 0.00003	0.95265 ± 0.00007
0.200	0.9393 ± 0.0001	0.9329 ± 0.0001	0.9252 ± 0.0006
0.300	0.91574 ± 0.00002	0.90823 ± 0.00008	0.9008 ± 0.0002
0.400	0.8929 ± 0.0001	0.8849 ± 0.0002	0.8767 ± 0.0002
0.500	0.87111 ± 0.00008	0.86236 ± 0.00006	0.8536 ± 0.0002
1.000	0.77239 ± 0.00006	0.7633 ± 0.0004	0.75257 ± 0.00009
	Ethanol		
0.100	0.9552 ± 0.0002	0.94867 ± 0.00009	0.9420 ± 0.0003
0.200	0.9222 ± 0.0001	0.9146 ± 0.0002	0.9063 ± 0.0002
0.300	0.8933 ± 0.0001	0.88467 ± 0.00008	0.87586 ± 0.00001
0.400	0.8657 ± 0.0002	0.8565 ± 0.0004	0.8476 ± 0.0002
1.000	0.7713 ± 0.0002	0.76280 ± 0.00007	0.7538 ± 0.0002
	i-Propanol		
0.050	0.9689 ± 0.0007	0.9635 ± 0.0007	0.9573 ± 0.0008
0.100	0.9489 ± 0.0006	0.9416 ± 0.0008	0.9341 ± 0.0008
0.200	0.9051 ± 0.0002	0.8963 ± 0.0002	0.8883 ± 0.0004
0.300	0.87251 ± 0.00008	0.86354 ± 0.00004	0.85521 ± 0.0002
0.400	0.8489 ± 0.0001	0.8400 ± 0.0001	0.8304 ± 0.0002
1.000	0.7713 ± 0.0001	0.7618 ± 0.0003	0.7530 ± 0.0003
	t-Butanol		
0.050	0.9618 ± 0.0002	0.9548 ± 0.0001	0.94805 ± 0.00006
0.100	0.9310 ± 0.0004	0.9231 ± 0.0002	0.9150 ± 0.0004
0.200	0.8803 ± 0.0008	0.8712 ± 0.0007	0.8625 ± 0.0009
0.300	0.8528 ± 0.0001	0.84324 ± 0.00008	0.8344 ± 0.0002
1.000	0.7660 ± 0.0002	0.75530 ± 0.00006	0.7443 ± 0.0002

[a] Data from ref. 152a.

The thermal expansivity, α, is defined as

$$\alpha = \left(\frac{\partial \ln V}{\partial T}\right)_p. \tag{74}$$

Since

$$\ln V = \text{const.} - \ln d \tag{75}$$

where d is the density of the liquid, then

$$\alpha = -\left(\frac{\partial \ln d}{\partial T}\right)_p. \tag{76}$$

The density vs. temperature data for each liquid were fitted to the linear equation

$$\ln d = A + BT \tag{77}$$

by the method of least squares (Appendix IX). It follows that

$$\alpha = -B. \tag{78}$$

The values of the thermal expansivities were calculated for each pycometer individually, and the results were averaged. This gave rise to the values shown in Table XIV together with their average deviations. The value for water was calculated from the densities reported in the literature.[152a]

PART IV

DISCUSSION

CHAPTER 9

CONSTANT PRESSURE ACTIVATION PARAMETERS

Activation parameters for reactions in solution are generally obtained at atmospheric pressure, and refer to processes not accompanied by a change in pressure. These are the familiar parameters ΔH^{*}, ΔS^{*} and ΔC_p^{*}, and those specifically highlighted in this work, ΔV_o^{*} and $(\partial \Delta V^{*}/\partial p)_T$. Recently Whalley and co-workers[110,156] advanced the proposal that the activation parameters at constant volume, derivable from those at constant pressure, are less dependent upon the solvent medium than are those at constant pressure and therefore are easier to understand. The constant volume parameters are the internal energy, ΔU_v^{*}, and entropy, ΔS_v^{*}, of activation. In the present chapter the constant pressure parameters will be considered while the constant volume parameters will be presented in Chapter 10. The subscripts "p" and "v" will be used to avoid confusion when necessary. In the absence of these subscripts the constant pressure parameter will be implied. The subscript "v" is also used to denote a thermodynamic parameter of vaporization, but the context of the material should suffice to avoid confusion with the constant volume parameters.

The present chapter consists of three main parts. The first deals with the elucidation of the mechanism for benzyl chloride solvolysis using the activation volume data of Table V (p. 90). The second part discusses the dependence of the various activation parameters on the solvent, and the third is concerned with the thermodynamic properties of the binary solvent systems.

Mechanistic Implications

As can be seen in Table V (p. 90), the activation volume, $\Delta V_0^{\ddagger}$, is always negative. As demonstrated in Chapter 1, this is consistent with an ionogenic mechanism where the solvent becomes more highly electrostricted about the transition state as compared with the initial state.[2,3,6] The question arises as to whether the sign and magnitude of the activation volume can be used to classify the benzyl chloride solvolysis into an operative S_N1 or S_N2 category. Since the present reaction is a "neutral" solvolysis, this may be rephrased by asking whether a solvent molecule is incorporated into the transition state.

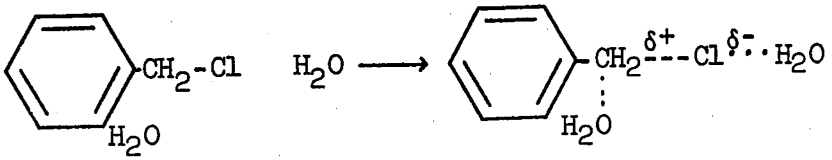
Baliga and Whalley[47] have studied the acid catalyzed hydration of olefins with a similar view in mind. Since no charge destruction or creation was involved, the activation volumes were not complicated by large solvent electrostriction changes. They concluded that the observed negative activation volumes, for the non-ionogenic reactions, are the result of incorporation of a water molecule into the transition state.

One problem in this type of inquiry is that of a precise definition of a reaction mechanism. Does the mechanistic picture of a reaction include the precise knowledge of the immediate solvent environment, or does the solvent merely provide a convenient bulk medium for studying the reaction? This may, at first, seem to be a trivial point, however, closer scrutiny shows it to be more significant.

As was pointed out in Chapter 2, Evans[69] and Franklin[70] demonstrated that the energies required for ionization of alkyl halides are readily available in solution. No such process is conceivable in the gas phase without providing an external energy source, e.g. irradiation. Therefore, the solvent medium is a <u>necessary</u> factor for ionization. If we accept that the solvent environment, and the molecules of which it consists, is an intimate part of the reaction mechanism, then a detailed account of its behavior is necessary in order to understand an activation process. Clearly, in the extreme sense, no reaction mechanism can be considered to be fully understood since, at present, we do not have a completely satisfactory theory of solutions. However, if we do not accept the solvent as playing an essential role in the mechanism, and thus being an intrinsic part thereof, then we neglect most of the energetics involved, thereby not only admitting of our ignorance, but suppressing any instinct or desire to fill this gap in our knowledge. This point will again arise when we discuss the activation parameters at constant volume (Chapter 10).

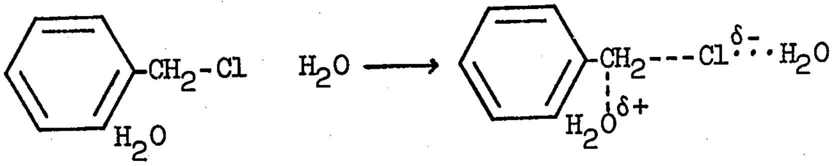
Returning to the problem at hand, and considering the solvent to be intimately related to the reaction mechanism, the only difference between the S_N1 and S_N2 mechanism for the present reaction is the degree of interaction between the substrate and the solvent molecules. In other words the mechanistic classification becomes trivial in the sense that the difference is one of degree rather than kind. This is pictorially demonstrated in eqs. 79 and 80 where --- represents a partial co-valent bond and ··· represents a coulombic interaction.

S_N1:



(79)

S_N2:



(80)

In both mechanisms, there is a stretching of the carbon to halogen bond accompanied by a concomitant development of charge. This charge development serves to increase the dipole moment of the substrate, which in turn increases the strength and extent of interaction between the substrate and solvent molecules. These phenomena are reflected in a positive contribution to the activation volume from the bond stretching and a negative contribution from the increased solvent electrostriction, the latter predominating (see Chapter 1). If there is partial covalent bond formation between the $\underline{\alpha}$-carbon atom and the water molecule, as in the S_N2 case, a further decrease in volume is to be expected. This arises because covalent type interaction is generally of shorter range than electrostatic interaction (as in the S_N1 case), so the two entities must approach each other to a closer distance thereby decreasing the amount of free volume between them.

The difference in the distance between the $\underline{\alpha}$-carbon atom and the solvent oxygen atom in the transition state of eq. 79 (S_N1) and that of eq. 80 (S_N2) cannot be very large; in any case probably no more than a fraction of an Angstrom. In order to detect the volume change due to this small difference, two things are needed. First, kinetic data are required of such a high degree of precision that the activation volumes derived have errors smaller than this volume difference. It is highly questionable that the present data are of sufficient precision for detecting such a small magnitude. Murr and Shiner[137] have demonstrated that such precision is attainable at atmospheric pressure, and, in principle, can be attained at higher pressures. The second necessity is a criterion for determining the demarcation between the two mechanisms. In other words we must know precisely what magnitude of activation volume encompasses S_N1 mechanisms and what magnitude encompasses S_N2 mechanisms. This treatment of course assumes no intermediate type mechanism. Such criteria are generally obtained by studying systems which are known to undergo one or the other mechanism. Unfortunately, because of differences in charge development and bond extension among systems reacting by the same mechanism, there is a large range of ΔV^* magnitudes, and the values for the two types of mechanism are not distinct. Buchanan and Hamann's data for the S_N1 solvolysis of t-butyl chloride in 80% aqueous ethanol[6] gives a value of -21 ml./mole for ΔV_0^* (see p. 75). David and Hamann's data for the S_N2 solvolysis of ethyl bromide[157] gives a ΔV_0^* of -15 ml./mole in 80% aqueous ethanol and -24 ml./mole in methanol. Obviously, this parameter, by itself, cannot be used to distinguish between the two mechanisms of neutral solvolysis.

We can therefore conclude that the activation volume for the solvolysis of benzyl chloride reported here does not shed any further light on the mechanism of this reaction, and activation volumes generally must be treated with some scepticism as parameters for distinguishing between operative S_N1 and S_N2 mechanisms in neutral solvolyses. It is suggested, however, that, while no classification as to degree of bond formation can be made, the present results are in agreement with an ionogenic reaction involving a highly polar transition state.

Although no mechanistic conclusions can be drawn from the behavior of the activation volume, its dependence upon the nature and composition of the solvent should be indicative of the role played by the solvent during the activation process.

Solvent Dependence of Activation Parameters

As activation enthalpies and entropies have been used widely in the past for studying the effect of solvent on chemical reactions (see Chapter 2), these parameters are best considered before dealing with the activation volume.

Enthalpy

The dependence of ΔH^{*} on the composition and chemical nature of the solvent is illustrated in Fig. 30. It can be seen that in each of the four systems a minimum occurs. As was pointed out in Chapter 2, this behavior is typical of reactions in aqueous binary solvents. It is interesting that a measureable minimum is also observed in aqueous

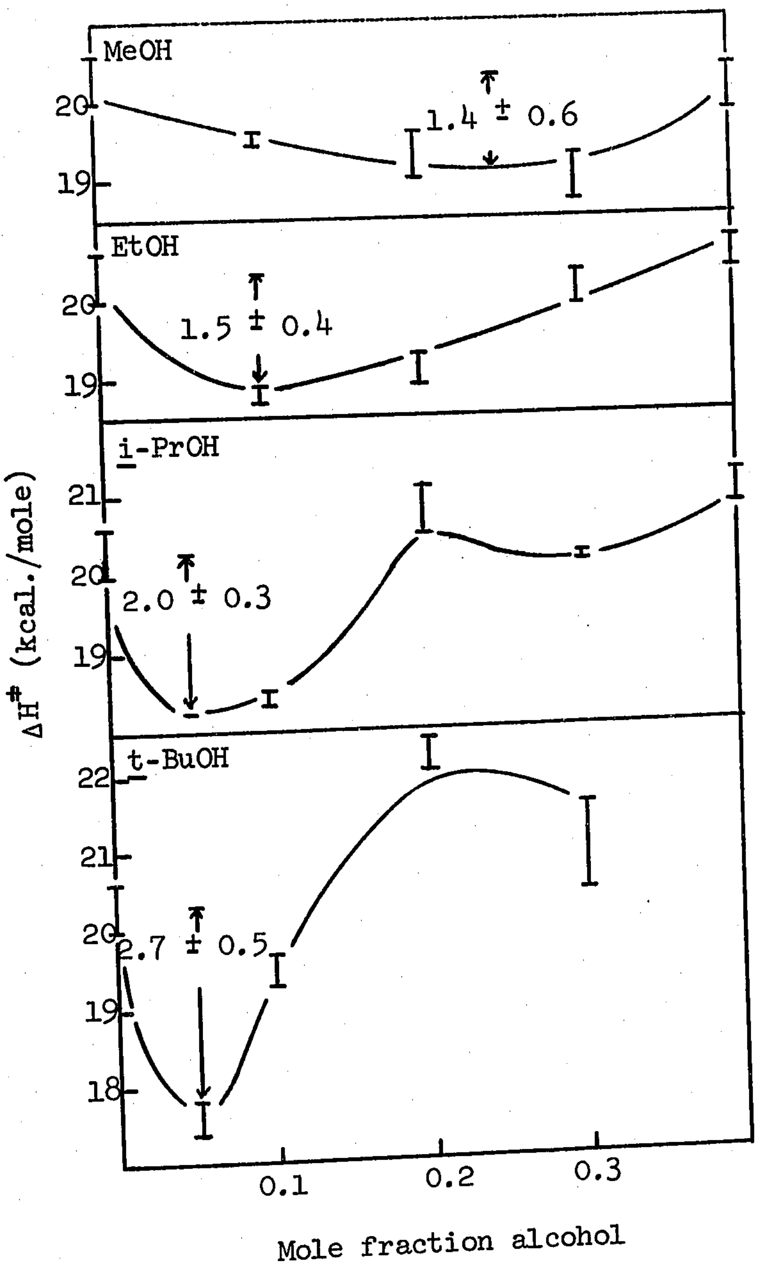


Fig. 30. Solvent dependence of the activation enthalpy for benzyl chloride solvolysis in aqueous alcohol.

methanol, contrary to the observations of Tommila, *et al*.[92,94,96] Tommila concluded that both the substrate and the organic solvent had to possess large hydrophobic groups in order that a minimum be observed[95] (p. 32). If this is correct then no minimum should be observed here for the methanol-water system.

The depth of the minimum in $\Delta H^{\ddagger}$ increases as the alcohol molecule becomes larger. This is also reflected in the results of Hyne and Wills for *p*-methylbenzyl chloride.[107] However, the latter shows a much more marked dependence on the organic solvent component in that for methanol-water the depth of the minimum $\Delta\Delta H^{\ddagger} = 1.7$ kcal./mole[158] while that for *t*-butanol-water is 5.0 kcal./mole.[107] Although these values are for 30°C., the difference between them and the present ones for benzyl chloride at 50.25°C. cannot be attributed solely to a difference in temperature. Hyne, Wills and Wonkka have shown that a change in temperature of 20° causes a change of only about 340 cal./mole in $\Delta\Delta H^{\ddagger}$.[106]

Comparing the value of $\Delta\Delta H^{\ddagger}$ in ethanol-water with those of Hyne, Wills and Wonkka[106] we find excellent agreement--1.5 ± 0.4 kcal./mole (present work) as compared with 1.8 kcal./mole (ref. 106).

It is apparent from Fig. 30 that the position of the minimum is shifted toward more aqueous solvents as the depth is increased. This same general behavior was observed for *p*-methylbenzyl chloride.[107,158] However, the exact positions of the extrema cannot be determined from the present data, but are probably within 0.03 mole fraction of the positions indicated in Fig. 30.

Arnett, *et al*.,[108,109] have measured the enthalpy of solution, $\Delta\bar{H}_s^g$, for various reactive substrates in aqueous ethanol. The most complete treatment was for *t*-butyl chloride.[159]

Fig. 31 shows that the minimum observed in $\Delta H^{\ddagger}$ for the solvolysis of *t*-butyl chloride in aqueous ethanol[101] is almost completely due to the endothermic maximum observed by Arnett, *et al.*, in the heat of solution of *t*-butyl chloride in these solvents.[109] The cycle below shows the relationship between these parameters where ΔH_V is the enthalpy of vaporization of

$$\begin{tikzcd}
\underline{t}\text{-BuCl(g)} \arrow[r, "\Delta H_g^{\ddagger}"] & \underline{t}\text{-Bu}^{\delta+}\text{---Cl}^{\delta-}\text{(g)} \arrow[dd, "\Delta\bar{H}_s^{t}"] \\
\underline{t}\text{-BuCl(l)} \arrow[u, "\Delta H_V"'] \arrow[d, "\Delta\bar{H}_s^{g}"'] & \\
\underline{t}\text{-BuCl(s)} \arrow[r, "\Delta H^{\ddagger}"] & \underline{t}\text{-Bu}^{\delta+}\text{---Cl}^{\delta-}\text{(s)}
\end{tikzcd} \qquad (81)$$

the liquid halide, $\Delta H_g^{\ddagger}$ is the gas phase activation energy for the reaction, and $\Delta\bar{H}_s^{t}$ is the enthalpy of solution of the gaseous transition state. The sum of $\Delta H^{\ddagger} + \Delta\bar{H}_s^{g}$ must equal $\Delta H_V + \Delta H_g^{\ddagger} + \Delta\bar{H}_s^{t}$. According to Fig. 31 this sum does not possess the deep extremum of the two components, but nevertheless is itself a somewhat complex function as regards its dependence on solvent composition. Since $\Delta H_g^{\ddagger}$ is a constant under the assumption of constancy of the transition state configuration as the solvent is varied and ΔH_V is a constant for any solute, the complex behavior of the summation must be due to $\Delta\bar{H}_s^{t}$.

Similar dissections for the solvolyses of *t*-butyldimethylsulfonium iodide and methyl benzenesulfonate do not appear to give such clear cut

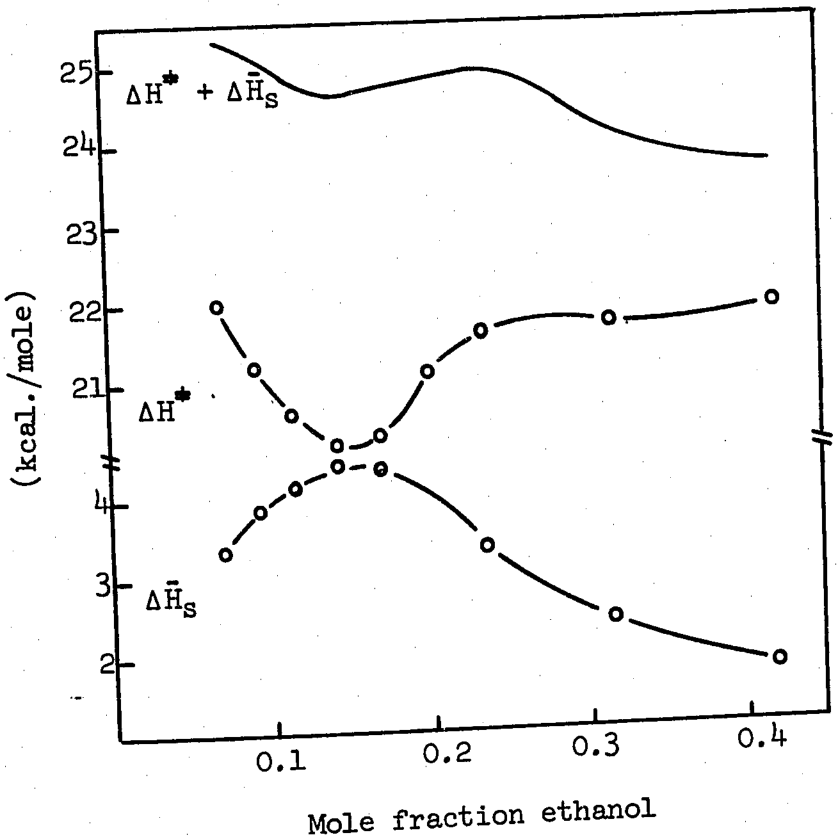


Fig. 31. Solvent dependence of t-butyl chloride enthalpy parameters in aqueous ethanol at 25°C.

($\Delta\bar{H}_S$ from ref. 109, ΔH^{*} from ref. 108) compensation.[109] The former has endothermic maxima in both $\Delta \bar{H}_s^g$ and $\Delta H^{\ddagger} + \Delta \bar{H}_s^g$, while the latter has two monotonically increasing curves. These dissections are not rigorous since the $\Delta \bar{H}_s^g$ and $\Delta H^{\ddagger}$ were measured at different temperatures.

A breakdown of the benzyl chloride system cannot be rigorously performed because the $\Delta \bar{H}_s^g$ is available only at 25°C.[109] while the present kinetic results are at 50.25°C. (Table V, p. 90). Nevertheless, an analogous treatment is illustrated in Fig. 32. Again an endothermic maximum is observed in $\Delta \bar{H}_s^g$ which compensates for the extremum in $\Delta H^{\ddagger}$. The v-shaped dip in $\Delta \bar{H}_s^g$ is reflected in the quantity $\Delta H^{\ddagger} + \Delta \bar{H}_s^g$, but the reality of this may be open to question as Arnett and co-workers encountered solubility problems in the measurement of $\Delta \bar{H}_s^g$ of benzyl chloride on the aqueous side of 0.143 mole fraction ethanol.[109] It is apparent, on comparison with Fig. 31, that the behavior of $\Delta H_v + \Delta H_g^{\ddagger} + \Delta \bar{H}_s^t$ is much simpler for benzyl chloride than for t-butyl chloride. The reason for this is presently unknown.

Since the $\Delta H^{\ddagger} + \Delta \bar{H}_s^g$ variation for benzyl chloride is analogous to that for t-butyl chloride in that it does not possess the deep extremum of the two components, it is tempting to suggest that the benzyl chloride transition state is of the S_N1 type. However, there are two very good reasons why such a rationalization is dangerous. First of all there is no precedent for using the $\Delta H^{\ddagger} + \Delta \bar{H}_s^g$ variation as a criterion of mechanism. In order to determine whether it is useful in this manner, a large number of compounds whose solvolytic mechanism is known would need to be studied. Secondly, t-butyldimethylsulfonium iodide, which undergoes S_N1 solvolysis,[160]

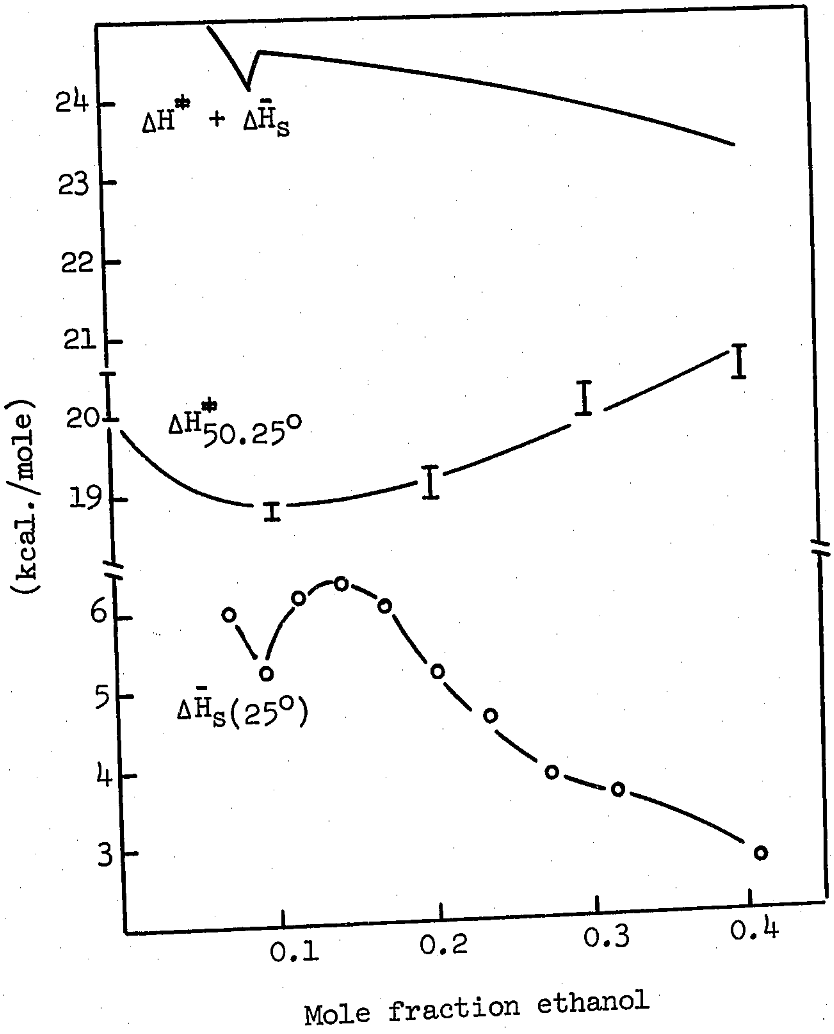


Fig. 32. Solvent dependence of benzyl chloride enthalpy parameters in aqueous ethanol.

($\Delta\bar{H}_s$ from ref. 109.)

possesses an endothermic maximum in $\Delta H^* + \Delta \bar{H}^g_s$ which is larger than that observed in ΔH^* alone.

Entropy

The variance of ΔS^* with solvent composition is shown in Fig. 33. It is apparent that the behavior of this parameter parallels that of ΔH^* (Fig. 30) in that a minimum is observed and the depth of the minimum, $\Delta\Delta S^*$, and its position are dependent upon the nature of the alcohol. Again aqueous methanol gives rise to an extremum contrary to Tommila's observations.[92,94,96]

Comparison of Fig. 33 with Fig. 30 shows a curious disparity between the positions of the ΔS^* extremum and the corresponding ΔH^* extremum in the ethanol and i-propanol solvents--the entropy minimum occurring at higher alcohol concentrations. The data of Hyne and Wills[133] indicate that the positions of the two minima do not always coincide. However, in two of the examples reported by these authors (o-nitro and p-methylbenzyl chloride) there is coincidence. Therefore, coincidence between the two extrema is neither an expected nor an unexpected phenomenon. It would seem that if the two extrema arise from the same physical effect they should coincide. However, the factors which cause these extrema are probably different in the two activation parameters of interest. This arises because the enthalpies depend merely on the interaction energies of the various molecules and the internal energy of the reacting substrate, whereas the entropies, in addition to this, depend upon the movements of the atoms within the molecules and of the molecules with respect to one

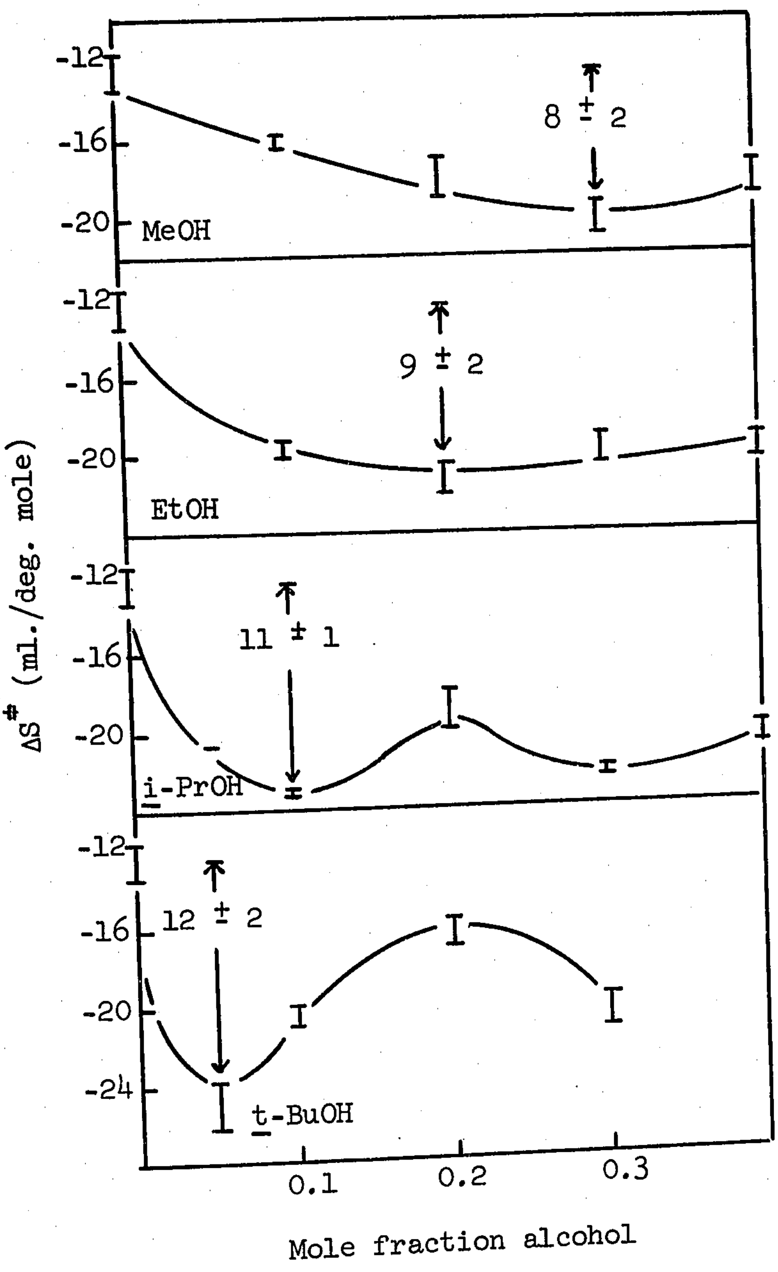


Fig. 33. Solvent dependence of the activation entropy for benzyl chloride solvolysis in aqueous alcohol.

another. From this viewpoint it would seem that any agreement between the positions of the two extrema is fortuitous unless the movements of the molecules are independent of the solvent components--a highly improbable situation.

It is also of interest to comment here that the positions of the $\Delta V_o^{\ddagger}$ minima, to be discussed below, are different again from that of either $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$.

It would seem that if the initial state solvation is capable of explaining the extremum in the activation enthalpy, the entropy of solution should be capable of explaining the corresponding extremum in $\Delta S^{\ddagger}$. The only attempt to dissect $\Delta S^{\ddagger}$ into its components is that of Arnett, *et al.*,[159] for *t*-butyl chloride. However, the data are available only on the non-aqueous side of 40% (v/v) ethanol (0.172 mole fraction ethanol), whereas the minimum in $\Delta S^{\ddagger}$ occurs near 0.17 mole fraction ethanol. Since there is a shortage of data in the region of interest, it is not possible to determine whether the same compensatory behavior occurs here as occurs in the enthalpy (*vide supra*). No data whatsoever are available for the entropy of solution of benzyl chloride in the solvents of interest.

Volume

Figs. 34 to 37 show the dependence of $\Delta V_o^{\ddagger}$ on solvent. Once again minimum values are observed, and the extremum size and position are dependent upon the nature of the organic solvent component. As pointed out in Chapter 1, $\Delta V_o^{\ddagger}$ reflects the behavior of the solvent during the activation process of ionic reactions. Since $\Delta S^{\ddagger}$ is also known to reflect

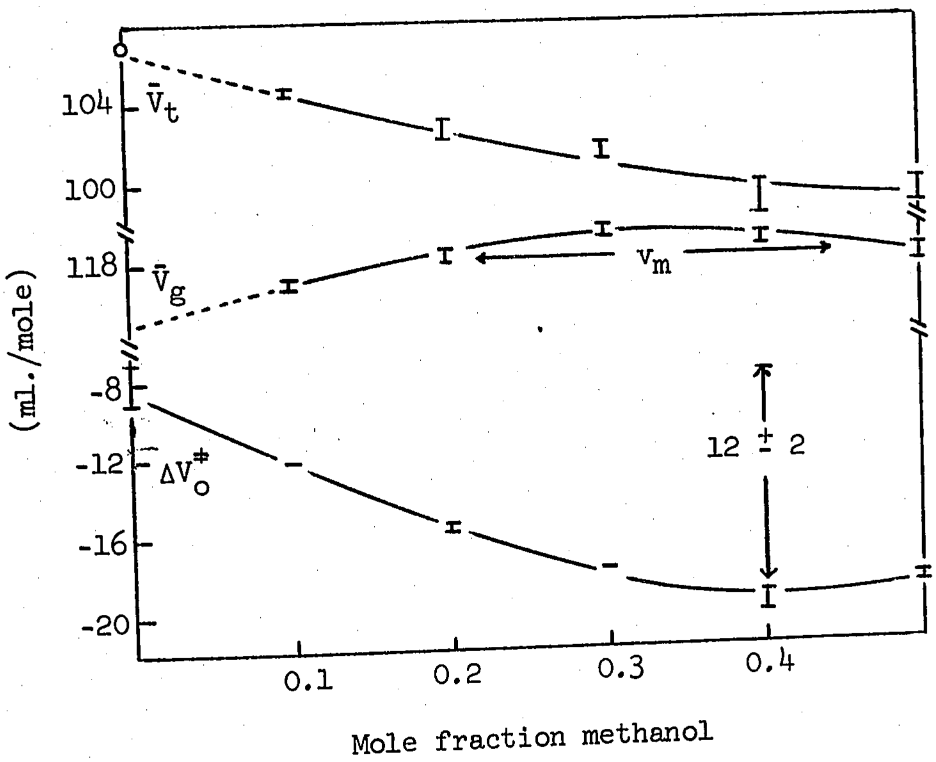


Fig. 34. Solvent dependence of benzyl chloride volume parameters in aqueous methanol. v_m is the molal volume of pure benzyl chloride.

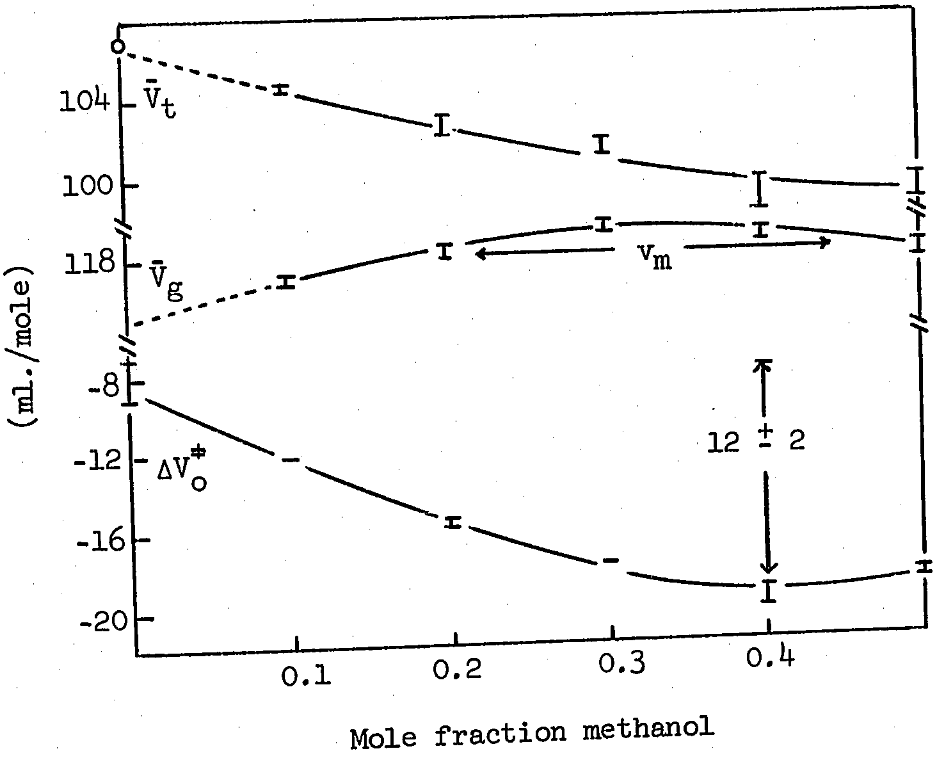


Fig. 34. Solvent dependence of benzyl chloride volume parameters in aqueous methanol. v_m is the molal volume of pure benzyl chloride.

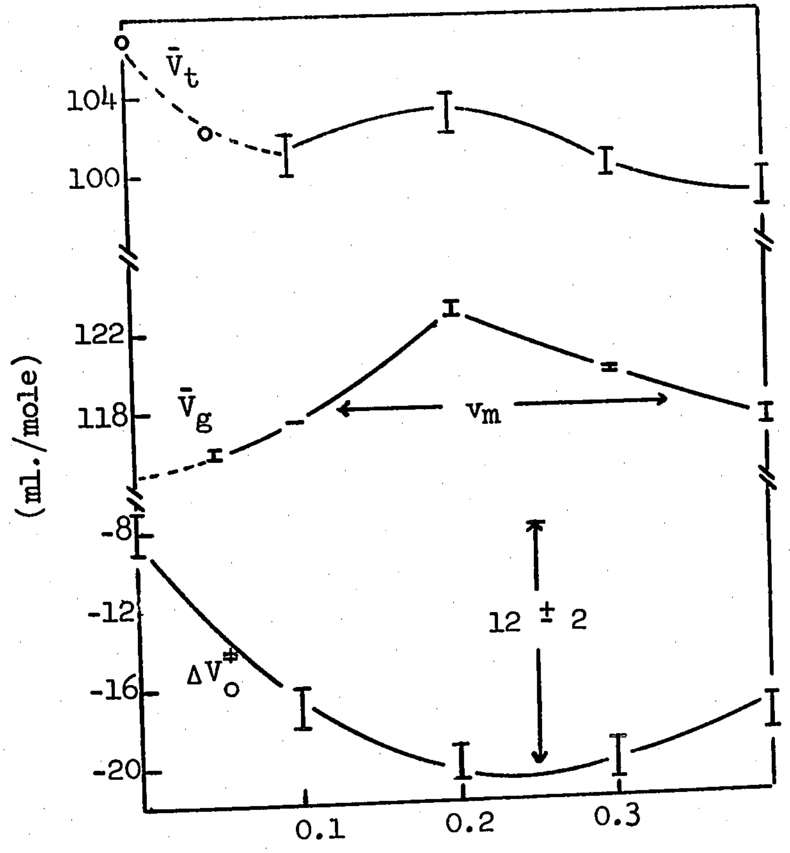


Fig. 35. Solvent dependence of benzyl chloride volume parameters in aqueous ethanol.
v_m is the molal volume of pure benzyl chloride.

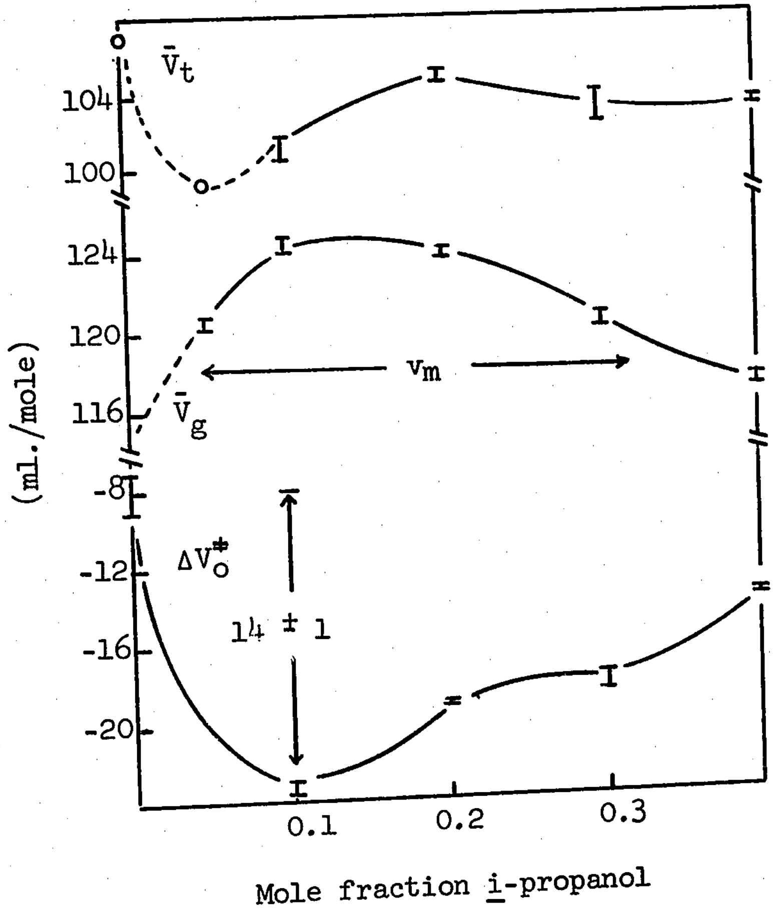


Fig. 36. Solvent dependence of benzyl chloride volume parameters in aqueous i-propanol. v_m is the molal volume of pure benzyl chloride.

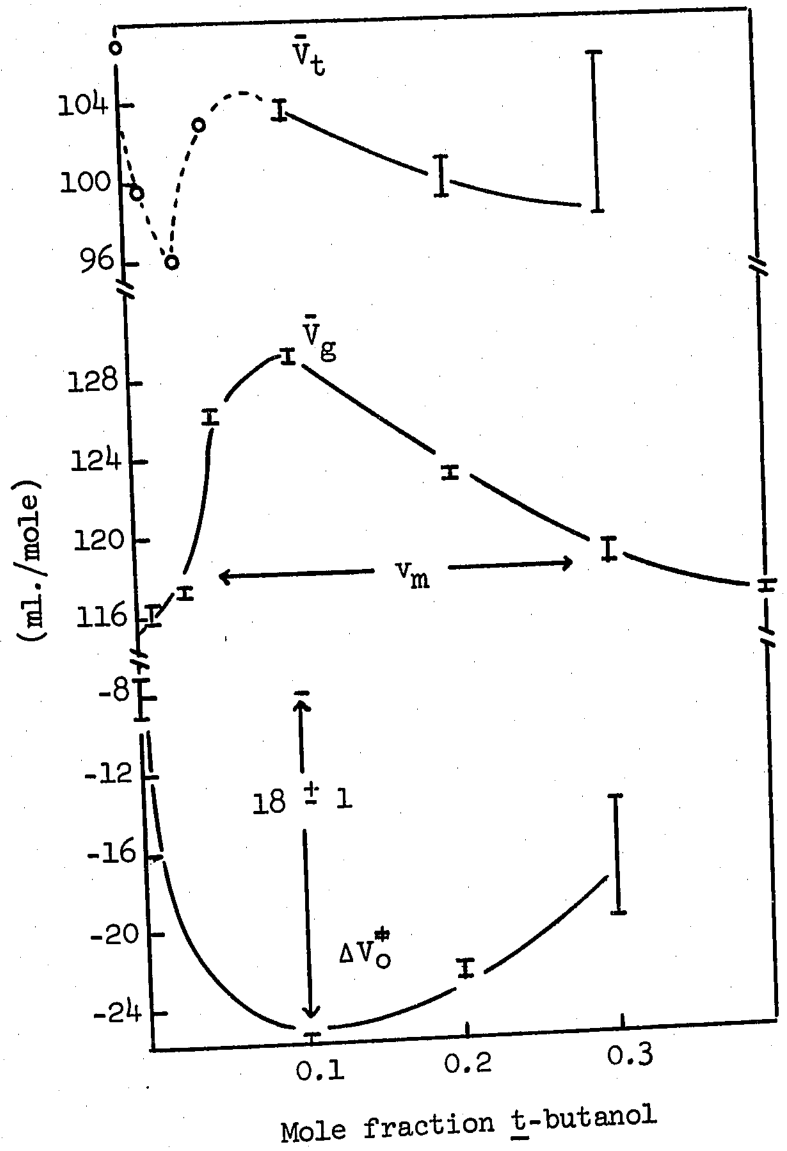


Fig. 37. Solvent dependence of benzyl chloride volume parameters in aqueous t-butanol. v_m is the molal volume of pure benzyl chloride.

this behavior,[45] a parallelism between the extremum behavior of these parameters ($\Delta S^{\ddagger}$ and $\Delta V_o^{\ddagger}$) might be expected. A comparison of Figs. 33 and 34 to 37, however, shows coincidence of extremum position only for i-propanol, and this may be fortuitous. The activation volume depends upon the relative positions of the atoms and the molecules in the initial and transition states and therefore should not strictly parallel the $\Delta S^{\ddagger}$ behavior which, in addition, depends upon the movements of the atoms and molecules (vide supra). However, some slight tendency toward parallel behavior might be expected since the amount of volume available to a molecule may affect its motions. For example, dissolution of a molecule in a liquid generally suppresses the rotational degrees of freedom.

As the enthalpy and entropy of activation can be broken down into several contributing factors, and can be understood in terms of these factors, a similar breakdown of the volume of activation is desireable in view of the possible understanding of the phenomena in the $\Delta V_o^{\ddagger}$ behavior. By definition, the activation volume is the difference between the partial molal volumes of the transition state, $\bar{V}_t$, and the initial state, $\bar{V}_g$. The measurement of $\bar{V}_g$ was described in Chapters 7 and 8, and its dependence on

$$\Delta V_o^{\ddagger} = \bar{V}_t - \bar{V}_g \tag{82}$$

solvent composition is shown in Figs. 34 to 37.

As was observed with the enthalpies of solution, there is a maximum in $\bar{V}_g$ for each solvent system. It is also apparent that the depth of the extremum increases and its position moves to higher aqueous solvents as the alcohol increases in molecular size. This is analogous to the behavior observed for ΔV_o^* itself. The question arises as to whether the behavior of $\bar{V}_g$ fully compensates for that of ΔV_o^* as was found for the activation enthalpy (Fig. 32).

By adding $\bar{V}_g$ to ΔV_o^*, $\bar{V}_t$ is obtained (see eq. 82). The results of this addition can be seen in Figs. 34 to 37. The broken curves are derived from interpolated values of ΔV_o^* and the experimental values of $\bar{V}_g$ except for the pure water point for which the experimental value of ΔV_o^* is available while that for $\bar{V}_g$ is not. It is apparent that only the methanol-water system gives a simple dependence of $\bar{V}_t$ on solvent composition. The other three curves are somewhat complex--even to the point of exhibiting relatively large minima[c] for which the depth is an increasing function of the size of the alcohol molecule, and the position approaches pure water as the alcohol becomes larger. It can be concluded that the large maximum found in the $\bar{V}_g$ dependence for benzyl chloride on solvent composition accounts for most of the extremum in ΔV_o^* (100% for aqueous methanol, 70% for aqueous ethanol, and 50% for aqueous i-propanol and aqueous t-butanol). This is similar to the enthalpy behavior found in ethanol (Fig. 32). The $\bar{V}_t$ curve for benzyl chloride in aqueous ethanol (Fig. 35) is not as complex as in the i-propanol (Fig. 36) or t-butanol (Fig. 37) systems.

It is interesting to note that Bateman's densities for aqueous ethanolic solutions of barium chloride[161] give rise to $\bar{V}_{BaCl_2}$ values having a shallow minimum at 0.08 mole fraction ethanol and a maximum at

---

[c] Note that $\bar{V}_t$ in pure water is about 107 ml./mole.

0.28 mole fraction (Fig. 38). The behavior of $\bar{V}_t$ for benzyl chloride in aqueous ethanol is seen to be very similar in that a shallow minimum followed by a low maximum appears as the concentration of ethanol increases. This suggests that the benzyl chloride solvolytic transition state behaves as a salt--i.e. a fully ionic species. Two problems arise in this comparison. First, association of the barium and chloride ions by the equilibria

$$Ba^{++} + Cl^{-} \rightleftharpoons BaCl^{+} \qquad (83)$$

$$BaCl^{+} + Cl^{-} \rightleftharpoons BaCl_2 \qquad (84)$$

may be great enough in the more ethanolic solvents to persist to infinite dilution. The presence of $BaCl^+$ and $BaCl_2$ would then be reflected in the ethanolic end of the curve of Fig. 38. The benzyl chloride transition state does not consist of two dissociated ions, but probably resembles some form of ion pair and thus may parallel the behavior of $BaCl_2$ in highly ethanolic solutions. Secondly, however, in the highly aqueous solvents, barium chloride undoubtedly exists as three separated ions while the benzyl chloride transition state does not.

Having established the extremum in $\bar{V}_g$, knowledge of the cause is desireable. In order to determine the factors involved, it is necessary to first consider the cycle involved. This is shown in eq. 85 where ΔV_{hf} measures the formation of holes of sufficient size and shape to accept the solute, and allows for any reorientation of solvent molecules in order to obtain that configuration most favorable for interaction with the solute.

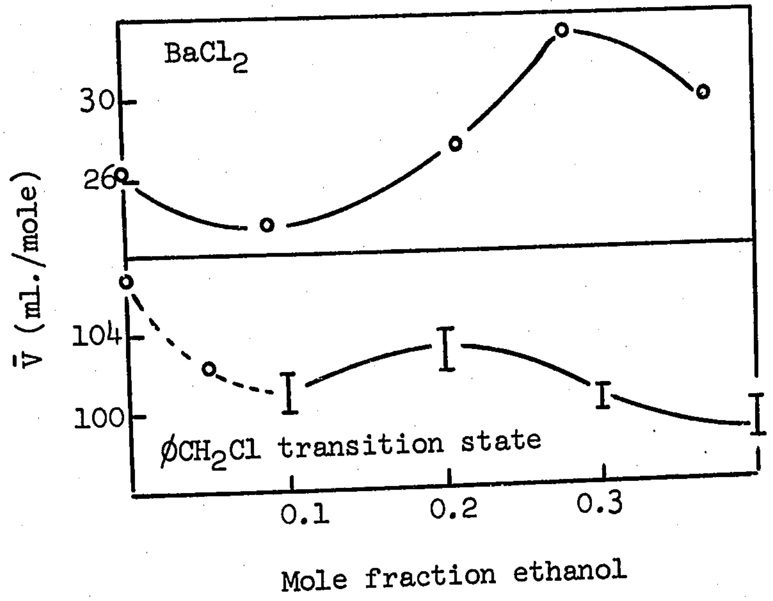
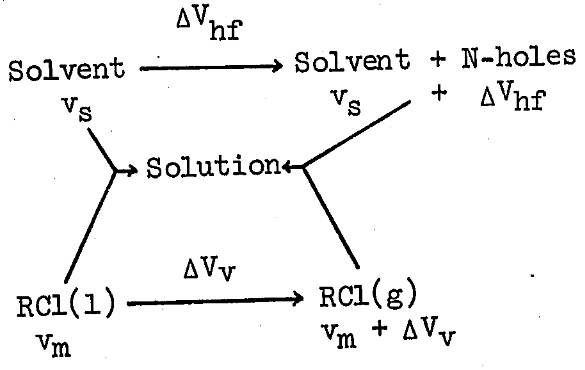


Fig. 38. Comparison of the benzyl chloride solvolytic transition state with barium chloride.

($\bar{V}_{BaCl_2}$ from ref. 161)



(85)

By definition, the partial molal volume of the solute is the change in volume of the solvent on addition of one mole of the solute to make an infinitely dilute solution. Three possible cases may be cited for illustration of the sign of the partial molal volume of a solute. If a golf ball is buried in a pile of sand, the increase in size of the sand pile exactly equals the volume of the golf ball--$\bar{V} > 0$. Such a situation would be expected for dissolution of a nonpolar solute in a dielectric continuum if no interaction between the solute and the solvent occurred. On the other hand, if honey (solute) is placed inside a honeycomb (solvent) there is no change in the volume of the honeycomb--$\bar{V} = 0$. Clathrate formation of a nonpolar solute in a highly structured solvent could produce this effect. Finally, if a magnet is placed in a loose pile of iron filings the strong attractive interaction may cause a decrease in volume giving a negative $\bar{V}$.

It is therefore apparent that the only factor in eq. 85 of significance to the value of $\bar{V}$ is ΔV_{hf}. In the present instance both $\bar{V}_g$ and $\bar{V}_t$ are positive. This may be due to the solvent behaving as a dielectric continuum with, or without, some form of solute-solvent interaction. The knowledge that these solvents are molecular in nature does not preclude such continuum behavior for as Bell pointed out[162] continuum behavior is observable when the particles of the solvent are much smaller than those of the solute. Obviously, the benzyl chloride molecule is much larger than a water molecule, and also is probably larger than the largest alcohol molecule of this study--t-butanol.

In order to determine how solute-solvent interactions affect the partial molal volumes, it is necessary to ascertain the molal volumes of the pure solutes. Since the density and effective molecular weight of the transition state are unknown, its molal volume in the hypothetical pure form cannot be determined. Using the density of benzyl chloride[151] as 1.0718 g./ml. at 50.25°C., and the molecular weight as 126.587 g./mole, the molal volume is $v_m = 118.1$ ml./mole. As can readily be seen in Figs. 34 to 37, $\bar{V}_g$ in the region of the maximum is always greater than v_m, whereas on either side of the maximum it is smaller. Obviously the disruption of the solvent structure near the maximum is somewhat greater than necessary in order to accommodate the non-interacting solute molecule. This could arise from a repulsive interaction between the solute and the solvent, or disruption of attractive interaction between solvent molecules. However, in the region where $\bar{V}_g - v_m$ is negative, attractive interaction would have to be postulated. It is difficult to envision any explanation for a change in sense of the solute-solvent or solvent-solvent interactions by slightly altering the solvent composition on both sides of the maximum. It must be noted that this treatment neglects any free volume contribution to v_m. Since the pure liquid has a non-zero compressibility and thermal expansivity this is a poor assumption. In fact, the benzyl chloride molecule is probably a great deal smaller than is implied by the value of 118.1 ml./mole.

Thermodynamics of the Binary Solvents

Since the extrema so far discussed occur as a result of altering the composition of the binary solvent, it is probable that these extrema reflect some physical property of the solvent. Recently, Franks and Ives reviewed the structural properties of aqueous alcohols.[163] The behavior of the thermodynamic parameters of these systems shows a surprising similarity to the activation and dissolution parameters discussed above. The variation of the heat of mixing, ΔH^M, and excess entropy of mixing, ΔS_E^M, with composition are shown in Fig. 39.

The first feature noticeable in Fig. 39 is that each of the thermodynamic parameters of mixing passes through a minimum value in the highly aqueous end of the scale the relative position of which is similar to that observed for the activation parameter extrema (vide supra). Secondly, for the two systems where data are available, the positions of the $T\Delta S_E^M$ minima occur at higher alcohol concentrations than do the ΔH^M minima. This is in accord with the observations discussed above (see Figs. 30 and 33) for the activation parameters.

It is interesting to note that the relative positions of the minima in Fig. 39 for the ΔH^M are the same as in Fig. 30 for the $\Delta H^{\ddagger}$, indicating that similar factors are probably responsible for the extrema. However,

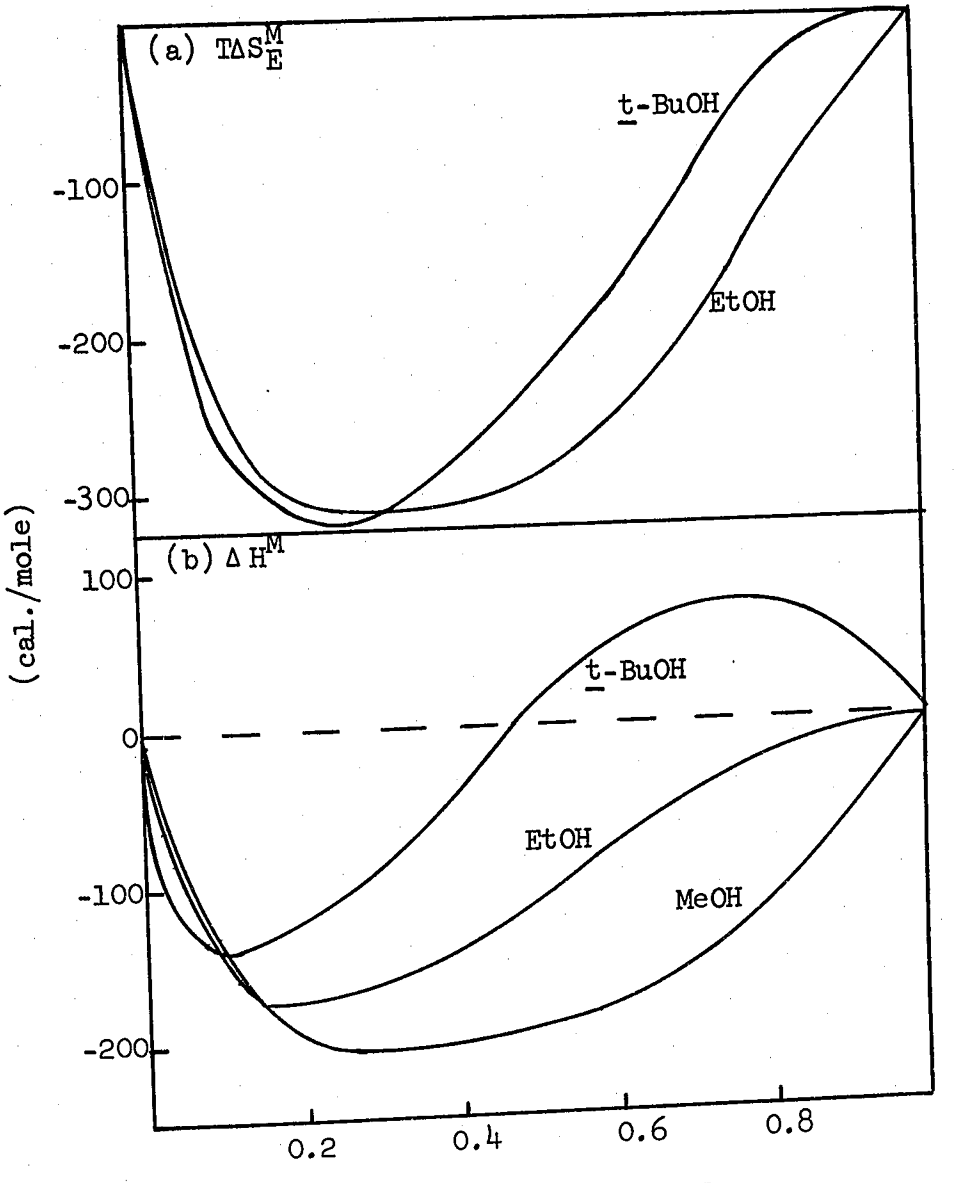


Fig. 39. Variation of the parameters of mixing of alcohol-water mixtures with solvent composition at 25°C.

(Data from ref. 163)

the relative depths of the minima are in the opposite sense.

Franks and Ives[163] have explained these minima in the thermodynamic parameters of mixing on the basis of an increase in the structure of the solvent (water) on addition of the first increments of added co-solvent (alcohol). Such phenomena arise from a combination of two factors --depolymerization of a highly associated component (water) and strong inter-component attraction. Since the increasing order of proton accepting facility in hydrogen bonding is MeOH < EtOH < i-PrOH < t-BuOH,[164] hydrogen bonding between water and t-butanol should be favored, however, steric limitations may prevent such association. That the minima occur in the high aqueous end of the composition parameter was explained on the basis that water, resisting any disturbance to its inherent structure, is able to act as host to molecules which have some affinity for it.[163] With addition of more of the foreign species, the failure of water to maintain its structure is expected. The more "foreign" the added molecules, the sooner the structure breakdown occurs. This is evidenced in Fig. 39 since the larger the alkyl group of the alcohol molecule, the less favorable it is to an aqueous environment, and the more willing it is to interact with water as a hydrogen bond acceptor.

In an analogous manner to the enthalpy and entropy considerations, it is to be expected that the excess volume of mixing, ΔV^M, of the solvents would show extremum behavior in the same solvent composition region as observed for the $\Delta V_0^{\ddagger}$ and $\bar{V}$'s. Utilizing the density data of Table XVI (p. 156), the excess volume of mixing can be calculated by means of eq. 86. The results of these calculations are illustrated in Fig. 40.

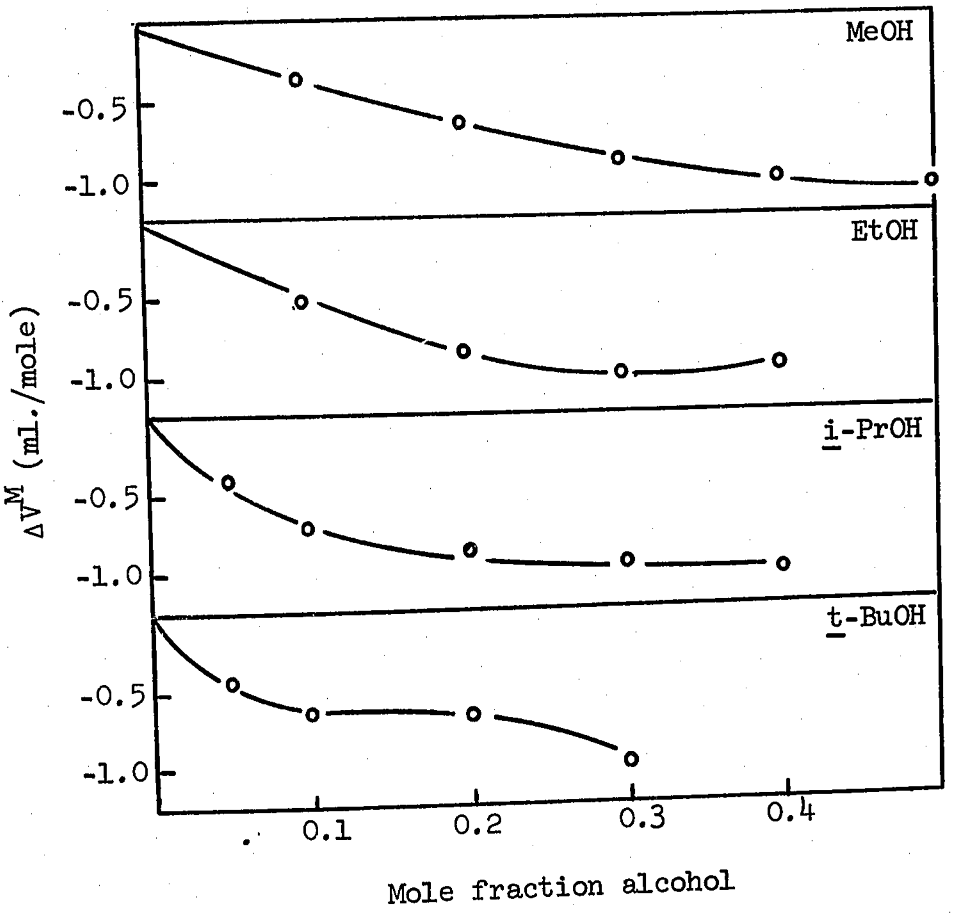


Fig. 40. Variation of the volume of mixing of alcohol-water mixtures with solvent composition at 50.25°C.

$$\Delta V^M = M_1X_1(\frac{1}{d} - \frac{1}{d_1}) + M_2X_2(\frac{1}{d} - \frac{1}{d_2}) \qquad (86)$$

It is apparent that, with the possible exception of ethanol, no extremum exists in the composition region of interest to the present study. Since ΔV^M must be zero at $X_{ROH} = 1$, there obviously is a minimum at some solvent composition beyond the range considered here.

If the partial molal volumes of the alcohols in these solvent mixtures are considered,[163] minima are indeed observed in the region of interest (Fig. 41). Surprisingly, however, these minima appear at higher water concentrations than those of either $\Delta V_0^{\ddagger}$ or the $\bar{V}$'s. No explanation for this anomaly is presently apparent.

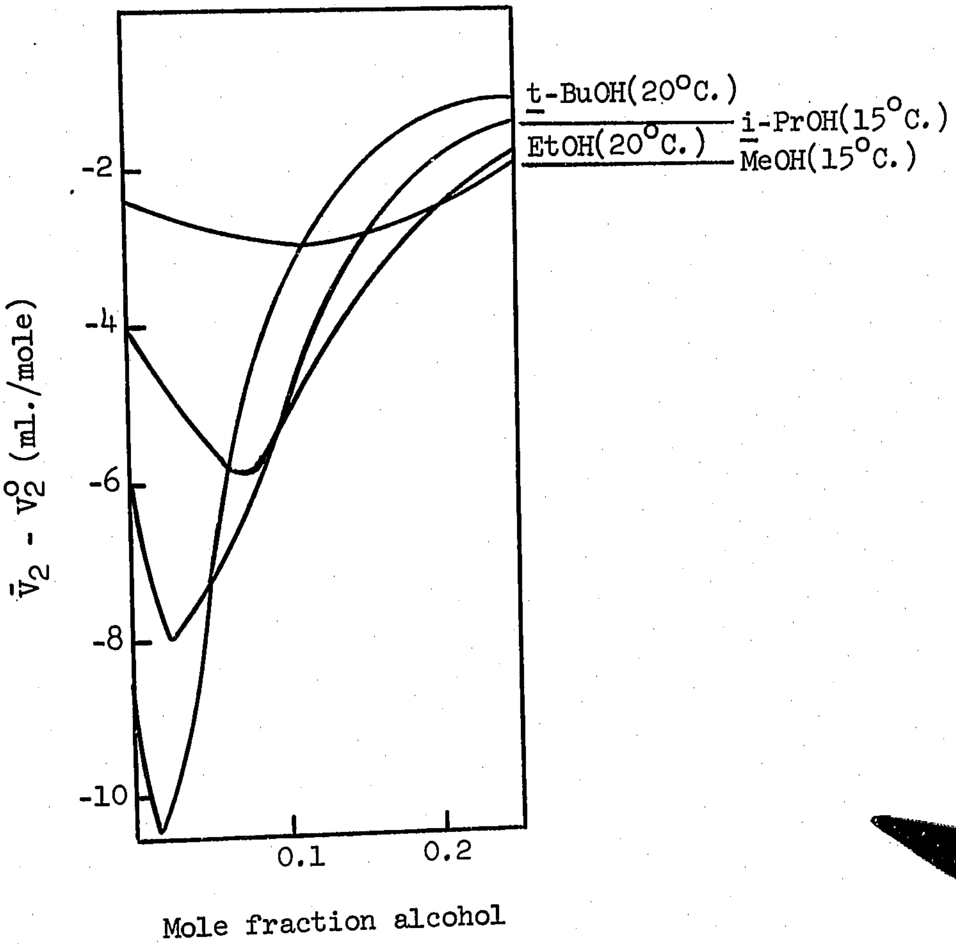


Fig. 41. Variation of the partial molal volume of alcohols with solvent composition in aqueous mixtures.

(Data from ref. 163)

CHAPTER 10

CONSTANT VOLUME ACTIVATION PARAMETERS

Whalley, et al.,[135] have recently advocated the use of activation parameters at constant volume for describing the activation process of reactions in binary solvent media. Their reason for this proposal is that these parameters generally vary in a simpler manner with solvent composition than do the constant pressure parameters normally studied. In particular, these authors found no extrema behavior in the activation energy at constant volume, $\Delta U_v^{\ddagger}$, or the activation entropy at constant volume, $\Delta S_v^{\ddagger}$, for the acid hydrolyses of methyl acetate and ethylene oxide in aqueous acetone. The method of calculating these parameters from the measureable constant pressure parameters is as follows.

For any parameter X which is a function of both T and p

$$dX = \left(\frac{\partial X}{\partial T}\right)_p dT + \left(\frac{\partial X}{\partial p}\right)_T dp. \tag{87}$$

Therefore

$$\left(\frac{\partial X}{\partial T}\right)_v = \left(\frac{\partial X}{\partial T}\right)_p + \left(\frac{\partial X}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v. \tag{88}$$

Since

$$\left(\frac{\partial p}{\partial T}\right)_v = - \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T = \frac{\alpha}{\kappa} \tag{89}$$

Then

$$\left(\frac{\partial X}{\partial T}\right)_V = \left(\frac{\partial X}{\partial T}\right)_p + \frac{\alpha}{\kappa}\left(\frac{\partial X}{\partial p}\right)_T. \tag{90}$$

If X is taken as equal to the free energy, F, and since $(\partial F/\partial T)_p = - S_p$ and $(\partial F/\partial p)_T = V$

$$\left(\frac{\partial F}{\partial T}\right)_V = - S_p + \frac{\alpha}{\kappa}V \tag{91}$$

or

$$- S_V = - S_p + \frac{\alpha}{\kappa}V. \tag{92}$$

At this point, Whalley, et al.,[135] assumed that the bulk solvent compressibility, κ, and thermal expansivity, α, could be taken as equalling the partial molal quantities of the solute. This then led to

$$T\Delta S_V^{\ddagger} = T\Delta S_p^{\ddagger} - \frac{T\alpha}{\kappa}\Delta V^{\ddagger}. \tag{93}$$

At constant volume, $\Delta S_V = \Delta U_V/T$, and at constant pressure $\Delta S_p = \Delta H_p/T$, therefore

$$\Delta U_V^{\ddagger} = \Delta H_p^{\ddagger} - \frac{T\alpha}{\kappa}\Delta V^{\ddagger}. \tag{94}$$

Since it is well known that the solvent structure and composition in the vicinity of a solute molecule is altered by the presence of the solute, there does not appear to be any justification for using the bulk solvent parameters in these calculations. Indeed, the partial molal expansivity, $\bar{\alpha}$, and the compressibility, $\bar{\kappa}$, of the solute in the appropriate solvents should be used. Such partial molal quantities reflect the nature of the reorganized solvent. Eqs. 93 and 94 then would be replaced by eqs. 95 and 96 respectively.

$$T\Delta S_v^{\neq} = T\Delta S_p^{\neq} - T\Delta\left(\frac{\bar{\alpha}}{\bar{\kappa}}\bar{V}\right)^{\neq} = T\Delta S_p^{\neq} - T\left(\frac{\bar{\alpha}_t}{\bar{\kappa}_t}\bar{V}_t - \frac{\bar{\alpha}_g}{\bar{\kappa}_g}\bar{V}_g\right) \qquad (95)$$

$$\Delta U_v^{\neq} = \Delta H_p^{\neq} - T\Delta\left(\frac{\bar{\alpha}}{\bar{\kappa}}\bar{V}\right)^{\neq} = \Delta H_p^{\neq} - T\left(\frac{\bar{\alpha}_t}{\bar{\kappa}_t}\bar{V}_t - \frac{\bar{\alpha}_g}{\bar{\kappa}_g}\bar{V}_g\right) \qquad (96)$$

Furthermore, just as $\bar{V}$ has different values for the transition and initial states (Figs. 34 to 37), $\bar{\alpha}$ and $\bar{\kappa}$ are expected to have different values for these same two states. Therefore, these parameters cannot justifiably be removed from the parentheses. Unfortunately, $\bar{\alpha}_t$ and $\bar{\kappa}_t$ can never be measured, and for solutes which react with the solvent $\bar{\alpha}_g$ and $\bar{\kappa}_g$ can also not be easily measured. Using the dilatometer technique for measuring $\bar{V}_g$ (Chapter 7) at different temperatures would indeed permit evaluation of $\bar{\alpha}_g$. However, compressibility measurements cannot at present be made "instantaneously" so that $\bar{\kappa}_g$ is still elusive. It was felt premature, therefore, to attempt to measure $\bar{\alpha}_g$ in this work since the other parameter, $\bar{\kappa}_g$, necessary for complete evaluation of eqs. 95 and 96 is unobtainable. It may be noted that highly accurate rate data at various pressures and temperatures may permit an indirect evaluation of $\Delta\alpha^{\neq}$. This work is currently underway in this laboratory by Mr. Stuart Dickson.

In view of the current inability to use the rigorously correct equations (95 and 96), the constant volume parameters were calculated by means of eqs. 93 and 94 for the solvolysis of benzyl chloride. The results are shown in Figs. 42 and 43. On comparing these figures with Figs. 30 and 33 (pp. 165 and 172), respectively, it is immediately obvious that the constant volume parameter dependence on solvent composition is indeed much simpler as pointed out by Whalley.[135] The minima observed in $\Delta S_p^{\ddagger}$ are entirely absent in Fig. 43. However, extrema do persist in the activation energy (Fig. 42), contrary to the observation of Whalley, et al.[135]

One immediate question is why Whalley did not observe extrema behavior in his systems. The data reported by these authors[135] were taken only to 0.2 mole fraction aqueous acetone--the $\Delta H_p^{\ddagger}$ and $\Delta S_p^{\ddagger}$ extrema occurring near 0.1 mole fraction. In the present study it was found that $\Delta V_o^{\ddagger}$ has extremum values at higher non-aqueous component concentrations than do $\Delta H_p^{\ddagger}$ or $\Delta S_p^{\ddagger}$. Consequently, the constant volume parameters, being a function of both $\Delta V_o^{\ddagger}$ and $\Delta H_p^{\ddagger}$ or $\Delta S_p^{\ddagger}$, have extrema at higher organic solvent component mole fractions than $\Delta H_p^{\ddagger}$ or $\Delta S_p^{\ddagger}$.

As a result of their observations, Whalley and his group concluded that "the existence of the minimum is therefore best considered as a trivial fact, not related to mechanism except insofar as changes in $T\alpha\Delta V^{\ddagger}/\kappa$ are related to mechanism",[135] and that most of the compensation in the extremum behavior of $\Delta H_p^{\ddagger}$ is "due to changes in the thermal expansivity α of the solvent...[while] changes of the volume of activation contribute to a smaller extent, and changes of the compressibility are of little

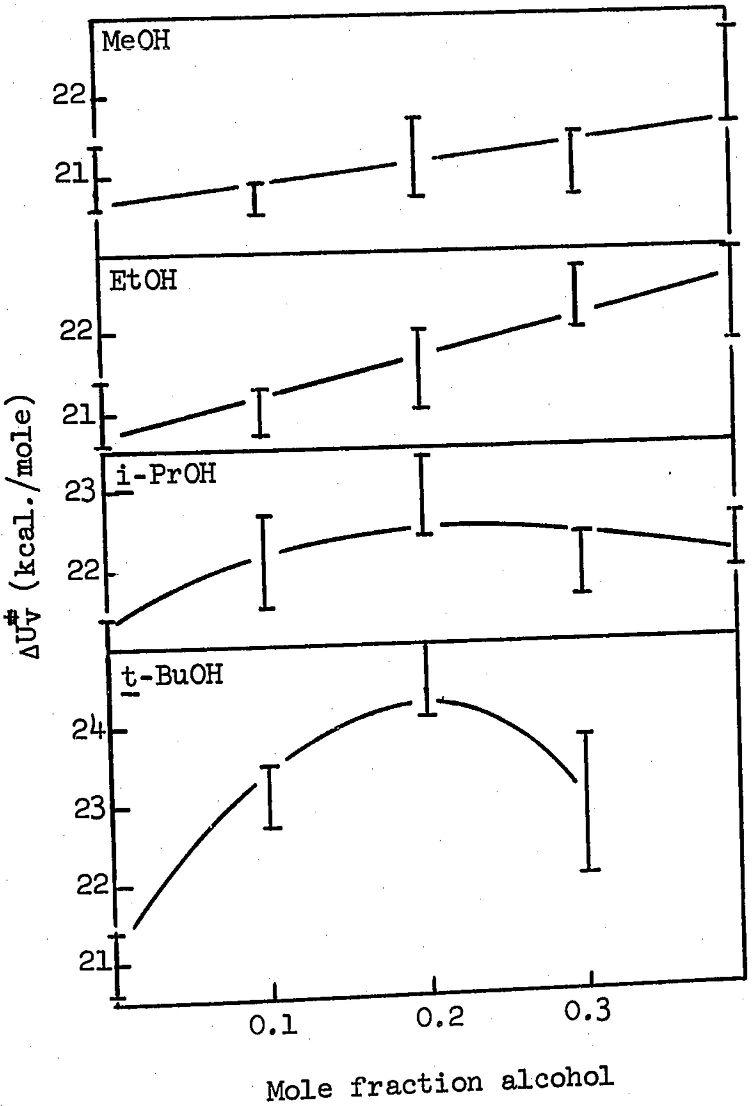


Fig. 42. Variation of $\Delta U_v^{\ddagger}$ with solvent composition for the solvolysis of benzyl chloride in aqueous alcohols.

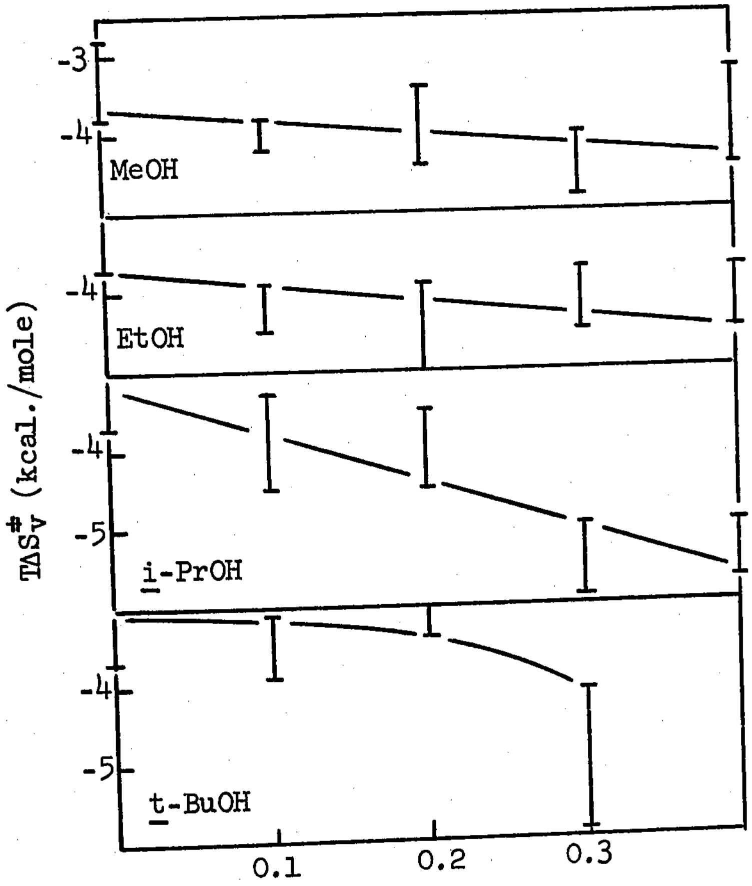


Fig. 43. Variation of $T\Delta S_v^{\neq}$ with solvent composition for the solvolysis of benzyl chloride in aqueous alcohols.

consequence."[135]

In view of the fact that ΔV_0^* for the present reaction, benzyl chloride solvolysis, exhibits extremum behavior (Figs. 34 to 37, pp. 174 to 177) whereas α changes monotonically with solvent composition (Table XIV p. 151), any compensatory behavior must be due to ΔV_0^* and not to α. The concept of the solvent being unrelated to mechanism was treated earlier (p. 161). Suffice it to repeat here that a precise definition of what constitutes a reaction "mechanism" is necessary in order to avoid a semantic argument. Once a definition is accepted, the current argument should be resolvable.

CHAPTER 11

ACTIVATION PARAMETER RELATIONSHIPS

It is well known that changes in substrate structure or solvent usually change both ΔH^* and ΔS^*, and that large values of one tend to accompany large values of the other. Such knowledge has led to considerations of the so-called "isokinetic relationship" between extrathermodynamic parameters (eq. 97).[165,166]

$$\Delta H^* = \Delta H_o^* + \beta \Delta S^* \tag{97}$$

In eq. 97 ΔH_o^* is simply the value of ΔH^* corresponding to $\Delta S^* = 0$, and has no physical meaning. The slope, β, is a quantity having dimensions of absolute temperature.

Leffler[165] found that 81 reactions of 103 for which sufficient data were available could be represented by eq. 97. Although linear relationships between ΔH^* and ΔS^* are frequently found, curves of various shapes are not uncommon.[166] In particular, eq. 97 for the solvolysis of t-butyl chloride in various binary solvents was observed to have peculiar shapes.[167] That the benzyl chloride solvolysis is not unlike the t-butyl chloride behavior in this respect is readily seen in Fig. 44. The dotted line is an arbitrary line of slope $\beta = 323^{o}$A.--the experimental temperature. It has been demonstrated[166] that strong solute-solvent interaction leads to a linear isokinetic relationship, whereas more complicated curves are

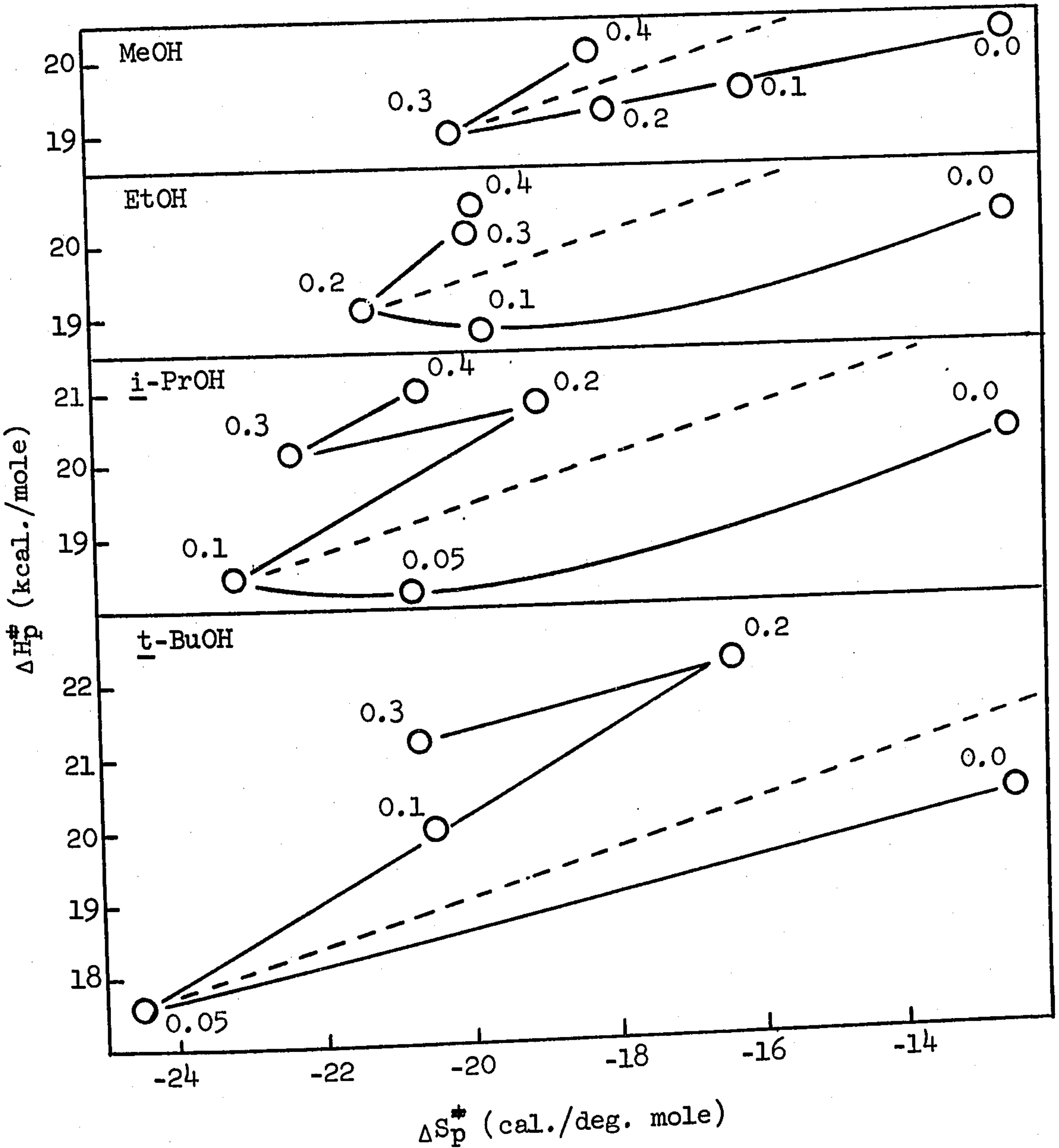


Fig. 44. Relationship between $\Delta H_p^{\ddagger}$ and $\Delta S_p^{\ddagger}$ for the solvolysis of benzyl chloride in aqueous alcohols.

(Numbers refer to mole fraction alcohol. Dotted lines are of slope β = 323°A., the experimental temperature) obtained when solvent-solvent interactions are also important. Apparently, for n distinct and important interactions there are n-1 inflection points observable.

Burris and Laidler[44] have observed that since $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ both reflect solvent behavior for ionic reactions, they should parallel one another in sign and magnitude. In fact they obtained a linear correlation between these two parameters for six different reactions in water. It is interesting to consider that if six different reactions in one solvent give a linear relationship, would one reaction in various solvents also give a linear correlation. In point of fact, the present data (Table V, p. 90) represent a fair test of this possibility since 17 solvent compositions are available. The appropriate graphs, one for each alcohol system, are presented in Fig. 45.

It is at once apparent that linearity is not observed. Rather do we find quite complex curves similar to the isokinetic relationship illustrated in Fig. 44. Furthermore, in at least two instances, the curves tend to cross themselves--a situation not previously reported for the $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ curves. Although this phenomenon is rather curious, it is doubtful whether any effort spent in trying to understand this cross over would be profitable. This is especially true in view of the empirical nature of the relationship.

The activation parameters at constant volume also display rather complex inter-relationships, as can be seen in Figs. 46 and 47. This contrasts the simple behavior observed by Whalley, et al.,[135] which may have been due to the limited solvent composition range studied by these authors.

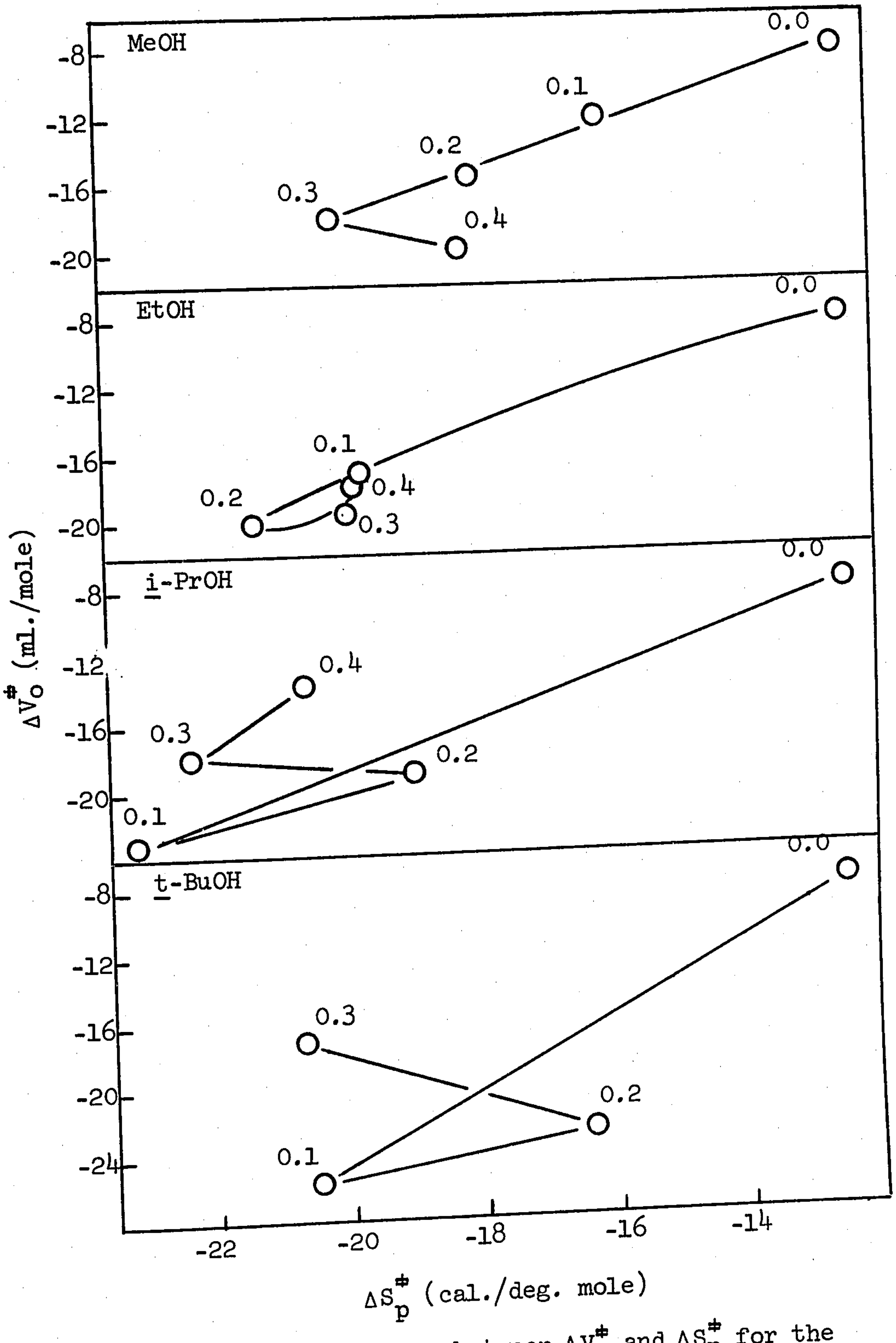


Fig. 45. Relationship between $\Delta V_o^{\ddagger}$ and $\Delta S_p^{\ddagger}$ for the solvolysis of benzyl chloride in aqueous alcohols.

(Numbers refer to mole fraction alcohol.)

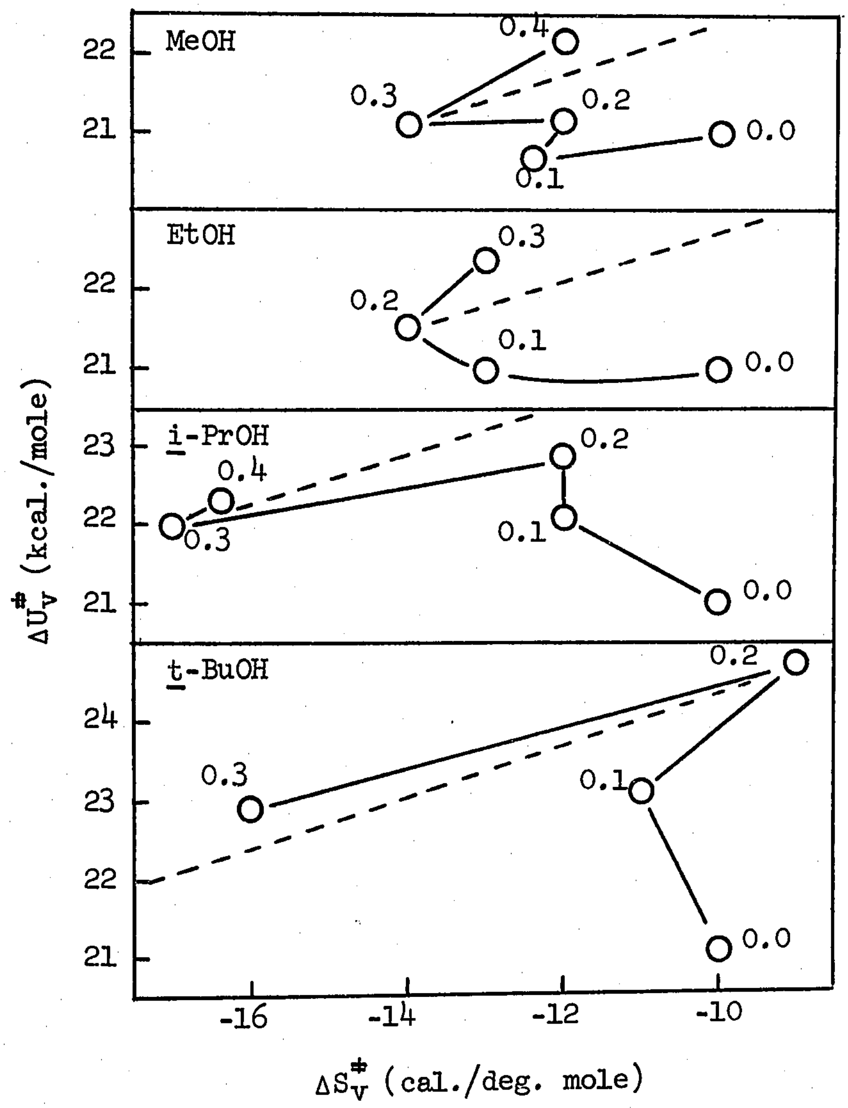


Fig. 46. Relationship between $\Delta U_V^{\ddagger}$ and $\Delta S_V^{\ddagger}$ for the solvolysis of benzyl chloride in aqueous alcohols.

(numbers refer to mole fraction alcohol. Dotted lines are of slope $\beta = 323^{o}$A., the experimental temperature.)

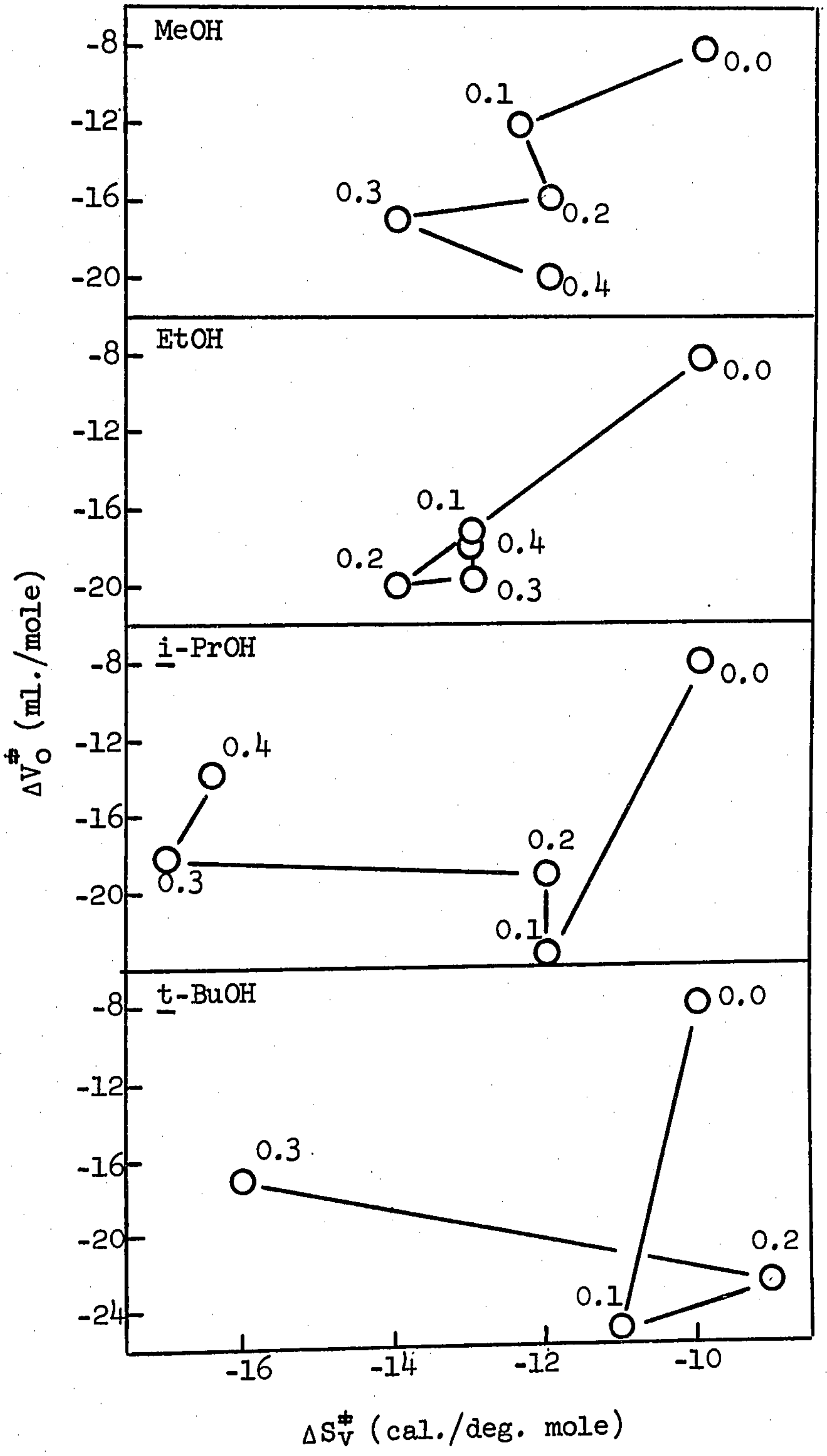


Fig. 47. Relationship between $\Delta V_o^{\neq}$ and $\Delta S_v^{\neq}$ for the solvolysis of benzyl chloride in aqueous alcohols.

(numbers refer to mole fraction alcohol)

CHAPTER 12

SECOND DERIVATIVE PARAMETERS - $(\partial\Delta V^{\ddagger}/\partial p)_T$

Having established that the pressure dependence of the activation volume, $(\partial\Delta V^{\ddagger}/\partial p)_T$, is measureable (Chapter 6), it is of interest to the present study to determine whether this parameter exhibits extremum behavior as a function of solvent composition. In Fig. 48 it is seen that an extremum in fact does occur for each solvent system near the region where $\Delta V_0^{\ddagger}$ has its minimum. It is interesting that the extremum in $(\partial\Delta V^{\ddagger}/\partial p)_T$ is a maximum rather than a minimum, but it is not unexpected in that $\Delta C_p^{\ddagger}$, the temperature dependence of $\Delta H^{\ddagger}$, for benzyl chloride solvolysis in aqueous ethanol also has a maximum where $\Delta H^{\ddagger}$ shows minimum behavior (Fig. 49).[106] Unfortunately, until more is understood about the extrema in $\Delta V_0^{\ddagger}$ and $\Delta H^{\ddagger}$, no explanation for those in the second derivatives of the rate constant is possible. However, accepting that the extrema behavior in $\Delta H^{\ddagger}$ and $\Delta V_0^{\ddagger}$ is a reflection of the structure of the binary solvent medium, then it would appear reasonable to conclude that similar effects are responsible for the extrema observed in the second derivative parameters $\Delta C_p^{\ddagger}$ and $(\partial\Delta V^{\ddagger}/\partial p)_T$. It is at least comforting to know that a further pair of measureable pseudo thermodynamic parameters of activation reflect these effects and their behavior will be available in the future to test any hypotheses presented to account for the observed extremum phenomena.

As was stated earlier (Chapter 6), $(\partial\Delta V^{\ddagger}/\partial p)_T$ is related to the compressibilities of the transition and initial states by

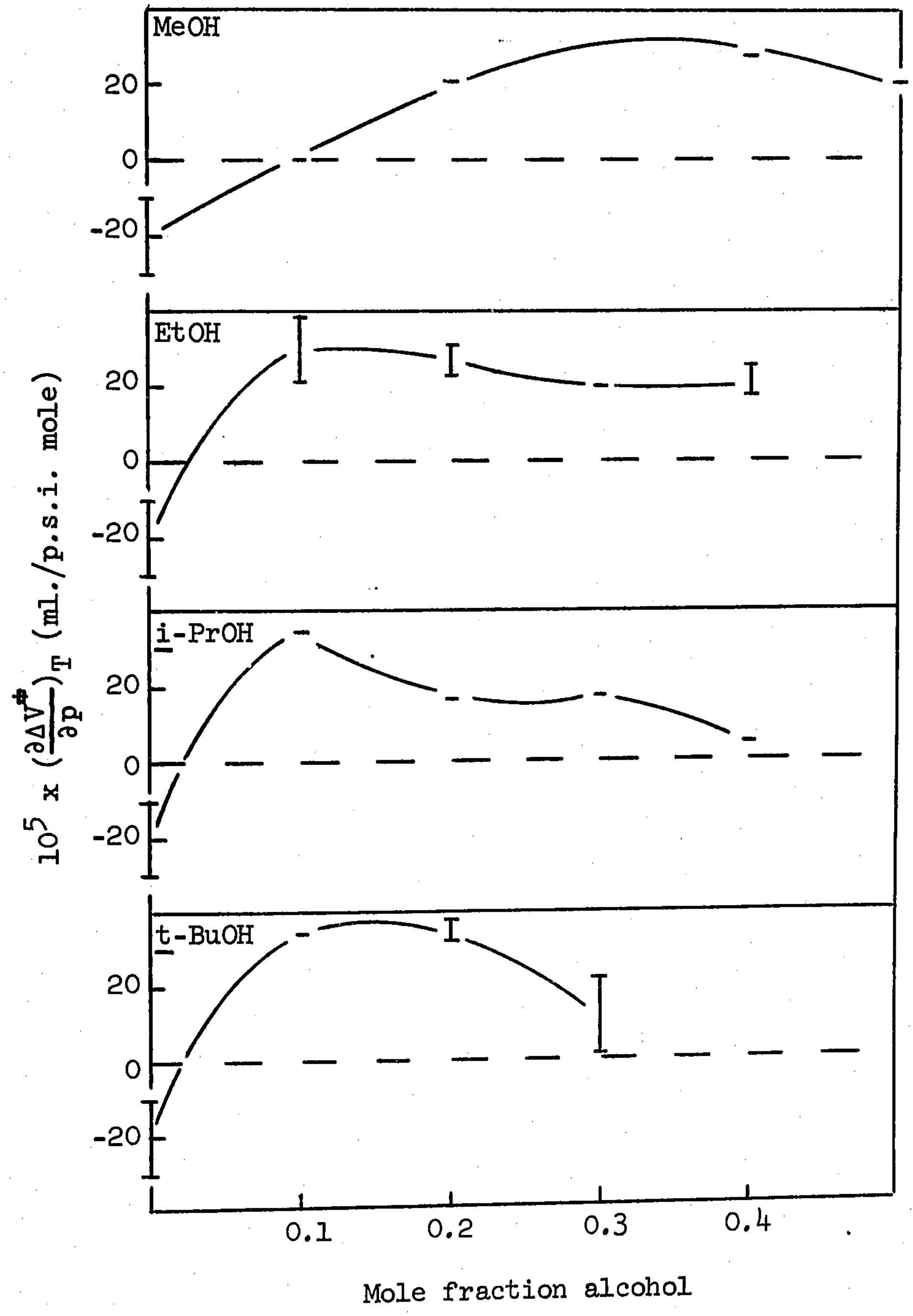
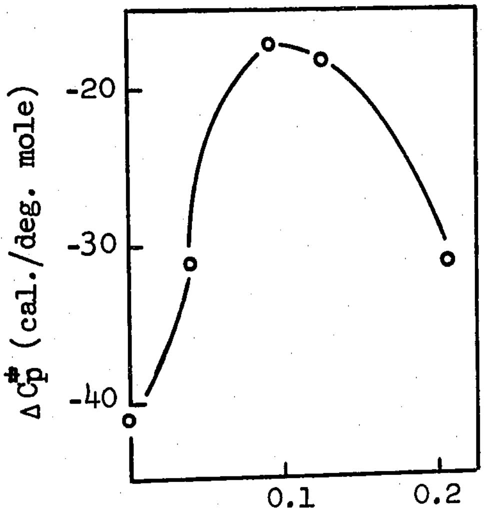


Fig. 48. Variation of $(\partial \Delta V^{\neq}/\partial p)_T$ with solvent composition in aqueous alcohol for benzyl chloride solvolysis.



Mole fraction ethanol

Fig. 49. Variation of $\Delta C_p^{\neq}$ with solvent composition for the solvolysis of benzyl chloride in aqueous ethanol.

(Data from ref. 106.)

$$\left(\frac{\partial \Delta V^{\ddagger}}{\partial p}\right)_T = -\bar{\kappa}_t \bar{V}_o^t \exp(-\bar{\kappa}_t p) + \bar{\kappa}_g \bar{V}_o^g \exp(-\bar{\kappa}_g p). \tag{98}$$

However, since $\bar{\kappa}_g$ cannot be measured by present techniques, this relationship is of no current practical value.

It is more profitable to consider this parameter as in eq. 99, since the effect of pressure on a volume is intuitively easier to comprehend.

$$\left(\frac{\partial \Delta V^{\ddagger}}{\partial p}\right)_T = \left(\frac{\partial \bar{V}_t}{\partial p}\right)_T - \left(\frac{\partial \bar{V}_g}{\partial p}\right)_T \tag{99}$$

Over most of the solvent range of interest, $(\partial \Delta V^{\ddagger}/\partial p)_T$ is positive, i.e. $(\partial \bar{V}_t/\partial p)_T > (\partial \bar{V}_g/\partial p)_T$. However, $(\partial \bar{V}/\partial p)_T < 0$. Therefore, $|(\partial \bar{V}_g/\partial p)_T| > |(\partial \bar{V}_t/\partial p)_T|$ implying that the volume of the initial state is more easily affected by the application of pressure. Since a more rigidly structured system would be expected to be only slightly compressed by pressure, while a less rigidly structured system would be more susceptible, it must follow that the transition state, defined as the solute plus its solvent environment, is held together by stronger interactions than is the initial state. The fact that $\Delta S^{\ddagger}$ is negative for this reaction (Table V, p. 90) certainly indicates that the transition state is in a more constrained environment.

The question of course arises as to the sign change in $(\partial \Delta V^{\ddagger}/\partial p)_T$ on addition of alcohol to water. Such circumstances are not entirely new, $\Delta S^{\ddagger}$ for t-butyl chloride solvolysis being positive in water and becoming negative on addition of a co-solvent.[160] In pure water the initial state is less compressible than the transition state. As alcohol is added the reverse occurs. At some solvent composition $(\partial \Delta V^{\ddagger}/\partial p)_T = 0$, that is

$$\left(\frac{\partial \bar{V}_g}{\partial p}\right)_T = \left(\frac{\partial \bar{V}_t}{\partial p}\right)_T. \tag{100}$$

The curves in Fig. 48 indicate that this "equicompressibility" composition[d] approaches pure water as the alcohol becomes more efficient in disrupting the water structure (see Chapter 9 and ref. 163). However, the data are not complete enough to elaborate on this observation. More values of $(\partial \Delta V^{\ddagger}/\partial p)_T$ in the region of pure water to 0.1 mole fraction alcohol are necessary.

Franks and Ives pointed out that as an alcohol is added to water a "maximum structuredness" ensues in the region of 0.0

---

[d] The equicompressibility composition is that solvent composition where $\bar{\kappa}_g = \bar{\kappa}_t$ rather than that solvent composition where eq. 100 is valid. Since $1/\bar{V}_g \neq 1/\bar{V}_t$ and since

$$\bar{\kappa} = -\frac{1}{\bar{V}}\left(\frac{\partial \bar{V}}{\partial p}\right)_T \tag{101}$$

these two solvent compositions are not identical, so that the term "equicompressibility" is incorrectly used in the text. However for lack of a better word, equicompressibility will be used with quotation marks to indicate the criterion of eq. 100.

to 0.1 X_{ROH}.[163] Such increase in the structure implies a loss of flexibility of the solvent. Therefore, κ of the solvent should decrease. As more alcohol is added, causing a breakdown of the structure, and more random distribution of the molecules, κ should begin to increase resulting in a minimum value at some solvent composition. The data in Table XIV (p. 151) do not display extrema behavior in κ, but rather show a monotonic behavior with solvent composition. Such behavior could nevertheless arise from a concomitant weakening of the molecular interactions coupled with an increase of structure as the first increments of alcohol are added followed by complete structure breakdown. The net effect of these changes would be increasing flexibility giving rise to monotonic κ behavior.

In dilute solutions, solute-solvent and solvent-solvent interactions are virtually the only existing ones. It is, therefore, reasonable to assume that $\bar{\kappa}$ of the solute parallels the solvent compressibility behavior--i.e. increases monotonically on addition of alcohol. Since

$$\left(\frac{\partial \bar{V}}{\partial p}\right)_T = - \bar{\kappa}\bar{V} \qquad (102)$$

and since $\bar{V}$ of the solute has a maximum value (Figs. 34 to 37, pp. 174 to 177), $(\partial\bar{V}/\partial p)_T$ must decrease until that solvent composition is reached where $\bar{V}$ maximizes. Beyond this solvent composition the behavior of $(\partial\bar{V}/\partial p)_T$ will depend upon the relative rate of increase of $\bar{\kappa}$ and decrease in $\bar{V}$. However, the "equicompressibility" composition occurs prior to this (Figs. 34 to 37 and 48). Therefore, over the range containing the solvent composition in which eq. 100 is valid, the $(\partial\bar{V}/\partial p)_T$ decreases monotonically. Furthermore, since $(\partial\Delta V^{\ddagger}/\partial p)_T = 0$ at some solvent composition and since $(\partial\bar{V}_g/\partial p)_T > (\partial\bar{V}_t/\partial p)_T$ in pure water, $(\partial\bar{V}_g/\partial p)_T$ must decrease faster than $(\partial\bar{V}_t/\partial p)_T$ with increasing alcohol concentration. Such a situation is illustrated in Fig. 50. The extrema in $(\partial\Delta V^{\ddagger}/\partial p)_T$ of course indicates that the two curves in Fig. 50 are not linear over a large composition range if in fact they are linear at all.

That $(\partial\bar{V}_g/\partial p)_T$ is more solvent dependent than $(\partial\bar{V}_t/\partial p)_T$ is not unreasonable from the viewpoint of the structuredness of the microscopic solvent region. The initial state solvent-solvent interactions are strong because they are not disrupted by the very weak solute-solvent interactions. As large amounts of alcohol are added, however, the structure is broken down giving rise to large changes in $(\partial\bar{V}_g/\partial p)_T$. On the other hand, the polar transition state interacts strongly with the solvent environment causing a weakening or increased flexibility of the solvent-solvent interactions. Any further disruption of structure due to added alcohol will be superimposed on the already disrupted solvent structure. Thus, $(\partial\bar{V}_t/\partial p)_T$ will show only a slight dependence on solvent composition.

Irrespective of the lack of complete understanding of the maxima discussed in Chapters 9 and 10, it appears that the pressure dependence of the activation volume gives rise to two points of

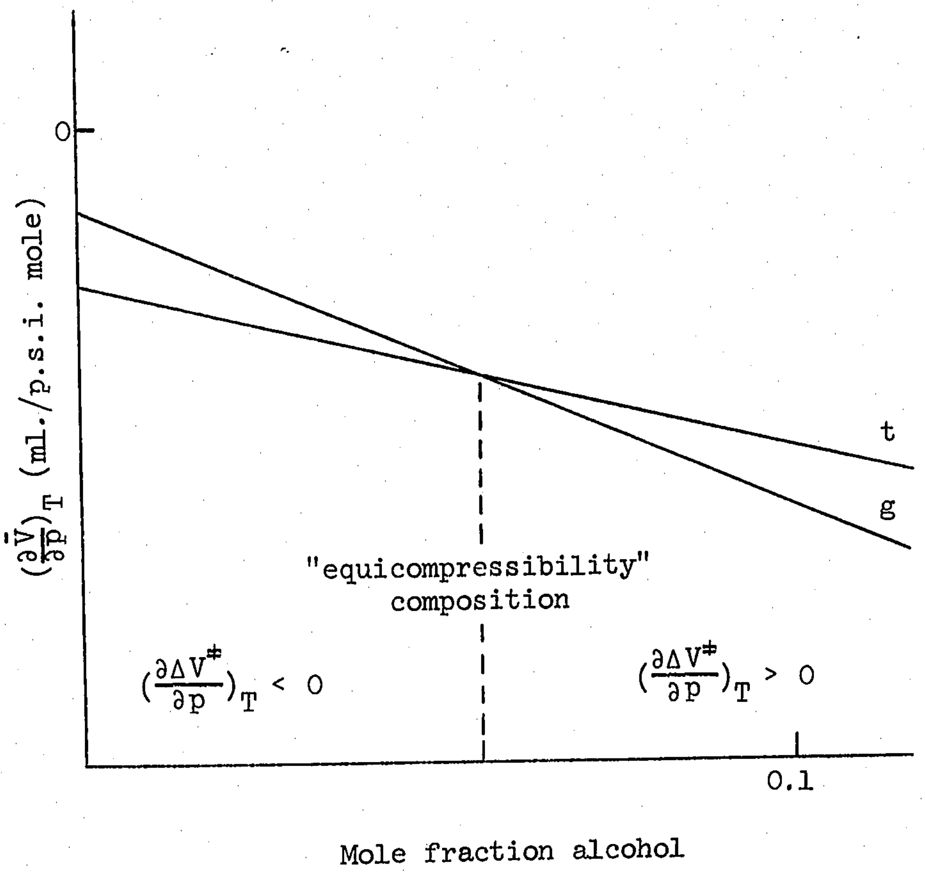


Fig. 50. Schematic diagram of the variation of $(\partial\bar{V}/\partial p)_T$ with solvent composition for the initial and transition states of benzyl chloride solvolysis.

interest--extremum behavior as a function of solvent composition and an "equicompressibility" solvent composition. Although no added understanding of solute-solvent interactions may be presently available from the behavior of $(\partial \Delta V^{\ddagger}/\partial p)_T$ as a function of solvent composition, it offers two further tests of any theory which may be proposed to account for the observed peculiarities.

CHAPTER 13

CONCLUSIONS

As the principal findings of this work are scattered amongst the various chapters, it is convenient to compile them into one section. Since these conclusions refer to experimental, analytical and interpretative aspects, it is advantageous to consider each separately.

Experimental

1. *In situ* conductimetric studies under pressure can yield rate constants of an accuracy comparable with that normally obtainable at atmospheric pressure.

2. Partial molal volumes can be measured for species which react with the solvent of interest, and meaningful results are obtainable.

Analytical

1. A quadratic function is generally the most useful for expressing the dependence of a reaction rate constant upon pressure and for extracting the volume of activation.

2. It is both necessary and sufficient to allow for the pressure dependence of the activation volume in analyzing a set of kinetic data as a function of pressure.

3. It is possible, in practice, to determine the pressure dependence of activation volumes with sufficiently small errors as to yield meaningful

$(\partial \Delta V^{\ddagger}/\partial p)_T$ values--the ability, or lack thereof, to interpret them notwithstanding.

4. Differentiation of an appropriate analytical function is a convenient and reliable method for estimating the errors associated with activation parameters.

Interpretative

1. Activation volumes, like activation enthalpies and entropies, show extrema behavior as a function of the composition of the binary solvent medium in which the reaction takes place.

2. A large part of the extremum behavior in $\Delta V_0^{\ddagger}$ is accounted for by the extremum behavior of the partial molal volume of the initial state. In the present instance, 50% to 100% compensation was observed.

3. The observance of extremum behavior in aqueous methanol casts doubt on Tommila's conclusion[96] that the organic solvent component must have a large hydrophobic group for extremum behavior to be observed and lends support to the hypothesis that the structural nature of the solvent is the major, if not the sole, cause of the extremum.

4. The extremum behavior of the activation parameters is similar to that found for the thermodynamic parameters of mixing of the binary solvent systems.

5. Contrary to the findings of Whalley, *et al.*,[135] the activation energy and entropy *at constant volume* were found to exhibit extremum behavior. The extrathermodynamic relationships also were found to be no simpler for the constant volume parameters than they are for the constant

pressure parameters. Consequently, the existence of these extrema is a reality of the chemical system, and these extrema must be considered as being related to the reaction mechanism insofar as the solvent itself is an intimate part of the mechanism.

6. The linear correlation between ΔS^* and ΔV^* observed by Burris and Laidler[44] was not found in the present instance of one reaction in a series of solvents. Rather very complex curves were obtained, the meaning of which is not apparent.

7. The pressure dependence of the activation volume undergoes a change in sign in highly aqueous media with increasing co-solvent concentration and also exhibits extremum behavior. Although this behavior is not fully understood at present, it will provide a further test of any hypothesis proposed to explain the extremum behavior of the activation parameters.

REFERENCES

1. S. D. Hamann, "Physico-Chemical Effects of Pressure", Butterworths Scientific Publications, London, England, 1957, (a) p. 165, (b) pp. 104f, (c) pp. 191ff.

2. R. S. Bradley, "High Pressure Physics and Chemistry", Academic Press Inc., Ltd., London, England, 1963, (a) v. 2, p. 172.

3. E. Whalley in "Advances in Physical Organic Chemistry", v. 2, V. Gold ed., Academic Press Inc., New York, N. Y., 1964.

4. W. Strauss, Fuel Soc. J., 8, 69 (1957).

5. B. B. Owen and S. R. Brinkley, Jr., Chem. Rev., 29, 461 (1941).

6. J. Buchanan and S. D. Hamann, Trans. Faraday Soc., 49, 1425 (1953).

7. S. D. Hamann and W. Strauss, Trans. Faraday Soc., 51, 1684 (1955).

8. P. W. Bridgman, Proc. Am. Acad. Arts and Sci., 67, 345 (1932).

9. D. Colladon and C. Sturm, Annes. Chim. (Phys.), 36, 231 (1827).

10. J. Fink, Ann. Phys., Lpz., 26, 481 (1855).

11. S. Lusanna, Nuovo Cim., 2, 263 (1895).

12. G. Tammann, Ann. Phys., Lpz., 69, 767 (1899).

13. W. Zisman, Phys. Rev., 39, 151 (1932).

14. S. D. Hamann and W. Strauss, Disc. Faraday Soc., 22, 70 (1956).

15. E. U. Franck, Z. Phys. Chem., Frankfurt, 8, 92 (1956).

16. F. T. Wall and S. J. Gill, J. Phys. Chem., 58, 740 (1954).

17. R. P. Bell, Trans. Faraday Soc., 37, 493 (1941).

18. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 3rd. ed., Reinhold Publishing Corporation, New York, N. Y., 1958, (a) p. 213, (b) p. 379, (c) p. 62.

19. M. Berthelot and L. Pean de Saint Gilles, Annes. Chim. (Phys.), 36, 231 (1862).

20. W. C. Röentgen, Ann. Phys., Lpz., 45, 98 (1892).

21. O. Stern, Ann. Phys., Lpz., 59, 659 (1896).

22. V. Rothmund, Z. Phys. Chem., 20, 168 (1896).

23 J. H. van't Hoff,"Vorlesungen über Theoretische und Physikalische Chemie", Friedrich Vieweg und Sohn, Braunschweig, 1898, pp. 236-8.

24. M. G. Evans and M. Polanyi, Trans. Faraday Soc., 31 875 (1935).

25. E. Cohen,"Problems in Piezochemistry", McGraw-Hill Book Co., New York, N.Y., 1926.

26. E. W. Fawcett and R. O. Gibson, J. Chem. Soc., 386 (1934).

27. M. W. Perrin, Trans. Faraday Soc., 34, 144 (1938).

28. A. E. Stearn and H. Eyring, Chem. Rev., 29, 509 (1941).

29. A. H. Ewald, Disc. Faraday Soc., 22, 138 (1956).

30. C. Walling and J. Pellon, J. Am. Chem. Soc., 79, 4786 (1957).

31. A. E. Nicholson and R. G. W. Norrish, Disc. Faraday Soc., 22, 97 (1956).

32. A. H. Ewald, Disc. Faraday Soc., 22, 146 (1956).

33. C. Walling and G. Metzger, J. Am. Chem. Soc., 81, 5365 (1959).

34. G. M. Burnett,"Mechanism of Polymer Reactions," Interscience, New York, N. Y., 1954, p. 228.

35. A. E. Nicholson and R. G. W. Norrish, Disc. Faraday Soc., 22, 104 (1956).

36. B. Raistrick, R. H. Sapiro and D. M. Newitt, J. Chem. Soc., 1761 (1939).

37. M. G. Gonikberg,"Chemical Equilibria and Reaction Rates at High Pressures", Israel Program for Scientific Translations Ltd., Jerusalem, Israel, 1963, (a) pp. 100f, (b) p. 106, (c) p. 113.

38. C. Walling and J. Peisach, J. Am. Chem. Soc., 80, 5819 (1958).

39. S. W. Benson and J. A. Berson, J. Am. Chem. Soc., 84, 152 (1962).

40. K. R. Brower, J. Am. Chem. Soc., 83, 4370 (1961).

41. E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, (a) pp. 644ff, (b) chap. 8, (c) p. 254.

42. A. M. Couture and K. J. Laidler, Can. J. Chem., 35, 207 (1957).

43. S. D. Hamann and D. R. Teplitzky, Disc. Faraday Soc., 22, 114 (1956).

44. C. T. Burris and K. J. Laidler, Trans. Faraday Soc., 51, 1497 (1955).

45. A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1961 p. 134.

46. K. R. Brower, J. Am. Chem. Soc., 85, 1401 (1963).

47. B. T. Baliga and E. Whalley, Can. J. Chem., 42, 1019 (1964).

48. S. D. Hamann, private communication.

49. H. G. David and S. D. Hamann, Trans. Faraday Soc., 50, 1188 (1954).

50. R. O. Gibson, E. W. Fawcett and M. W. Perrin, Proc. Roy. Soc., A150, 223 (1935).

51. E. G. Williams, M. W. Perrin and R. O. Gibson, Proc. Roy. Soc., A154, 684 (1936).

52. K. J. Laidler and D. Chen, Trans. Faraday Soc., 54, 1026 (1958).

53. W. J. le Noble and B. L. Yates, J. Am. Chem. Soc., 87, 3515 (1965).

54. A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, (a) chap. 4, (b) p. 45.

55. E. R. Thornton, "Solvolysis Mechanisms," Ronald Press, New York, N. Y., 1964.

56. E. D. Hughes, Quart. Rev., 5. 245 (1951).

57. C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithica, N. Y., 1953.

58. J. Hine, "Physical Organic Chemistry," 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

59. L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

60. A. R. Olson and R. S. Halford, J. Am. Chem. Soc., 59, 2644 (1937).

61. W. Taylor, J. Chem. Soc., 1853 (1938).

62. W. Taylor, J. Chem. Soc., 840 (1938).

63. W. Taylor, J. Am. Chem. Soc., 60, 2094 (1938).

64. R. A. Ogg, Jr., J. Am. Chem. Soc., 61, 1946 (1939).

65. L. C. Bateman, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 881 (1938).

66. A. M. Ward, J. Chem. Soc., 2285 (1927).

67. C. K. Ingold, Ann. Reports on Progress Chem. (Chem. Soc., London) 24, 156 (1927).

68. J. L. Gleave, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 236 (1935).

69. A. G. Evans, Trans. Faraday Soc., 42, 719 (1946).

70. J. L. Franklin, Trans. Faraday Soc., 48, 443 (1952).

71. S. Winston, E. Clippinger, A. H. Fainberg and G. C. Robinson, J. Am. Chem. Soc., 76, 2597 (1954).

72. A. G. Ogston, E. R. Holiday, J. S. L. Philpot and L. A. Stocken, Trans. Faraday Soc., 44, 45 (1948).

73. J. G. Kirkwood, J. Chem. Phys., 2, 351 (1934).

74. L. C. Bateman, E. D. Hughes and C. K. Ingold, J. Am. Chem. Soc., 60, 3080 (1938).

75. N. T. Farianacci and L. P. Hammett, J. Am. Chem. Soc., 59, 2542 (1937).

76. R. F. Hudson and B. Saville, J. Chem. Soc., 4114 (1955).

77. R. A. Fairclough and C. N. Hinshelwood, J. Chem. Soc., 538 (1937).

78. E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70, 846 (1948).

79. S. Winstein, E. Grunwald and H. W. Jones, J. Am. Chem. Soc., 73, 2700 (1951).

80. E. M. Kosower, J. Am. Chem. Soc., 80 3253 (1958).

81. E. M. Kosower, J. Am. Chem. Soc., 80, 3267 (1958).

82. J. B. Hyne and J. H. Jensen, Can. J. Chem., 41, 1679 (1963).

83. C. G. Swain and C. B. Scott, J. Am. Chem. Soc., 75, 141 (1953).

84. C. G. Swain and D. C. Dittmer, J. Am. Chem. Soc., 75, 4627 (1953).

85. J. O. Edwards, J. Am. Chem. Soc., 76, 1540 (1954).

86. C. G. Swain, R. B. Mosely and D. E. Brown, J. Am. Chem. Soc., 77, 3731 (1955).

87. H. G. Davis and V. K. LaMer, J. Chem. Phys., 10, 585 (1942).

88. E. Tommila, M. Tiilikainen and A. Voipio, Ann. Acad. Sci. Fennicae A II, 65, (1955).

89. A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 78, 2770 (1956).

90. R. E. Robertson, Suomen Kemistilehti, 33A, 63 (1960).

91. R. A. Fairclough and C. N. Hinshelwood, J. Chem. Soc., 1573 (1937).

92. E. Tommila, A. Koivisto, J. P. Lyyra, L. Antell and S. Heimo, Ann. Acad. Sci. Fennicae A II, 47, (1952).

93. K. J. Laidler and H. Eyring, Ann. N. Y. Acad. Sci., 39, 303 (1940).

94. L. Pekkarinen and E. Tommila, Acta. Chem. Scand., 13, 1019 (1955).

95. E. Tommila and S. Maltamo, Suomen Kemistilehti, B28, 73 (1955).

96. E. Tommila and S. Maltamo, Suomen Kemistilehti, B28, 118 (1955).

97. E. Tommila, L. Takanen and K. Salomen, Suomen Kemistilehti, B31, 37 (1958).

98. "Handbook of Chemistry and Physics", 39th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1957, (a) pp. 2350ff, (b) pp. 830f, (c) p. 1577, (d) p. 2001

99. E. Tommila and P. J. Antikainen, Acta Chem. Scand., 9, 825 (1955).

100. J. B. Hyne and R. E. Robertson, Can. J. Chem., 34, 931 (1956).

101. A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 79, 1602 (1957).

102. A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 79, 1597 (1957).

103. J. B. Hyne, J. Am. Chem. Soc., 82, 5219 (1960).

104. P. Debye, Z. physik. Chem., 130, 56 (1927).

105. G. Scatchard, J. Chem. Phys., 9, 34 (1941).

106. J. B. Hyne, R. Wills and R. E. Wonkka, J. Am. Chem. Soc., 84, 2914 (1962).

107. J. B. Hyne and R. Wills, Unpublished results.

108. E. M. Arnett, P. M. Duggleby and J. J. Burke, J. Am. Chem. Soc., 85, 1350 (1963).

109. E. M. Arnett, W. G. Bentrude, J. J. Burke and P. M. Duggleby, J. Am. Chem. Soc., 87, 1541 (1965).

110. B. T. Baliga, R. J. Withey, D. Polton and E. Whalley, Trans. Faraday Soc., 61, 517 (1964).

111. A. R. Olson and H. H. Voge, J. Am. Chem. Soc., 56, 1690 (1934).

112. C. G. Swain, J. Am. Chem. Soc., 70, 1119 (1948).

113. S. C. J. Olivier, Rec. trav. chim., 41, 303 (1922).

114. S. C. J. Olivier and G. Berger, Rec. trav. chim., 41, 637 (1922).

115. S. C. J. Olivier, Rec. trav. chim., 42, 775 (1923).

116. S. C. J. Olivier, and G. Berger, Rec. trav. chim., 45, 452 (1926).

117. S. C. J. Olivier and A. P. Weber, Rec. trav. chim., 53, 869 (1934).

118. G. M. Bennett and B. Jones, J. Chem. Soc., 1815 (1935).

119. I. Roberts and L. P. Hammett, J. Am. Chem. Soc., 59, 1063 (1937).

120. G. W. Beste and L. P. Hammett, J. Am. Chem. Soc., 62, 2481 (1940).

121. G. R. Lucas and L. P. Hammett, J. Am. Chem. Soc., 64, 1928 (1942).

122. W. T. Miller and J. Bernstein, J. Am. Chem. Soc., 70, 3600 (1948).

123. C. G. Swain and W. P. Langsdorf, Jr., J. Am. Chem. Soc., 73, 2813 (1951).

124. J. K. Kochi and G. S. Hammond, J. Am. Chem. Soc., 75, 3445 (1953).

125. J. C. Charlton and E. D. Hughes, J. Chem. Soc., 850 (1956).

126. B. Bensley and G. Kohnstam, J. Chem. Soc., 4747 (1957).

127. B. Bensley and G. Kohnstam, J. Chem. Soc., 287 (1956).

128. R. E. Robertson and J. M. W. Scott, J. Chem. Soc., 1596 (1961).

129. G. Kohnstam and P. R. Robinson, J. Chem. Soc., 4970 (1957).

130. M. J. Bird, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 255 (1943).

131. E. Tommila, E Paakkala, U. K. Virtanen, A. Erva and S. Varila, Ann. Acad. Sci. Fennicae A II, 91 (1959).

132. R. E. Robertson, Can. J. Chem., 33, 1536 (1955).

133. J. B. Hyne and R. Wills, J. Am. Chem. Soc., 85, 3650 (1963).

134. K. Shinoda and J. H. Hildebrand, J. Phys. Chem., 62, 295 (1958).

135. B. T. Baliga, R. J. Withey, D. Poulton and E. Whalley, Trans. Faraday Soc., 61, 517 (1964).

136. R. Wills, M.Sc. Thesis, Department of Chemistry, University of Alberta at Calgary (1963).

137. B. L. Murr, Jr. and V. J. Shiner, Jr., J. Am. Chem. Soc., 84, 4672 (1962).

138. G. A. Hulett and W. D. Bonner, J. Am. Chem. Soc., 31, 390 (1909).

139. A. I. Vogel, "A Text-Book of Practical Organic Chemistry", 3rd ed., Longmans, Green and Co., Ltd., London, 1961, pp. 167f.

140. E. A. Guggenheim, Phil. Mag. (7), 2, 538 (1926).

141. S. D. Hamann, Private communication.

142. J. B. Hyne and R. E. Robertson, Can. J. Chem., 33, 1544 (1955).

143. K. T. Leffek, R. E. Robertson and S. Sugamori, J. Am. Chem. Soc., 87, 2097 (1965).

144. R. E. Robertson, R. L. Heppolette and J. M. W. Scott, Can J. Chem., 37, 803 (1959).

145. F. Daniels, *et al.*, "Experimental Physical Chemistry", 5th ed., McGraw-Hill Book Co., New York, N. Y., 1956, p. 326.

146. S. D. Hamann, Australia J. Chem., 9, 533 (1956).

147. C. Walling and D. D. Tanner, J. Am. Chem. Soc., 85, 612 (1963).

148. P. W. Bridgman, "The Physics of High Pressure", G. Bell and Sons, Ltd., London, 1958, Chaps. V and VI.

149. B. B. Owen and S. R. Brinkley, Jr., Phys. Rev., 64, 32 (1943).

150. S. D. Hamann, Trans. Faraday Soc., 54, 507 (1958).

151. A. I. Vogel, J. Chem. Soc., 644 (1948).

152. "International Critical Tables", McGraw-Hill Book Co., Inc., New York, N. Y., 1933, (a) v. III, p. 25, (b) v. III, p. 27, (c) v. III, p. 41, (d) v. III, p. 36.

153. A. G. Mitchell and W. F. K. Wynne-Jones, Disc. Faraday Soc., 15, 161 (1953).

154. M. B. Volf, "Technical Glasses", Sir Isaac Pitman and Sons, Ltd., London, England, 1961, Appendix Table XV.

155. Fisher Scientific Co., Ltd., Private communication.

156. B. T. Baliga and E. Whalley, Can. J. Chem., 42, 1835 (1964).

157. H. G. David and S. D. Hamann, Trans. Faraday Soc., 50, 1188 (1954).

158. J. B. Hyne and P. Wales, Unpublished results.

159. E. M. Arnett, W. G. Bentrude and P. M. Duggleby, J. Am. Chem. Soc., 87, 2048 (1965).

160. E. D. Hughes and C. K. Ingold, J. Chem. Soc., 1571 (1933).

161. R. L. Bateman, J. Am. Chem. Soc., 74, 5516 (1962).

162. R. P. Bell, Trans. Faraday Soc., 33, 496 (1937).

163. F. Franks and D. J. G. Ives, Quart. Rev., 20, 1 (1966).

164. W. Gerrard and E. D. Macklen, Chem. Rev., 59, 1105 (1959).

165. J. E. Leffler, J. Org. Chem., 20, 1202 (1955).

166. J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", John Wiley and Sons, Inc., New York, N. Y., 1963, Chap. 9.

167. S. Winstein and A. H. Fainberg, J. Am. Chem. Soc., 79, 5937 (1957).

PART V

APPENDICES

APPENDIX I

PRESSURE UNITS

The majority of present day literature uses the units of atmospheres or bars in reporting piezochemical data. For the reader who is more familiar with these units the following table is included.

TABLE XVII

Pressure Units

p.s.i.g.	Atmospheres	Bars
0	1	1
122	9	9
510	36	36
1008	70	71
1507	103	104
2002	136	138
2500	171	173
3000	205	207
5000	341	346
10000	681	690
15000	1022	1036
20000	1362	1380
30000	2043	2070
40000	2722	2758
60000	4083	4137

APPENDIX II

RATE CONSTANT CALCULATION

```
C     GUGGENHEIM ANALYSIS FOR CONDUCTIMETRIC RATE STUDIES
      DIMENSION R1(20), R2(20), T(20), P(20), D(20), TM(20), CP(20),
     1HEAD(80)
1     READ 200, HEAD
200   FORMAT (80A1)
      PRINT 201, HEAD
201   FORMAT (1H1, 80A1)
2     READ 100, N
100   FORMAT (I3)
      DO 10 I=1,N
10    READ 101, TM(I), R1(I), R2(I)
101   FORMAT (16X,F5.0,15X,F6.0,16X,F5.0)
      IRC = 1
      IPPO = 1
      ISTEP = 1
16    J = 1
      NLO = 0
      NE = 0
      KA = N - J + 1
      FN = KA
C     CONVERT THE TIME TO SECONDS AND COMPUTE THE POINTS
9     CONTINUE
      DO 11 I=J,N
      T(I) = TM(I)*60.
11    P(I) = LOGF(1./R2(I) - 1./R1(I))
C     INITIALIZE THE SUMS
18    TS = 0.
      PTS = 0.
      PS = 0.
      T2S = 0.
      DS = 0.
      K = KA
C     COMPUTE THE SUMS
      DO 15 I=J,N
      IF(P(I)) 17,19,17
19    K = K-1
      FN = K
17    TS = TS + T(I)
      PTS = PTS + P(I)*T(I)
      PS = PS + P(I)
15    T2S = T2S + T(I)**2
C     COMPUTE REQUIRED STATISTICS
      DIV = FN*T2S - TS**2
```

```
      IF(DIV) 20,70,20
20    S = (FN*PTS - TS*PS)/DIV
      CI = (T2S*PS - TS*PTS)/DIV
      K = KA
      DO 21 I=J,N
      IF(P(I)) 22,23,22
23    D(I) = 0.
      K = K - 1
      FN = K
      GO TO 21
22    CP(I) = S*T(I) + CI
      D(I) = CP(I) - P(I)
21    DS = DS + D(I)**2
      DS = SQRTF(DS/FN)
C     OUTPUT REGION
      IF(IPPO) 26,27,26
26    PRINT 110
110   FORMAT (1HO, 6X, 4HTIME, 8X, 2HR1, 8X, 2HR2, 9X, 5HOBS P, 9X,
     15HCAL P, 9X, 5HERROR)
      DO 25 I = J,N
25    PRINT 103, TM(I), R1(I), R2(I), P(I), CP(I), D(I)
103   FORMAT (1H , 3F10.2,2F14.6, F14.8)
      PRINT 115
115   FORMAT (1HO)
      IPPO = 0
27    PRINT 102, K, S, DS, CI
102   FORMAT (1H ,4HNP= , I3,2X,3HS= ,E14.7,2X,4HDS= ,E14.7,2X,3HI= ,
     1F10.6)
      IF(DS - 1.*10.**(-3)) 1,24,24
24    GO TO (42,41), ISTEP
C     REMOVE INITIAL POINT BY INCREMENTING J
41    J = J + 1
      IF(N-J-7) 1,1,44
44    KA = N-J+1
      FN = KA
      IF(IRC) 60,61,60
60    IRC = 0
      GO TO 9
61    GO TO 18
42    DS2 = DS*2. + .001
      DO 50 I=J,N
      CPF = ABSF(D(I))
      IF(CPF - DS2) 50,52,52
52    T(I) = 0.
      P(I) = 0.
50    CONTINUE
      KA = N-J+1
      FN = KA
      ISTEP = 2
```

```
      GO TO 18
70    PRINT 106
106   FORMAT (1H ,19HDIVISOR EQUALS ZERO)
      GO TO 1
      END
```

INPUT DATA

```
RUN 288 BENZYL CHLORIDE/0.10004 I-PROH/50.25 DEG./20,000 PSIG
020
                  3          72620          27289
                 18          65865          27088
                 33          61196          26867
                 48          56223          26665
                 63          52630          26493
                 78          49426          26337
                 93          46867          26192
                108          44678          26053
                123          42785          25924
                138          41225          25794
                153          39814          25689
                168          38451          25582
                183          37294          25486
                198          36246          25390
                213          35311          25291
                228          34401          25205
                243          33653          25126
                258          32956          25050
                273          32314          24978
                288          31737          24910
```

OUTPUT

```
RUN 288 BENZYL CHLORIDE/0.10004 I-PROH/50.25 DEG./20,000PSIG

   TIME        R1         R2          OBS P         CAL P          ERROR
    3.00   72620.00   27289.00    -10.685488    -10.680813      .00467500
   18.00   65865.00   27088.00    -10.736626    -10.732228      .00439800
   33.00   61196.00   26867.00    -10.776745    -10.783643     -.00689800
   48.00   56223.00   26665.00    -10.834078    -10.835058     -.00098000
   63.00   52630.00   26493.00    -10.884570    -10.886473     -.00190300
   78.00   49426.00   26337.00    -10.939850    -10.937888      .00196200
   93.00   46867.00   26192.00    -10.991597    -10.989303      .00229400
  108.00   44678.00   26053.00    -11.042864    -11.040718      .00214600
  123.00   42785.00   25924.00    -11.094108    -11.092132      .00197600
  138.00   41225.00   25794.00    -11.140563    -11.143547     -.00298400
  153.00   39814.00   25689.00    -11.190090    -11.194962     -.00487200
  168.00   38451.00   25582.00    -11.244207    -11.246377     -.00217000
  183.00   37294.00   25486.00    -11.295939    -11.297792     -.00185300
  198.00   36246.00   25390.00    -11.347721    -11.349207     -.00148600
  213.00   35311.00   25291.00    -11.397815    -11.400622     -.00280700
  228.00   34401.00   25205.00    -11.454114    -11.452037      .00207700
  243.00   33653.00   25126.00    -11.504523    -11.503451      .00107200
  258.00   32956.00   25050.00    -11.556180    -11.554866      .00131400
  273.00   32314.00   24978.00    -11.608457    -11.606281      .00217600
  288.00   31737.00   24910.00    -11.659622    -11.657696      .00192600

NP= 20   S= -5.7127633E-05   DS= 2.9789989E-03   I= -10.670531
NP= 20   S= -5.7127633E-05   DS= 2.9789989E-03   I= -10.670531
NP= 19   S= -5.7218517E-05   DS= 2.8162445E-03   I= -10.669451
NP= 18   S= -5.7335705E-05   DS= 2.5251574E-03   I= -10.668024
NP= 17   S= -5.7217665E-05   DS= 2.2459131E-03   I= -10.669496
NP= 16   S= -5.7212236E-05   DS= 2.3142965E-03   I= -10.669566
NP= 15   S= -5.7172545E-05   DS= 2.3612668E-03   I= -10.670085
NP= 14   S= -5.7252165E-05   DS= 2.3495936E-03   I= -10.669019
NP= 13   S= -5.7384448E-05   DS= 2.2235962E-03   I= -10.667204
NP= 12   S= -5.7576477E-05   DS= 1.9212044E-03   I= -10.664522
NP= 11   S= -5.7859402E-05   DS= 1.1005026E-03   I= -10.660483
NP= 10   S= -5.7934904E-05   DS= 1.0879776E-03   I= -10.659408
NP=  9   S= -5.7828074E-05   DS= 1.0465630E-03   I= -10.660951
```

APPENDIX III

ACTIVATION VOLUME ANALYSIS

```
C       QUADRATIC EQUATION FOR ACTIVATION VOLUMES WITH ERROR ANALYSIS
        DIMENSION P(10),DP(10),Y(10),DY(10),M(80),YY(10),DYY(10),PK(10),
       1D(10)
1       READ 100, M
100     FORMAT (80A1)
        PRINT 99, (M(I),I=1,80)
99      FORMAT (1H1,80A1, 7X,18HQUADRATIC ANALYSIS)
        PRINT 98
98      FORMAT (1H ,82X,23HLN(K) = A + B*P + C*P*P//)
2       READ 101,N
101     FORMAT (I2)
        READ 102, (P(I), DP(I), Y(I), DY(I), I=1,N)
102     FORMAT (F5.0,10X,I3,10X,E9.3,10X,E6.0)
        SP = 0.
        SPP = 0.
        SPPP = 0.
        SPPPP = 0.
        SPPLY = 0.
        SPLY = 0.
        SLY = 0.
        SDP = 0.
        SPDP = 0.
        SPPDP = 0.
        SPPPDP = 0.
        SDYY = 0.
        SPDYY = 0.
        SPPDYY = 0.
        SLYDP = 0.
        SPLYDP = 0.
C       CALCULATE THE SUMS
        DO 3 I=1,N
        SP = SP + P(I)
        SPP = SPP + P(I)*P(I)
        SPPP = SPPP + P(I)*P(I)*P(I)
        SPPPP = SPPPP + P(I)*P(I)*P(I)*P(I)
        SPPLY = SPPLY + P(I)*P(I)*LOGF(Y(I))
        SPLY = SPLY + P(I)*LOGF(Y(I))
        SLY = SLY + LOGF(Y(I))
        YY(I) = LOGF(Y(I))
        SDP = SDP + DP(I)
        SPDP = SPDP + P(I)*DP(I)
        SPPDP = SPPDP + P(I)*P(I)*DP(I)
        SPPPDP = SPPPDP + P(I)*P(I)*P(I)*DP(I)
```

```
      SDYY = SDYY + DY(I)/Y(I)
      DYY(I) = DY(I)/Y(I)
      SLYDP = SLYDP + LOGF(Y(I))*DP(I)
      SPLYDP = SPLYDP + P(I)*LOGF(Y(I))*DP(I)
      SPDYY = SPDYY + (P(I)*DY(I))/Y(I)
3     SPPDYY = SPPDYY + (P(I)*P(I)*DY(I))/Y(I)
      FN = N
C     CALCULATE THE PARAMETERS
      DENOM = FN*SPP*SPPPP - FN*SPPP*SPPP - SP*SP*SPPPP + 2.*SP*SPP*SPPP
     1- SPP**3.
      C = (FN*SPP*SPPLY - FN*SPPP*SPLY - SP*SP*SPPLY + SP*SPPP*SLY +
     1SP*SPP*SPLY - SPP*SPP*SLY)/DENOM
      B = (FN*SPLY - FN*C*SPPP - SP*SLY + C*SP*SPP)/(FN*SPP - SP*SP)
      A = (SLY - B*SP - C*SPP)/FN
      DDENOM = FN*(2.*SPDP*SPPPP + 4.*SPP*SPPPDP - 6.*SPPP*SPPDP) - 2.*
     1SDP*SP*SPPPP - 4.*SP*SP*SPPPDP + 2.*(SDP*SPP*SPPP + 2.*SP*SPDP*SPP
     2P + 3.*SP*SPP*SPPDP) - 6.*SPP*SPP*SPDP
      DC = (2.*SPDP*(FN*SPPLY - 2.*SPP*SLY + SP*SPLY) - (SLYDP + SPDYY)*
     1(FN*SPPP - SP*SPP) + SDP*(SPPP*SLY - 2.*SP*SPPLY + SPP*SPLY) - 3.*
     2SPPDP*(FN*SPLY - SP*SLY) + (2.*SPLYDP + SPPDYY)*(FN*SPP - SP*SP) -
     3SDYY*(SPP*SPP - SP*SPPP))/DENOM - C*DDENOM/DENOM
      DB = (FN*(SPDYY + SLYDP - DC*SPPP - 3.*C*SPPDP) - SDP*SLY - SP*SDY
     1Y + C*SDP*SPP + 2.*C*SP*SPDP)/(FN*SPP - SP*SP) - B*(3.*FN*SPDP -
     22.*SP*SDP)/(FN*SPP - SP*SP)
      DA = (SDYY - DB*SP - B*SDP - DC*SPP - 2.*C*SPDP)/FN
C     OUTPUT REGION
      PRINT 103, A, B, C
103   FORMAT (17HOVALUE OF A IS = ,F8.4,2X,7HB IS =,E11.4,2X,7HC IS = ,
     1E11.4//)
      PRINT 104, DA, DB, DC
104   FORMAT (18H VALUE OF DA IS = ,E11.4,2X,8HDB IS = ,E11.4,2X,8HDC IS
     1 = ,E11.4//)
      PRINT 105
105   FORMAT (11H INPUT DATA/)
      PRINT 107
107   FORMAT (2X,4H   P,6X,2HDP,9H        K,12H           DK/)
      PRINT 106, (P(I),DP(I),Y(I),DY(I),I=1,N)
106   FORMAT (1H ,F7.0,2X,F5.0,2X,E10.3,2X,E8.1)
      DO 6 I=1,N
      PK(I) = A + B*P(I) + C*P(I)*P(I)
6     D(I) = YY(I) - PK(I)
      PRINT 108
108   FORMAT (/1H ,11H LOGF(K(I)),5X,11H DK(I)/K(I), 5X, 12HLOG(K(CALC))
     1,5X,10HOBS - CALC/)
      PRINT 109,(YY(I),DYY(I),PK(I),D(I),I=1,N)
109   FORMAT (1H ,1X,F9.5,7X,F9.5,7X,F9.5,7X,F9.5)
      GO TO 1
5     CALL EXIT
4     END
```

INPUT DATA

```
BENZYL CHLORIDE AT 50.25 DEG. C. IN 0.1 MOLE FRACTION METHANOL
04
    0          0          1.247E-04          4.E-07
10000        200          1.749E-04          4.E-07
20000        200          2.310E-04          4.E-06
40000        200          4.400E-04          1.E-05
```

OUTPUT

```
                                                                    QUADRATIC ANALYSIS
BENZYL CHLORIDE AT 50.25 DEG. C. IN 0.1 MOLE FRACTION METHANOL   LN(K) = A + B*P + C*P*P


VALUE OF A IS =  -8.9822  B IS =  3.1104E-05  C IS =  4.3408E-12

VALUE OF DA IS =  5.9574E-04  DB IS =  1.4472E-07  DC IS =  6.7809E-12

INPUT DATA

   P       DP        K          DK

    0.      0.    1.247E-04   4.0E-07
 10000.   200.    1.749E-04   4.0E-07
 20000.   200.    2.310E-04   4.0E-06
 40000.   200.    4.400E-04   1.0E-05

  LOGF(K(I))      DK(I)/K(I)     LOG(K(CALC))      OBS - CALC

  -8.98959          .00320        -8.98228          -.00731
  -8.65129          .00228        -8.67080           .01950
  -8.37309          .01731        -8.35846          -.01463
  -7.72873          .02272        -7.73117           .00243
```

TABLE XVIII

Parameters of the Quadratic Analysis for the Activation Volume for Benzyl Chloride Solvolysis

Mole Fraction	A	10^5 x B ($p.s.i.^{-1}$)	10^{10} x C ($p.s.i.^{-2}$)	10^3 x DA	10^6 x DB ($p.s.i.^{-1}$)	10^{11} x DC ($p.s.i.^{-2}$)
			Methanol			
0.000	- 8.3892	2.1397	3.1243	15.399	-3.2626	12.917
0.100	- 8.9822	3.1104	0.043408	0.59574	0.14472	0.67809
0.200	- 9.5484	4.0040	-2.6917	7.8976	0.48277	- 1.9267
0.300	-10.1875	4.5902	-3.2790	4.6235	-0.26667	0.16402
0.400	-10.7991	5.0803	-3.6152	4.5759	-1.2303	2.7951
0.500	-11.2814	4.8129	-2.7865	4.1431	-0.38839	0.56710
			Ethanol			
0.100	- 9.5980	4.3631	-3.8665	2.9596	-2.5655	11.974
0.200	-10.8655	5.1348	-3.4390	12.460	-2.2125	5.4441
0.300	-11.7187	4.9910	-2.6134	10.594	-1.2901	2.9915
0.400	-12.3016	4.5923	-2.8106	29.155	-2.3974	5.1408
			i-Propanol			
0.100	-10.7656	5.9260	-4.4925	2.4303	-0.50203	0.92072
0.200	-12.2540	4.8742	-2.1507	5.2533	0.28072	- 0.67278
0.300	-12.9702	4.6290	-2.2969	- 1.2813	1.3631	- 1.4550
0.400	-13.5418	3.4912	-5.8555	5.8413	0.11378	1.2490
			t-Butanol			
0.100	-11.8621	6.5336	-4.2974	18.361	-0.28550	- 0.092910
0.200	-13.1801	5.8219	-4.4509	11.069	2.0480	- 3.9407
0.300	-13.9175	4.3386	-1.4676	13.078	8.8350	-15.883

APPENDIX IV

ACTIVATION ENTHALPY AND ENTROPY CALCULATION

```
C     ENTHALPY AND ENTROPY OF ACTIVATION
      DIMENSION HEAD(20),T(3),DT(3),FK(3),DFK(3),FLNK(3),RT(3),FLNT(3),
     1DFLNK(3),DFLNT(3)
      R = 1.98726
      BK = 1.3805E-16
      H = 6.625E-27
      BKRH = BK/H
1     READ 100, HEAD
100   FORMAT (20A4)
      READ 101, (T(I),DT(I),FK(I),DFK(I),I=1,3)
101   FORMAT (F7.3,5X,F5.3,6X,E9.3,5X,E6.0)
      PRINT 200, HEAD
200   FORMAT (1H1, 20A4)
      PRINT 201
201   FORMAT (//1HO,11HTEMPERATURE,5X,21HTEMPERATURE DEVIATION,5X,13HRAT
     1E CONSTANT,5X,23HRATE CONSTANT DEVIATION,/)
      DO 2 I=1,3
      PRINT 202,T(I),DT(I),FK(I),DFK(I)
202   FORMAT (1H ,1X,F8.3,14X,F6.3,15X,E10.3,14X,E7.0)
      T(I) = T(I) + 273.16
      RT(I) = 1./T(I)
      FLNT(I) = LOGF(T(I))
      FLNK(I) = LOGF(FK(I))
      DFLNT(I) = DT(I)/T(I)
2     DFLNK(I) = DFK(I)/FK(I)
      FT = RT(3) - RT(1)
      ENTHAL = -R*(FLNK(3) - FLNK(1) - FLNT(3) + FLNT(1))/FT
      ENTROP = R*(-LOGF(BKRH) + FLNK(2) + ENTHAL*RT(2)/R - FLNT(2))
      DENTHA = -R*(DFLNK(3) - DFLNK(1) - DT(3)/T(3) + DT(1)/T(1))/FT +
     1ENTHAL*(DT(3)*RT(3) - DT(1)*RT(1))/FT
      DENTRO = R*(DFLNK(2) - DFLNT(2) + DENTHA*RT(2)/R - ENTHAL*RT(2)*
     1RT(2)*DT(2)/R)
      PRINT 203
203   FORMAT (//1HO,20HABSOLUTE TEMPERATURE,5X,17HLN(RATE CONSTANT),5X,
     19HDEVIATION,5X,22HRECIPROCAL TEMPERATURE,/)
      PRINT 204,(T(I),FLNK(I),DFLNK(I),RT(I),I=1,3)
204   FORMAT (1H ,6X,F8.3,15X,F9.5,9X,F9.5,11X,F10.7)
      PRINT 205, ENTHAL, DENTHA, ENTROP, DENTRO
205   FORMAT(/1HO,24HENTHALPY OF ACTIVATION = ,F7.0,14H CALORIES/MOLE,
     15X,12HDEVIATION = ,F7.0,//,25H ENTROPY OF ACTIVATION = ,F6.2,21HCA
     2LORIES/DEGREE MOLE,5X,12HDEVIATION = ,F6.2)
      GO TO 1
999   CALL EXIT
      END
```

INPUT DATA

```
BENZYL CHLORIDE IN WATER
 40.050       0.010       7.527E-05      2.E-08
 50.250       0.010       2.310E-04      4.E-06
 60.500       0.010       5.940E-04      5.E-06
```

OUTPUT

```
BENZYL CHLORIDE IN WATER

TEMPERATURE     TEMPERATURE DEVIATION     RATE CONSTANT     RATE CONSTANT DEVIATION

  40.050                 .010              7.527E-05               2.E-08
  50.250                 .010              2.310E-04               4.E-06
  60.500                 .010              5.940E-04               5.E-06


ABSOLUTE TEMPERATURE     LN(RATE CONSTANT)     DEVIATION     RECIPROCAL TEMPERATURE

     313.210                 -9.49442            .00026             .0031927
     323.410                 -8.37309            .01731             .0030920
     333.660                 -7.42863            .00841             .0029970

ENTHALPY OF ACTIVATION = 20336. CALORIES/MOLE     DEVIATION =    286.

ENTROPY OF ACTIVATION = -12.45 CALORIES/DEGREE MOLE     DEVIATION =    .91
```

APPENDIX V

POLYNOMIAL ACTIVATION VOLUME ANALYSIS

```
C     ACTIVATION VOLUME ANALYSIS WITH THE OPTION OF USING LINEAR OR
C     CURVILINEAR FUNCTIONS AND THE SECOND OPTION OF FORCING THE
C     FUNCTION TO PASS THROUGH THE EXPERIMENTAL LOG(K(0)) OR ALLOWING
C     IT TO FIND THE LEAST SQUARE INTERCEPT
C
C     FIRST DATA CARD - COL. 1, 1 FOR LINEAR CASE, 3 FOR CURVILINEAR.
C     COL. 2 to 15, COEFFICIENT IF ANY OF FORMAT E14.8.
C     DIGIT IN COL. 20 SKIPS TO A NEW PAGE, 30 PRINTS DATA, 40 REREADS
C     DATA.  EACH DATA CARD TO HAVE ONE PAIR OF DATA OF FORMAT 2E14.8
C     A BLANK CARD SIGNIFIES THE END OF DATA
C
      DIMENSION X(1),P(1),XX(20),PP(20),CALC(20),D(20),HEAD(20)
C     INITIALIZE THE SUMS
10    SX = 0.
      N = 0.
      SP = 0.
      SXP = 0.
      SX2 = 0.
      SX3 = 0.
      SX4 = 0.
      SX2P = 0.
      GO TO 12
11    CALL EXIT
12    READ 112, HEAD
112   FORMAT (20A4)
      READ 100, L, CSTK, IS, IP, IX
100   FORMAT (I1,E14.8,4X,I1,9X,I1,9X,I1)
      IF(CSTK) 37,37,36
36    CST = LOGF(CSTK)
37    IF(IS) 34,35,34
34    PRINT 105
105   FORMAT (1H1)
      PRINT 113, HEAD
113   FORMAT (1H0, 20A4)
35    IF(IP) 32,5,32
32    PRINT 106
106   FORMAT(21H      GIVEN DATA       ,/,28H PRESSURE        RATE CONSTAN
     1T,//)
5     READ 108,PQ,FK
108   FORMAT (2E14.8)
      IF(PQ**2 + FK**2) 1,2,1
1     P(1) = LOGF(FK)
      X(1) = PQ
```

```
      IF(IP) 30,31,30
30    PRINT 109, PQ, FK, P(1)
109   FORMAT (2E14.8, 10H  LN(K) = , E14.8)
31    N = N + 1
      XX(N) = X(1)
      PP(N) = P(1)
      FN = N
      DO 3 I=1,1
      SX = SX + X(I)
      SP = SP + P(I)
      SXP = SXP + X(I)*P(I)
      SX2 = SX2 + X(I)*X(I)
      IF(L-3) 3,4,3
4     SX3 = SX3 + X(I)**3
      SX4 = SX4 + X(I)**4
      SX2P = SX2P + P(I)*X(I)*X(I)
3     CONTINUE
      GO TO 5
2     PRINT 107
107   FORMAT (1H ,///)
      IF(L-3) 7,6,7
C     LINEAR CASES
7     IF(CSTK) 22,21,22
C     INPUT CONSTANT
22    B = (SXP - CST*SX)/SX2
      A = CST
      GO TO 23
C     FIND CONSTANT
21    DENOM = FN*SX2 - SX*SX
      A = (SX2*SP - SX*SXP)/DENOM
      B = (FN*SXP - SX*SP)/DENOM
23    DO 40 I=1,N
      CALC(I) = A + B*XX(I)
40    D(I) = PP(I) - CALC(I)
      PRINT 110
110   FORMAT (//1H ,1X,5HLN(K),5X,11HLN(K(CALC)),3X,10HOBS - CALC)
      PRINT 111,(PP(I),CALC(I),D(I),I=1,N)
111   FORMAT (1H ,F8.4,5X,F8.4,5X,F8.4)
      PRINT 103,A,B,N
103   FORMAT(//43H REPRESENTATIVE LINEAR REGRESSION EQUATION    ,/,9H LN
     1(K) = ,E14.8,3H    ,E14.8,2H P,22H     FOR DATA OF SIZE ,I3//)
1100  IF(IX) 10,11,10
C     QUADRATIC CASES
6     IF(CSTK) 25,24,25
C     INPUT CONSTANT
25    DENOM = SX2*SX4 - SX3*SX3
      B = (SX4*(SXP - SX*CST) - SX3*(SX2P - SX2*CST))/DENOM
      C = (SX2*(SX2P - SX2*CST) - SX3*(SXP - SX*CST))/DENOM
      A = CST
      GO TO 26
```

```
C       FIND THE CONSTANT
24      DENOM = FN*(SX2*SX4 - SX3*SX3) - SX*(SX*SX4 - SX2*SX3) +
       1SX2*(SX*SX3 - SX2*SX2)
        B = (FN*(SXP*SX4 - SX3*SX2P) - SX*(SP*SX4 - SX2*SX2P) +
       1SX2*(SP*SX3 - SXP*SX2))/DENOM
        C = (FN*(SX2*SX2P - SXP*SX3) - SX*(SX*SX2P - SP*SX3) +
       1SX2*(SX*SXP - SP*SX2))/DENOM
        A = (SX2*(SX4*SP - SX2*SX2P) - SX3*(SX3*SP - SX*SX2P) +
       1SXP*(SX3*SX2 - SX*SX4))/DENOM
26      DO 41 I=1,N
        CALC(I) = A + B*XX(I) + C*XX(I)*XX(I)
41      D(I) = PP(I) - CALC(I)
        PRINT 110
        PRINT 111, (PP(I),CALC(I),D(I),I=1,N)
        PRINT 104, A, B, C, N
104     FORMAT (//47H REPRESENTATIVE CURVILINEAR REGRESSION EQUATION,/,
       19H LN(K) = ,E14.8,      E14.8,2H P,E14.8,5H P**2, 12H  DATA SIZE
       2 ,I3,//)
        GO TO 1100
999     CALL EXIT
        END
```

INPUT DATA

```
BENZYL CHLORIDE IN 0.2 MOLE FRACTION ETHANOL
1                 1        1          1
0.00000000E-991.93000000E-05
5.00000000E+032.46000000E-05
1.00000000E+043.02000000E-05
2.00000000E+044.64000000E-05
4.00000000E+048.71200000E-05
6.00000000E+041.20000000E-04
```

OUTPUT

```
BENZYL CHLORIDE IN 0.2 MOLE FRACTION ETHANOL
    GIVEN DATA
PRESSURE      RATE CONSTANT

.00000000E-99 .19300000E-04  LN(K) = - .10855405E+02
.50000000E+04 .24600000E-04  LN(K) = - .10612764E+02
.10000000E+05 .30200000E-04  LN(K) = - .10407668E+02
.20000000E+05 .46400000E-04  LN(K) = - .99782110E+01
.40000000E+05 .87120000E-04  LN(K) = - .93482240E+01
.60000000E+05 .12000000E-03  LN(K) = - .90280188E+01



 LN(K)      LN(K(CALC))    OBS - CALC
-10.8554     -10.7321        -.1232
-10.6127     -10.5779        -.0347
-10.4076     -10.4238         .0161
- 9.9782     -10.1154         .1372
- 9.3482     - 9.4987         .1505
- 9.0280     - 8.8821        -.1459

REPRESENTATIVE LINEAR REGRESSION EQUATION
LN(K) = -.10732150E+02     .30834127E-04 P     FOR DATA OF SIZE   6
```

TABLE XIX

Parameters of the Linear Activation Volume Analysis

Mole Fraction	A	10^5 x B
		(p.s.i.$^{-1}$)
Benzyl Chloride Solvolysis at 50.25°C.		
	Methanol	
0.000	- 8.4048697	2.7869600
0.100	- 8.9831485	3.1283885
0.200	- 9.4946511	2.8888457
0.300	-10.121928	3.2317628
0.400	-10.640808	2.8862655
0.500	-11.159395	3.1218715
	Ethanol	
0.100	- 9.5231764	2.7681800
0.200	-10.732150	3.0834127
0.300	-11.617302	3.4321147
0.400	-12.178518	2.8866318
	i-Propanol	
0.100	-10.568869	3.1995301
0.200	-12.159830	3.5689396
0.300	-12.869631	3.2351094
0.400	-13.516210	3.1358396
	t-Butanol	
0.100	-11.673934	3.9255784
0.200	-12.985193	3.1206698
0.300	-13.853298	3.4479474
Reaction[a]		
1	- 4.5304444	1.3377925
4	1.6375928	- 2.3263220

TABLE XIX(con't)

Reaction	A	10^5 x B
		(atm.$^{-1}$)
2	-10.151181	6.1974674
3	- 0.81245665	-32.773932
5	- 6.8233352	-10.626058
		(cm.^{2}/Kg.)
6	-18.804322	69.677093

[a] Numbers refer to the reactions of Table VIII.

TABLE XX

Parameters of the Linear Forced Intercept Activation Volume Analysis

Mole Fraction	$\ln k_o$	10^5 x B (p.s.i.$^{-1}$)
Benzyl Chloride Solvolysis at 50.25°C.		
	Methanol	
0.000	- 8.3730928	2.5751123
0.100	- 8.9895997	3.1498919
0.200	- 9.5606073	3.1087000
0.300	-10.196249	3.4794995
0.400	-10.802429	3.2548736
0.500	-11.292987	3.4265526
	Ethanol	
0.100	- 9.5981006	3.0827755
0.200	-10.855405	3.3740576
0.300	-11.736069	3.7121746
0.400	-12.291630	3.1446052
	i-Propanol	
0.100	-10.773849	3.6670263
0.200	-12.285115	3.8546771
0.300	-13.038941	3.6212526
0.400	-13.562419	3.2412263
	t-Butanol	
0.100	-11.900059	4.4413000
0.200	-13.189037	3.5855754
0.300	-13.909821	3.5768578

Reaction[a]		
1	- 4.5282091	1.3218768
4	1.6448050	- 2.3741238

TABLE XX (con't)

Reaction	$\ln k_o$	$10^5 \times B$
		($atm.^{-1}$)
2	-10.747457	8.4551881
3	- 0.79850769	-34.141891
5	- 6.4253291	-14.348068
		($cm.^2/Kg.$)
6	-19.203752	76.691008

[a] Numbers refer to the reactions of Table VIII.

TABLE XXI

Parameters of the Quadratic Activation Volume Analysis[a]

Reaction[b]	A	10^5 x B	10^{10} x C
		(p.s.i.$^{-1}$)	(p.s.i.$^{-2}$)
1	- 4.5300550	1.3174046	0.23171728
4	1.6451140	- 2.8711931	3.1468576
		(atm.$^{-1}$)	(atm.$^{-2}$)
2	-10.437424	13.302875	- 19.123646
3	- 0.81500486	- 31.278797	-109.91510
5	- 6.5245967	- 27.022692	111.27858
		(cm.^{2}/Kg.)	(cm.^{4}/Kg.^{2})
6	-19.308841	107.51614	-461.48939

[a] The parameters for the solvolysis of benzyl chloride at 50.25°C. are given in Table XVIII.

[b] Numbers refer to the reactions of Table VIII.

TABLE XXII

Parameters of the Quadratic Forced Intercept Activation Volume Analysis

Mole Fraction	$\ln k_o$	$10^5 \times B$	$10^{10} \times C$
		(p.s.i.$^{-1}$)	(p.s.i.$^{-2}$)
	Benzyl Chloride Solvolysis at 50.25°C.		
	Methanol		
0.000	- 8.3730928	1.8373639	4.2445782
0.100	- 8.9895997	3.1788960	- 8.3430693
0.200	- 9.5606073	4.1174009	- 2.9017425
0.300	-10.196249	4.6720123	- 3.4305173
0.400	-10.802429	5.1022090	- 3.6435351
0.500	-11.292987	4.8895498	- 2.8856935
	Ethanol		
0.100	- 9.6123115	4.5174929	- 4.1692639
0.200	-10.855405	5.0592528	- 3.3368743
0.300	-11.736069	5.1200428	- 2.7877370
0.400	-12.291630	4.5261502	- 2.7248460
	_i_-Propanol		
0.100	-10.773849	5.9806782	- 4.5632594
0.200	-12.285115	5.0806207	- 2.4179499
0.300	-13.038941	5.0851945	- 2.8873612
0.400	-13.562419	3.6277503	- 0.76234776
	_t_-Butanol		
0.100	-11.900059	6.6801583	- 4.4325678
0.200	-13.189037	5.8811299	- 4.5275676
0.300	-13.909821	4.2871972	- 1.4010165
Reaction[a]			
1	- 4.5282091	1.3420309	- 0.13147878
4	1.6448050	- 2.8663446	3.1297005

TABLE XXII (con't)

Reaction	$\ln k_o$	$10^5 \times B$	$10^{10} \times C$
		(atm.^{-1})	(atm.^{-2})
2	-10.747457	17.045603	- 27.281641
3	- 0.79850769	- 35.513595	121.03117
5	- 6.4253291	- 29.677642	125.40572
		$(\text{cm.}^2/\text{Kg.})$	$(\text{cm.}^4/\text{Kg.}^2)$
6	-19.203752	102.91654	-417.61183

[a] Numbers refer to the reactions of Table VIII.

APPENDIX VI

BENSON-BERSON ACTIVATION VOLUME ANALYSIS

```
C     BENSON-BERSON EQUATION FOR ACTIVATION VOLUMES
      DIMENSION P(20),Y(20),YY(20),HEAD(20),PK(20),FK(20),CALC(20),
     1D(20)
1     READ 100, HEAD
100   FORMAT (20A4)
      PRINT 99, HEAD
99    FORMAT (1H1, 20A4, 5X,20HBENSON-BERSON METHOD,//)
      READ 101, N
101   FORMAT (I2)
      READ 102, (P(I),Y(I),I=1,N)
102   FORMAT (F5.0,7X,E9.3)
      Y1 = Y(1)
C     INITIALIZE SUMS
      SP = 0.
      SPP = 0.
      SLYYP = 0.
      SPLYYP = 0.
      PP(1) = 0.
      DO 2 I=2,N
      SP = SP + P(I)**0.523
      PP(I) = P(I)**0.523
      SPP = SPP + PP(I)*PP(I)
      SLYYP = SLYYP + LOGF(Y(I)/Y1)/P(I)
      YY(I) = LOGF(Y(I)/Y1)/P(I)
2     SPLYYP = SPLYYP + PP(I)*YY(I)
      FN = N
      A = (SPP*SLYYP - SP*SPLYYP)/((FN - 1.)*SPP - SP*SP)
      B = ((FN - 1.)*SPLYYP - SP*SLYYP)/((FN - 1.)*SPP - SP*SP)
      DO 4 I=1,N
      FK(I) = LOGF(Y(I))
      CALC(I) = (A + B*PP(I))*P(I) + LOGF(Y(1))
4     D(I) = FK(I) - CALC(I)
      PRINT 103, A, B
103   FORMAT (17H VALUE OF A IS = , E11.4, 3X,7HB IS = ,E11.4,//)
      PRINT 104
104   FORMAT(11H INPUT DATA,/)
      PRINT 105
105   FORMAT (5H    P,8X,1HK,12X,8HP**0.523,/)
      PRINT 106, (P(I),Y(I),PP(I),I=1,N)
106   FORMAT (F7.0,2X,E11.3,5X,F7.1)
      DO 5 I=2,N
5     PK(I) = A + B*PP(I)
      PRINT 107
```

```
107    FORMAT (/1H , 6HLOG(K), 5X, 12HLOG(K(CALC)), 5X, 10HOBS - CALC,/)
       PRINT 108, (FK(I), CALC(I), D(I), I=1,N)
108    FORMAT (1H , F8.4, 5X, F8.4, 8X, F8.4)
       GO TO 1
3      CALL EXIT
       END
```

INPUT DATA

```
BENZYL CHLORIDE IN 0.3 MOLE FRACTION I-PROPANOL
05
    0      2.174E-06
10000      3.870E-06
20000      5.800E-06
40000      9.100E-06
60000      1.710E-05
```

OUTPUT

```
                                                     BENSON-BERSON METHOD
BENZYL CHLORIDE IN 0.3 MOLE FRACTION I-PROPANOL

VALUE OF A IS =  7.2078E-05   B IS = -1.2778E-07

INPUT DATA

  P         K          P**0.523

    0.   2.174E-06       0.0
10000.   3.870E-06     123.5
20000.   5.800E-06     177.5
40000.   9.100E-06     255.1
60000.   1.710E-05     315.4

LOG(K)      LOG(K(CALC))     OBS - CALC

-13.0389    -13.0389          0.0000
-12.4622    -12.4760           .0138
-12.0576    -12.0512          -.0063
-11.6072    -11.4602          -.1470
-10.9764    -11.1330           .1566
```

TABLE XXIII

Parameters of the Benson-Berson Activation Volume Analysis

Mole Fraction	10^5 x A (p.s.i.$^{-1}$)	10^8 x B (p.s.i.$^{-1.523}$)
Benzyl Chloride Solvolysis at 50.25°C.		
Methanol		
0.000	0.093888	15.754
0.100	3.4969	- 1.5694
0.200	5.1785	- 8.9572
0.300	5.6958	- 9.5367
0.400	6.1505	- 9.9444
0.500	5.8118	- 8.3321
Ethanol		
0.100	5.6282	- 11.039
0.200	5.5193	- 7.3779
0.300	6.1487	- 8.6269
0.400	4.8746	- 5.9106
i-Propanol		
0.100	7.3088	- 12.717
0.200	6.2104	- 8.2769
0.300	7.2078	- 12.778
0.400	4.1704	- 3.2885
t-Butanol		
0.100	8.6135	- 14.631
0.200	7.2393	- 12.774
0.300	5.0011	- 5.1869
Reaction[a]		
1	0.97551	2.3556
4	- 3.2666	5.7245

TABLE XXIII (con't)

Reaction	$10^5 \times A$	$10^8 \times B$
	(atm.$^{-1}$)	(atm.$^{-1.523}$)
2	30.528	-101.91
3	54.798	546.55
5	-43.453	214.72
	(cm.^{2}/Kg.)	(cm.$^{3.046}$/Kg.$^{1.523}$)
6	104.92	-285.98

[a] Numbers refer to reactions of Table VIII.

APPENDIX VII

WHALLEY ACTIVATION VOLUME ANALYSIS

```
C     WHALLEY METHOD FOR ACTIVATION VOLUMES
      DIMENSION HEAD(20), X(20), Y(20), P(20), PK(20), OBS(20), CALC(20)
     1,D(20)
1     READ 99, HEAD
99    FORMAT (20A4)
      PRINT 98, HEAD
98    FORMAT (1H1, 20A4, 11X, 14HWHALLEY METHOD,//)
      READ 100, N
100   FORMAT (I2)
      READ 101, (P(I),PK(I),I=1,N)
101   FORMAT (F5.0, 7X, E9.3)
      J = N - 1
      DO 2 I=1,J
      Y(I) = (LOGF(PK(I+1)/PK(I)))/(P(I+1) - P(I))
2     X(I) = (P(I+1) + P(I))/2.
C     INITIALIZE SUMS
      SXX = 0.
      SY = 0.
      SX = 0.
      SXY = 0.
      FN = J
      DO 3 I=1,J
C     COMPUTE THE SUMS
      SX = SX + X(I)
      SXX = SXX + X(I)*X(I)
      SY = SY + Y(I)
3     SXY = SXY + X(I)*Y(I)
      SX2 = SX*SX
C     COMPUTE THE PARAMETERS
      A = (SXX*SY - SX*SXY)/(FN*SXX - SX2)
      B = (FN*SXY - SX*SY)/(FN*SXX - SX2)
      PRINT 102, A, B
102   FORMAT (1H , 20HTHE VALUE OF A IS = , E14.8, 5X, 7HB IS = , E14.8,
     1//)
      PRINT 103
103   FORMAT (11H INPUT DATA,//)
      PRINT 104
104   FORMAT (1H , 1X, 4HP(I), 13X, 4HK(I),//)
      PRINT 105, (P(I), PK(I), I=1,N)
105   FORMAT (1H , F7.0, 9X, E10.3)
      PRINT 106
106   FORMAT (//1H , 16H(P(I+1)+P(I))/2 ,5X, 30HLOG(K(I+1)/K(I))/(P(I+1)
     1-P(I)),/)
```

```
      PRINT 107, (X(I), Y(I), I=1,J)
107   FORMAT (1H , 1X, E14.8, 13X, E14.8)
      DO 4 I=1,J
      CALC(I) = A*(P(I+1) - P(I)) + B*X(I)*(P(I+1) - P(I))
      OBS(I) = LOGF(PK(I+1)/PK(I))
4     D(I) = OBS(I) - CALC(I)
      PRINT 108
108   FORMAT (//1H , 6X, 4HCALC, 20X, 3HOBS, 17X, 42HOBS LOG(K(I+1)/K(I)
     1)-CALC LOG(K(I+1)/K(I)),/)
      PRINT 109, (CALC(I), OBS(I), D(I), I=1,J)
109   FORMAT (1H , 3X, F8.4, 16X, F8.4, 28X, F8.4)
      GO TO 1
6     CALL EXIT
      END
```

INPUT DATA

```
BENZYL CHLORIDE IN 0.3 MOLE FRACTION T-BUTANOL
05
    0        9.100E-07
10000        1.490E-06
20000        1.700E-06
40000        4.590E-06
60000        6.920E-06
```

OUTPUT

```
                                                                          WHALLEY METHOD
BENZYL CHLORIDE IN 0.3 MOLE FRACTION T-BUTANOL

THE VALUE OF A IS =  .40921739E-04     B IS = -.31003739E-09

INPUT DATA

 P(I)             K(I)

    0.           9.100E-07
 10000.          1.490E-06
 20000.          1.700E-06
 40000.          4.590E-06
 60000.          6.920E-06

 (P(I+1)+P(I))/2      LOG(K(I+1)/K(I))/(P(I+1)-P(I))

  .50000000E+04            .49308677E-04
  .15000000E+05            .13185204E-04
  .30000000E+05            .49662588E-04
  .50000000E+05            .20526784E-04

     CALC                 OBS               OBS LOG(K(I+1)/K(I))-CALC LOG(K(I+1)/K(I))

     .3937               .4930                         .0993
     .3627               .1318                        -.2308
     .6324               .9932                         .3608
     .5083               .4105                        -.0978
```

TABLE XXIV

Parameters of the Whalley Activation Volume Analysis

Mole Fraction	$10^5 \times A$ (p.s.i.$^{-1}$)	$10^{10} \times B$ (p.s.i.$^{-2}$)
	Benzyl Chloride Solvolysis at 50.25°C.	
	Methanol	
0.000	1.7910741	10.217368
0.100	3.1893884	- 0.36262947
0.200	4.1347715	- 6.1277378
0.300	4.6845305	- 7.0947747
0.400	5.0933150	- 7.3101891
0.500	4.9209541	- 5.7502347
	Ethanol	
0.100	4.6180295	- 8.9260666
0.200	4.9619205	- 6.4850792
0.300	5.1378800	- 5.5560674
0.400	4.5411873	- 5.3992369
	i-Propanol	
0.100	5.9826302	- 9.1447521
0.200	5.1812778	- 4.7522326
0.300	5.2327169	- 5.7118760
0.400	3.6945343	- 1.4690304
	t-Butanol	
0.100	6.8939023	- 9.1679913
0.200	5.8763084	- 9.0861413
0.300	4.0921739	- 3.1003739
Reaction[a]		
1	1.2824759	0.58293993
4	- 2.8442783	5.9638146

TABLE XXIV (con't)

Reaction	10^5 x A	10^{10} x B
	($atm.^{-1}$)	($atm.^{-2}$)
2	23.082916	- 70.251293
3	-33.999402	-174.18695
5	-31.999152	260.30991
	($cm.^2$/Kg.)	($cm.^4$/$Kg.^2$)
6	97.521090	-971.44449

[a] Numbers refer to the reactions of Table VIII.

APPENDIX VIII

COMPRESSIBILITY CALCULATIONS

```
C      COMPRESSIBILITY PROGRAM
C      FOR THAT PVT CELL DESIGNATED AS NO. 1 BY ESSO RESEARCH,ONLY
C      REFERENCE PRESSURE IS 3000 P.S.I.G.
       DIMENSION HEAD(9), CP(7),PR(7)COL3(7),COL4(7),COL5A(7),COL5B(7),
      1COL5(7),COL6A(7),COL6B(7),COL6(7),COL7(7),COL8(7),Y(7),YCALC(7),
      2YDIF(7),YREL(7),DCP(7),DPR(7),DCOL3(7),DCOL4(7),DCOL5A(7),DCOL5B(7
      3),DCOL5(7),DCOL6A(7),DCOL6B(7),DCOL6(7),DCOL7(7),DCOL8(7),DY(7)
1      READ 102,(HEAD(I),I=1,9)
102    FORMAT(3X,9A4)
       PRINT 103, HEAD
103    FORMAT(1H1,19HCOMPRESSIBILITY OF , 9A4,27HLN(V) = A + B*P + C*(P**
      12.))
       READ 1041,RT
1041   FORMAT(20X,F4.1)
       READ 1042,CT
1042   FORMAT(20X,F6.2)
       READ 1043,VLIQ
1043   FORMAT(39X,F6.3)
       PRINT 113,RT,CT
113    FORMAT(1H0,19HROOM TEMPERATURE IS,F5.1,11H DEGREES F.,5X,19HCELL T
      1EMPERATURE IS,F7.2,11H DEGREES F.)
       PRINT 1133,VLIQ
1133   FORMAT(1H ,38HSAMPLE VOLUME AT REFERENCE PRESSURE IS,F7.3,5H C.C.)
       READ 105,N
105    FORMAT(I2)
       DO 5 I=1,N
5      READ 106,CP(I),PR(I),DCP(I),DPR(I)
106    FORMAT(F4.0,10X,F7.3,10X,I1,10X,F5.3)
C      CELL VOLUME IS 493.310 C.C.
       VO = 493.310 - VLIQ
       DO 6 I=1,N
6      COL3(I) = PR(1) - PR(I)
       DCOL3(1) = 0.000
       DO 51 I=2,N
51     DCOL3(I)=DPR(1) + DPR(I)
       BRT = (2.53 + 0.0031*RT)*1.E-7
       BCT = (2.53 + 0.0031*CT)*1.E-7
       VMCT=1. +(1.0086E-4)*(CT - 60.) + (2.4E-9)*(CT*(CT-320.) + 25600.)
       VMRT=1. +(1.0086E-4)*(RT - 60.) + (2.4E-9)*(RT*(RT-320.) + 25600.)
       PRINT 300
300    FORMAT(1H0,4H   1,8X,1H2,8X,1H3,11X,1H4,5X,2H5A,6X,2H5B,5X,1H5,5X,
      12H6A,5X,2H6B,6X,1H6,10X,1H7)
       PRINT 114
114    FORMAT(1H ,   1X,4HCELL,5X,4HPUMP,5X,17HMERCURY WITHDRAWN,3X,17HME
      1RCURY EXPANSION,3X,19HAPPARATUS EXPANSION,2X,13H,SAMPLE VOLUME)
```

```
      PRINT 115
115   FORMAT(1H ,8HPRESSURE, 2X,7HREADING,2X,4HPUMP,8X,4HCELL,3X,4HCELL,
     14X,4HLINE,2X,5HTOTAL,2X,4HCELL,3X,4HLINE,3X,5HTOTAL,4X,8HINCREASE)
      DO 7 I=1,N
      COL4(I) = COL3(I)*(1. + 3000.BRT)*(VMCT/VMRT)*(1. - BCT*CP(I))
      DCOL4(I)=DCOL3(I)*(1.+3000.BRT)*(VMCT/VMRT)*(1.-BCT*CP(I))+COL3(I)
     1*(1.+3000.*BRT)*(VMCT/VMRT)*(-BCT*DCP(I))
      DCOL4(I)=ABSF(DCOL4(I))
      COL5A(I) = VO*((1. +3000.*BCT)*(1. - BCT*CP(I)) - 1.)
      DVO = 0.004
      DCOL5A(I) = DVO*((1.+3000.*BCT)*(1.-BCT*CP(I))-1.) +VO*((1.+3000.*
     1BCT)*(-BCT*DCP(I)))
      DCOL5A(I) = ABSF(DCOL5A(I))
C     VOLUME OF LINE IS 10.768 C.C.
      COL5B(I) = 10.768*((1. + 3000.*BCT)*(1. - BCT*CP(I)) - 1.)
      DCOL5B(I) = 0.002*((1.+3000.*BCT)*(1.-BCT*CP(I))-1.)+10.768*((1.+
     13000.*BCT)*(-BCT*DCP(I)))
      DCOL5B(I) = ABSF(DCOL5B(I))
      COL5(I) = COL5A(I) + COL5B(I)
      DCOL5(I) = DCOL5A(I) + DCOL5B(I)
      COL6A(I)=8.3E-5*(CP(I) - 3000.)
      DCOL6A(I) = 8.3E-5*DCP(I)
      IF(CP(I) - 3000.) 10,11,11
11    COL6B(I) = 0.0
      DCOL6B(I)= 0.0
      GO TO 20
10    IF(CP(I) - 2002.) 14,13,12
13    COL6B(I) = -0.005
      DCOL6B(I) = 0.0002
      GO TO 20
12    COL6B(I) = -5.01002E-6*(3000. - CP(I))
      DCOL6B(I) = 5.01002E-6*DCP(I)
      GO TO 20
14    IF(CP(I) - 1008.) 17,16,15
16    COL6B(I) = -.011
      DCOL6B(I) = 0.0002
      GO TO 20
15    COL6B(I)=-0.005 - 6.0362E-6*(2002. -CP(I))
      DCOL6B(I) = 6.0362E-6*DCP(I)
      GO TO 20
17    IF(CP(I) - 122.) 19,19,18
19    COL6B(I) = -0.055
      DCOL6B(I) = 0.0002
      GO TO 20
18    COL6B(I) = -0.011 - 4.96614E-5*(1008. - CP(I))
      DCOL6B(I)=4.96614E-5*DCP(I)
20    COL6(I) = COL6A(I) + COL6B(I)
      DCOL6B(I) = ABSF(DCOL6B(I))
      DCOL6(I) = DCOL6A(I) + DCOL6B(I)
```

```
      COL7(I) = COL4(I) + COL6(I) -COL5(I)
      DCOL7(I) = DCOL4(I) + DCOL6(I) + DCOL5(I)
      COL8(I) = COL7(I) + VLIQ
      DCOL8(I) = DCOL7(I) + 0.002
7     PRINT 108,CP(I),PR(I),COL3(I),COL4(I),COL5A(I),COL5B(I),COL5(I),
     1COL6A(I),COL6B(I),COL6(I),COL7(I)
108   FORMAT(1H ,F6.0,4X,F6.3,2X,F6.3,6X,F6.3,1X,F6.3,1X,F6.3,1X,F6.3,1X
     1,F6.3,1X,F6.3,1X,F6.3,4X,F6.3)
      PRINT 201
201   FORMAT(1H0,10HSAMPLE VOL,2X,15HLOG(SAMPLE VOL),2X,18HD(LOG(SAMPLE
     1VOL)),2X,12HLOG(V(CALC)),2X,10HCALC - OBS,2X,12HRELATIVE VOL)
      DO 8 I=1,N
      Y(I) = LOGF(COL8(I))
8     DY(I) = DCOL8(I)/COL8(I)
      SP = 0.
      SPP = 0.
      SPPP = 0.
      SPPPP = 0.
      SY = 0.
      SPY = 0.
      SPPY = 0.
      DO 3 I=1,N
      SP = SP + CP(I)
      CPI2 = CP(I)*CP(I)
      SPP = SPP + CPI2
      SPPP = SPPP + CP(I)*CPI2
      SPPPP = SPPPP + CPI2*CPI2
      SY = SY + Y(I)
      SPY = SPY + CP(I)*Y(I)
3     SPPY = SPPY + CPI2*Y(I)
      FN = N
C     CALCULATIONS
      DENOM = FN*SPP*SPPPP - FN*SPPP*SPPP - SP*SP*SPPPP + 2.*SP*SPP*SPPP
     1-SPP*SPP*SPP
      C = (FN*SPP*SPPY - FN*SPPP*SPY - SP*SP*SPPY + SP*SPPP*SY + SP*SPP*
     1SPY - SPP*SPP*SY)/DENOM
      B = (FN*SPY - FN*C*SPPP - SP*SY + C*SP*SPP)/(FN*SPP - SP*SP)
      A = (SY - B*SP - C*SPP)/FN
      DO 9 I=1,N
      YCALC(I) = A + B*CP(I) + C*CP(I)*CP(I)
9     YDIF(I) = YCALC(I) - Y(I)
      DO 21 I=1,N
21    YREL(I) = COL8(I)/COL8(1)
      PRINT 111,(COL8(I),Y(I),DY(I),YCALC(I),YDIF(I),YREL(I),I=1,N)
111   FORMAT(1H ,F7.3,7X,F9.6,12X,F8.6,7X,F9.6,3X,F8.6,6X,F9.6)
      FA = EXPF(A)/COL8(1)
      PRINT 203,FA
203   FORMAT(1H ,41X,36HAT ATMOSPHERIC PRESSURE EXTRAPOLATED,F9.6)
      PRINT 109,A,B,C
```

```
109    FORMAT(1HO,7HLOGV = ,E14.7,2X,E14.7,2H*P,2X,E14.7,5H*P**2)
       DP = 0.
       DPP = 0.
       DPPP = 0.
       DPPPP = 0.
       DZ = 0.
       DPY = 0.
       DPPY = 0.
       DO 50 I=1,N
       DP = DP + DCP(I)
       DPP = DPP + 2.*DCP(I)*CP(I)
       CPI2 = CP(I)*CP(I)
       DPPP = DPPP + 3.*DCP(I)*CPI2
       DPPPP = DPPPP + 4.*CP(I)*CPI2*DCP(I)
       DZ = DZ + DY(I)
       DPY = DPY+DCP(I)*Y(I) + CP(I)*DY(I)
50     DPPY = DPPY + 2.*DCP(I)*CP(I)*Y(I) + CPI2*DY(I)
       DDENOM = FN*DPP*SPPPP + FN*SPP*DPPPP - 2.*FN*DPPP*SPPP - 2.*DP*SP*
      1SPPPP - SP*SP*DPPPP + 2.*DP*SPPY*SPPP + 2.*SP*DPP*SPPP + 2.*SP*SPP
      2*DPPP - 3.*DPP*SPP*SPP
       DC = (FN*DPP*SPPY + FN*SPP*DPPY - FN*DPPP*SPY - FN*SPPP*DPY - 2.*
      1DP*SP*SPPY - SP*SP*DPPY + DP*SPPP*SY + SP*DPPP*SY + SP*SPPP*DZ +
      2DP*SPP*SPY + SP*DPP*SPY + SP*SPP*DPY - 2.*DPP*SPP*SY - SPP*SPP*DZ)
      3/DENOM - C*DDENOM/DENOM
       DB = (FN*DPY - FN*DC*SPPP - FN*C*DPPP - DP*SY - SP*DZ + DC*SP*SPP
      1+ C*DP*SPP + C*SP*DPP)/(FN*SPP - SP*SP) - B*(FN*DPP - 2.*SP*DP)/(
      2FN*SPP - SP*SP)
       DA = (DZ - DB*SP - B*DP - DC*SPP - C*DPP)/FN
       DA = ABSF(DA)
       DB = ABSF(DB)
       DC = ABSF(DC)
       PRINT 202,DA,DB,DC
202    FORMAT(1HO, 4HDA =,E14.7,6H  DB =,E14.7,6H  DC =,E14.7)
       GO TO 1
999    CALL EXIT
       END
```

INPUT DATA

```
WATER
                    80.7
                    122.25
                              94.354

07                                  .001
3000           5.268          5     .001
2500           5.038          5     .001
2002           4.802          5     .001
1507           4.568          5     .001
1008           4.320          5     .001
 510           4.080          5     .001
 122           3.874          5
```

OUTPUT

```
                                                       LN(V) = A + B*P + C*(P**2.)
COMPRESSIBILITY OF WATER

ROOM TEMPERATURE IS 80.7 DEGREES F.     CELL TEMPERATURE IS 122.25 DEGREES F.
SAMPLE VOLUME AT REFERENCE PRESSURE IS 94.354 C.C.

                                 4        5A      5B      5        6A      6B      6        7
   1        2          3                                                               SAMPLE VOLUME
  CELL     PUMP     MERCURY WITHDRAWN  MERCURY  EXPANSION        APPARATUS  EXPANSION      INCREASE
PRESSURE  READING   PUMP        CELL   CELL     LINE    TOTAL    CELL     LINE    TOTAL
 3000.     5.268    0.000      0.000   0.000    0.000   0.000    0.000    0.000   0.000      0.000
 2500.     5.038     .230       .230    .057     .001    .059    -.041    -.002   -.044       .127
 2002.     4.802     .466       .468    .115     .003    .118    -.082    -.005   -.087       .261
 1507.     4.568     .700       .703    .173     .004    .177    -.123    -.007   -.131       .393
 1008.     4.320     .948       .952    .231     .006    .237    -.165    -.011   -.176       .538
  510.     4.080    1.188      1.193    .288     .007    .296    -.206    -.035   -.242       .654
  122.     3.874    1.394      1.400    .333     .009    .342    -.238    -.055   -.293       .764

SAMPLE VOL  LOG(SAMPLE VOL)  D(LOG(SAMPLE VOL))  LOG(V(CALC))  CALC - OBS  RELATIVE VOL
  94.354       4.547057           .000031          4.547012     -.000044     1.000000
  94.481       4.548406           .000053          4.548441      .000035     1.001349
  94.615       4.549821           .000055          4.549854      .000032     1.002768
  94.747       4.551215           .000053          4.551249      .000033     1.004167
  94.892       4.552748           .000054          4.552645     -.000102     1.005707
  95.008       4.553968           .000055          4.554029      .000061     1.006935
  95.118       4.555119           .000054          4.555101     -.000017     1.008094
                                   AT ATMOSPHERIC PRESSURE EXTRAPOLATED       1.008414

LOGV = 4.5554367E+00   -2.7494060E-06*P   -1.9530391E-11*P**2

DA = 1.0826149E-04   DB = 7.9836204E-08   DC = 2.4082247E-11
```

TABLE XXV

Parameters of the Compressibility Equation

Mole Fraction	A	10^{6} x B (p.s.i.$^{-1}$)	10^{11} x C (p.s.i.$^{-2}$)	10^{5} x DA	10^{7} x DB (p.s.i.$^{-1}$)	10^{11} x DC (p.s.i.$^{-2}$)
Methanol						
0.000	4.555	-2.749	- 1.953	10.826	0.798	2.408
0.100	4.536	-3.105	5.371	5.102	2.651	8.751
0.200	4.543	-3.218	4.394	2.944	2.195	7.274
0.300	4.554	-3.617	2.441	1.506	1.278	4.305
0.400	4.533	-4.474	10.741	16.228	5.167	16.887
0.500	4.547	-5.144	14.160	23.639	6.797	22.153
Ethanol						
0.100	4.556	-2.839	- 1.953	10.869	0.798	2.408
0.200	4.548	-3.666	5.371	4.918	2.657	8.766
0.300	4.546	-4.366	6.347	6.713	3.116	10.250
0.400	4.545	-5.190	14.160	23.579	6.791	22.135
i-Propanol						
0.100	4.558	-3.141	- 0.977	8.837	0.337	0.916
0.200	4.569	-4.334	10.253	15.666	4.987	16.297
0.300	4.553	-5.225	13.671	22.596	6.577	21.439
0.400	4.567	-5.984	20.995	38.695	10.064	32.713
t-Butanol						
0.100	4.546	-3.659	4.883	3.845	2.430	8.033
0.200	4.558	-4.803	9.277	13.122	4.511	14.758
0.300	4.569	-5.818	18.554	33.381	8.913	28.992

APPENDIX IX

THERMAL EXPANSIVITY CALCULATIONS

```
C     LINEAR THERMAL EXPANSIVITY PROGRAM
C     LN(DENSITY) = A + B*T
C     R = DENSITY
      DIMENSION R(3),T(3),HEAD(80),Y(3),CALC(3),DIF(3)
1     READ 100, HEAD
100   FORMAT(80A1)
      N = 3.
2     READ 101,(T(I),R(I),I=1,N)
101   FORMAT(F5.2,10X,F7.5)
      ST = 0.
      ST2 = 0.
      SY = 0.
      STY = 0.
      ST2Y = 0.
      DO 3 I=1,N
      Y(I) = LOGF(R(I))
      ST = ST + T(I)
      ST2 = ST2 + T(I)*T(I)
      SY = SY + Y(I)
      STY = STY + T(I)*Y(I)
 3    ST2Y = ST2Y + T(I)*T(I)*Y(I)
      Q = N
      DENOM = Q*ST2 - ST*ST
      B = (Q*STY - ST*SY)/DENOM
      A = (ST2*SY - ST*STY)/DENOM
C     OUTPUT
      PRINT 200
200   FORMAT(1H1, 19HTHERMAL EXPANSIVITY)
      PRINT 201, HEAD
201   FORMAT(1H0, 80A1)
      PRINT 202
202   FORMAT(1H0,3X,1HT,6X,7HDENSITY)
      PRINT 203,(T(I),R(I),I=1,N)
203   FORMAT(1H , F6.2, 4X, F8.5)
      DO 5 I=1,N
      CALC(I) = A + B*T(I)
 5    DIF(I) = Y(I) - CALC(I)
      PRINT 204
204   FORMAT(1H0,1X,11HLN(DENSITY),3X,17HLN(DENSITY CALC.),4X,10HOBS - C
     1ALC)
      PRINT 205,(Y(I),CALC(I),DIF(I),I=1,N)
205   FORMAT(1H ,2X,F8.5,9X,F8.5,9X,F9.6)
      PRINT 206
206   FORMAT(1H0, 21HLN(DENSITY) = A + B*T)
```

```
      PRINT 207, A,B
207   FORMAT(1H0,1X,4HA = ,F10.7,/,2X,4HB = ,F10.7)
      GO TO 1
999   CALL EXIT
      END
```

INPUT DATA

```
WATER, FROM INTERNATIONAL CRITICAL TABLES
40.05          .99225
50.25          .98796
60.50          .98298
```

OUTPUT

```
THERMAL EXPANSIVITY

WATER, FROM INTERNATIONAL CRITICAL TABLES

   T      DENSITY
 40.05     .99225
 50.25     .98796
 60.50     .98298

 LN(DENSITY)   LN(DENSITY CALC.)   OBS - CALC
   -.00778          -.00766          -.000116
   -.01211          -.01234           .000232
   -.01716          -.01705          -.000115

LN(DENSITY) = A + B*T

 A =   .0107199
 B =  -.0004590
```

TABLE XXVI

Parameters of the Thermal Expansivity Equation

Mole Fraction	10^2 x A	10^4 x B (deg.$^{-1}$)	10^2 x A	10^4 x B (deg.$^{-1}$)	10^2 x A	10^4 x B (deg.$^{-1}$)
			Methanol			
0.000	1.07199	-4.590				
0.100	-1.30717	-5.847	-1.46486	-5.547	-1.43156	-5.630
0.200	-3.15489	-7.689	-3.37207	-7.168	-3.30037	-7.326
0.300	-5.56488	-8.121	-5.63539	-7.918	-5.55281	-8.097
0.400	-7.73263	-8.923	-7.82547	-8.816	-7.69147	-9.059
0.500	-9.81015	-9.982	-9.88568	-9.762	-9.77400	-10.025
			Ethanol			
0.100	-1.89193	-6.689	-1.87513	-6.817	-1.80814	-6.897
0.200	-4.69227	-8.427	-4.74483	-8.387	-4.60504	-8.682
0.300	-7.54887	-9.503	-7.55799	-9.499	-7.67962	-9.657
0.400	-10.25821	-10.311	-10.33109	-10.276	-10.30937	-10.344
			i-Propanol			
0.050	-0.76599	-5.752	-0.79309	-5.843	-0.83174	-6.029
0.100	-2.17988	-7.612	-2.15054	-7.514		
0.200	-6.29293	-9.285	-6.39068	-8.974	-6.29961	-9.142
0.300	-9.73869	-9.751	-9.66454	-9.930	-9.77918	-9.697
0.400	-12.12553	-10.605	-12.10634	-10.657	-11.93387	-11.020
			t-Butanol			
0.050	-1.13378	-6.965	-1.07222	-7.066	-1.04489	-7.081
0.100	-3.68146	-8.519	-3.83084	-8.373	-3.75412	-8.533
0.200	-8.67136	-9.896	-8.82044	-9.937	-8.74352	-10.207
0.300	-11.63480	-10.741	-11.63480	-10.741	-11.70379	-10.610

APPENDIX X

ERROR MEASUREMENTS

Two types of error measurement have been used in this thesis. For the error associated with an experimental measurement, the average deviation from the mean has been used. This is defined as

$$\text{a.d.} = \frac{\Sigma|\bar{Q} - Q_j|}{n} \tag{103}$$

where $\bar{Q}$ represents the average value of the measured quantity, Q_j the j^{th} determination of that quantity and n the number of determinations.

In Chapter 6, the ability of the various functional forms of the pressure dependence of the reaction rate constant to reproduce the observed rate data was represent by the standard deviation. This measurement was defined as

$$\text{s.d.} = \sqrt{\frac{\Sigma(k_{obs} - k_{calc})^2}{n-1}}. \tag{104}$$

APPENDIX XI

REPRINTS

This appendix contains reprints of the articles by the author of this thesis which deal with solvent effects in reacting systems. These articles were published during his period of residence at the University of Calgary (previously called University of Alberta at Calgary).

[Reprinted from the Journal of the American Chemical Society, 88, 2104 (1966).]

The Effect of Pressure on the Rate of Solvolysis of Benzyl Chloride in Aqueous Ethanol

J. B. Hyne, H. S. Golinkin, and W. G. Laidlaw

Contribution from the Department of Chemistry, University of Alberta, Calgary, Alberta, Canada. *Received November 18, 1965*

Abstract: The high-pressure apparatus and associated conductometric technique for following rates of solvolysis of alkyl halides in ethanol–water mixtures as a function of pressure are described. Results of the redetermination of ΔV_0^* for *t*-butyl chloride in 80% aqueous ethanol are presented to establish the precision and accuracy of the method. The dependence of ΔV_0^* on the composition of the ethanol–water medium for solvolysis of benzyl chloride is reported. ΔV_0^* for this system passes through an extremum at approximately 0.3 mole fraction of ethanol.

The influence of solvent on the kinetics of reactions in solution has been the subject of intensive study for the past 4 decades. Over this period the progressive refinement of the arguments and rationalizations of observed effects has left little doubt that the major impediment to a detailed understanding of the phenomenon is the lack of a definitive description of the liquid state of the solvent system. As a result of these limitations the explanations offered for solvent effects on rate processes have been largely of the empirical type. Relationships between rate and expressions involving bulk dielectric constant[1-6] have been most commonly employed together with linear free energy relationships of the *mY* type as proposed by Winstein, *et al.*[7] The principal objection to the use of these parameters has been that they reflect the bulk properties of the solvent medium, but neglect any specific type of substrate–solvent interaction that may be of more than passing significance in determining solvent effects on the rate process. Recently, spectroscopically determined solvent parameters of the type proposed by Kosower[8] (*Z* values) appear to take better account of such specific interactions, but even in these cases the rate relationships with such parameters are essentially empirical in form.

Notwithstanding the apparent lack of understanding of the specific nature of the substrate–solvent interaction in single component solvent systems, there has recently been a considerable revival of interest in the effect of varying the composition of binary solvent media on the various kinetically measurable rate parameters, ΔH^*, ΔS^*, and ΔC_p^*.[9-13] These pseudo-thermodynamic parameters exhibit an extremum behavior as a function of solvent composition that is not manifest in the directly measurable log k or ΔF^*. Compensatory effects of ΔH^* and ΔS^* ($\Delta F^* = \Delta H^* - T\Delta S^*$) are generally accepted as the reason for this phenomenon.

The observed extremum behavior of these kinetic parameters in binary solvent systems has been ascribed to a specific interaction between the reacting substrate and the binary solvent environment. Until recently, however, there was no experimental evidence to indicate whether the initial or transition state, or both, of the reacting substrate is primarily influenced by these specific solvent effects since the various Δ parameters measure the *difference* between the initial and transition states. This difference could vary as a result of changes in either the initial or transition state or changes in both. Recently, however, Arnett and co-workers[14,15] have measured "instantaneous" heats of solution of reacting

---

(1) S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(2) G. Scatchard, *J. Chem. Phys.*, 7, 657 (1939).

(3) H. Bohme and W. Schurhoff, *Chem. Ber.*, **84**, 28 (1951).

(4) E. Tommila and A. Hella, *Ann. Acad. Sci. Fennicae, Ser. AII*, **53**, 3 (1954).

(5) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

(6) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(7) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, 73, 2700 (1951).

(8) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

(9) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956); **79**, 1597, 1602, 5937 (1957).

(10) J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **34**, 863 (1956).

(11) E. Tommila, *Suomen Kemistilehti*, **B25**, 37 (1952).

(12) E. Tommila and M. Murto, *Acta Chem. Scand.*, **17**, 1947, 1957, 1985 (1963).

(13) J. B. Hyne, *et al.*, *J. Am. Chem. Soc.*, (a) **85**, 3650 (1963); (b) **84**, 2914 (1962); (c) **82**, 5129 (1960).

(14) E. M. Arnett, P. M. Duggleby, and J. J. Burke, *ibid.*, **85**, 1350 (1963).

(15) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *ibid.*, **87**, 1541 (1965).

substrates in binary solvent mixtures, and thus have a measure of variation of the initial state end of the enthalpy difference. With this information available, Arnett, *et al.*, have shown that for a variety of reacting substrates in binary solvent mixtures the extremum behavior of ΔH^* can result from changes in substrate–solvent interaction at *either* the initial *or* transition state end of the differential, *or* both.

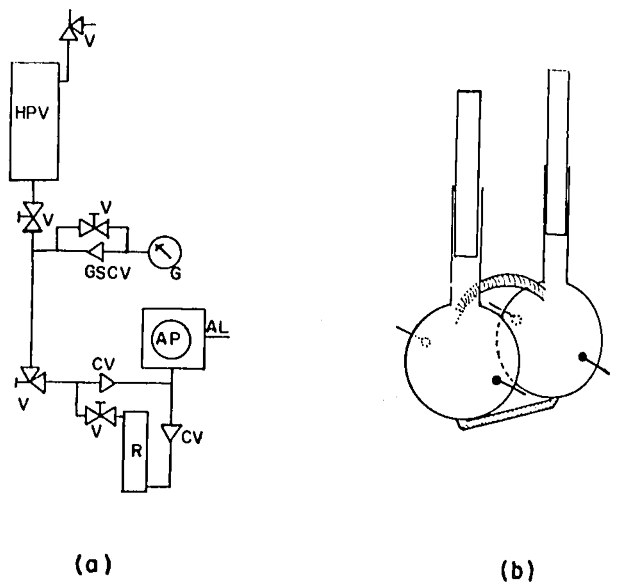
The apparent initial success of these attempts to interpret the behavior of ΔH^* with solvent composition variation in terms of specific solvent effects has led us to an examination of the solvent composition behavior of the one remaining, readily accessible, pseudo-thermodynamic parameter, ΔV^*, the volume change on activation. It is clear that if there is a significant change in substrate–solvent interaction through a series of solvents, either at the initial state or transition state end of the differential, such changes should be reflected in the volume change on activation. As in the case of ΔH^*, which results from the temperature dependence of log k, ΔV^* cannot be measured directly, but results from the pressure dependence of reaction rate. Since we are interested in the *variation* of this pressure dependence with the solvent composition, the required precision of measurement of the rate at various pressures is somewhat higher than has been previously common. In this paper we describe a precision conductometric method for measuring the rate of solvolysis of alkyl halides as a function of both binary solvent composition and pressure. The method is checked against the previously reported rate constants for *t*-butyl chloride in 80% ethanol–water, and the solvent composition dependence of ΔV_0^* for the solvolysis of benzyl chloride in ethanol–water mixtures is reported. In the benzyl chloride case, ΔV_0^* is found to exhibit an extremum as solvent composition is varied.

Experimental Section

High-Pressure Apparatus. A schematic diagram of the hydrostatic system is presented in Figure 1a. The high-pressure vessel is a modified version of the AEM series manufactured by Autoclave Engineers, Inc. (Erie, Pa.). It is equipped with four Covar leads which pass through the cover and are insulated from it by porcelain. A brass mounting fitted to the outside of the cover holds the BNC connectors which are connected to the leads. Pressurization of the reactor is accomplished by means of an air-driven pump manufactured by Autoclave Engineers, Inc. The pressurizing liquid is Blackhawk hydraulic fluid.

The pressure was measured by a 16-in. dial Bourdon tube gauge manufactured by Heise-Bourdon Tube Co. (Newark, N. J.) and calibrated in units of 3.402 atm. Automatic pressure control was accomplished by use of a micro switching mechanism inserted in the face plate of the gauge. An auxiliary pointer, equipped with a very light side arm, was preset to the desired pressure reading. When this pressure was reached in the system, the gauge needle lifted the side arm causing a break in the control circuit and closure of a solenoid valve in the air supply line. When the pressure fell, contact was remade and pressurization resumed. This method enabled the pressure to be controlled to better than ±15 atm over the entire range above atmospheric. It may be noted that a delicate balance of the watch spring system in the switching device was necessary to avoid distortion of the gauge reading.

Conductivity Apparatus. Twin high-pressure conductivity cells of the type shown in Figure 1b were used as reaction vessels, permitting two simultaneous kinetic determinations to be made. These were suspended in the pressurizing fluid of the hydrostatic vessel, and the platinum electrode terminals were connected to the Covar leads. Each compartment of the cell consisted of an 8-ml capacity bulb with two platinum bead electrodes sealed into the wall. The value of the cell constant was not required in the Guggenheim method of first-order rate analysis[16] employed. Pressure was transmitted to the cell contents by a 0.25-in. Teflon piston operating in a precision bore glass tube attached to each cell compartment. The pressure difference across the glass wall was therefore zero. Care had to be exercised in filling the cells so that no air bubbles remained in the cell compartments, and working solutions were degassed before use. Leakage past the Teflon piston was not a problem; the only operational problem arising in the system was the fracturing of the platinum to glass seals after several pressurizations, particularly at pressures above 1364 atm. This behavior, although inconvenient, was tolerated, and the cells simply were replaced at frequent intervals. The ac conductivity bridge was of conventional design, but specially constructed from high-precision components by Mr. T. Clement of this department. A sensitivity of 1 ohm in 80,000 was attainable.



(a) (b)

Figure 1. High-pressure apparatus. (a) Schematic diagram of the hydrostatic system: AL, air line; AP, air pump; CV, check valve; G, gauge; GSCV, gauge surge check valve; HPV, high pressure vessel; R, reservoir; V, valve. (b) High-pressure conductivity cell.

Temperature Control. Because of the temperature sensitivity of both conductance and rate, accurate control of this parameter is of crucial importance in obtaining precision conductometric rate constants. While for rate studies at atmospheric pressure such control can be conveniently accomplished by direct immersion of the conductance cell in a precision thermostat, the presence of the pressure vessel between the thermostating fluid and the reaction cell necessitated a careful check of temperature control in this work. In addition, heating effects due to pressurization further complicate the matter of temperature control.

A 50-gal oil thermostat capable of ±0.005° control at 50° in an air-conditioned room at 22° ambient temperature was used throughout this work. The complete pressure vessel assembly was immersed in the thermostat and could be raised by a chain hoist sufficiently to expose the removable head for cell loading. The vessel itself was never removed from the thermostating fluid. In order to determine the time interval required for thermal equilibration after loading and pressurizing, the following procedures were used.

A special cell containing water at 0° and equipped with a thermocouple was used as a "dummy" in the pressure vessel, and normal loading techniques followed. After 30 min no temperature difference between the cell contents and thermostat fluid at 50° could be detected. As an additional check of the thermal equilibration interval, a conductivity cell of the type used in the rate studies, but containing an aqueous solution of 5×10^{-4} mole/l. of KCl at 0°, was loaded into the pressure vessel in the normal manner. Resistance measurements were then taken at 1-min intervals. It was found that after 30 min the resistance changed by only 2 to 3 ohms between readings, indicating that the cell temperature was very close to equilibrium.

---

(16) E. A. Guggenheim, *Phil. Mag.*, (7) 2, 538 (1926).

Table I. Rate Constants fo
(v/v) Aqueous Ethanol at 30

Pressure, atm	Th
1	1.9
681	3.1
1362	4.9
2042	6.
ΔV_0^*,[a] ml/mole	−22.

[a] Throughout this series o
the volume of activation ex
ΔV^* will refer to an activati

Materials. Singly distille
deionizing resin. It was th
which atmospheric carbon
polyethylene containers.

Standard hydrochloric a
Hulett and Bonner.[17]

Table II. Rate Constants a

Pressure, atm	
1	
341	2
681	
1362	
2723	
4084	
ΔV_0^*, ml/mole	
$10^3(\partial\Delta V^*/\partial p)_T$, ml/atm mole	

[a] Mole fraction of ethano

The ethanol used was Re
was dried over magnesium
Bjerrum.[18]

Eastman White Label *t*-b
purification.

Eastman White Label b
quantities at 1×10^{-3} mm,

Kinetics. The mixtures o
weight to ±0.0002 mole frac
10^{-4} mole/l. of alkyl halide i
weight. These were filtered
standard taper joint enabli
vial was then closed with a
degassed by twice freezing,
and thawing. They were
water bath.

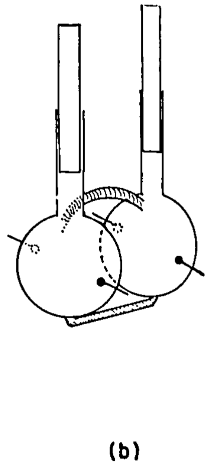
New conductivity cells w
trated nitric acid and distill
cell was aged with a soluti
desired solvent for a minim
perature to be used. The c
vessel, emptied, and rinsed t
with doubly distilled water (

The vacuum in the vial c
leased, after thorough agitat
extracted through the rubbe
cell was rinsed twice with t
The Teflon piston was ins
This method prevented the
was then placed in the high-
the thermostat and connec
vessel was brought up to t
was allowed for thermal e

---

(17) G. A. Hulett and W.
(1909).

(18) A. I. Vogel, "A Textb
ed, Longmans, Green and Co



apparatus. (a) Schematic diagram of the
air line; AP, air pump; CV, check valve;
surge check valve; HPV, high pressure
alve. (b) High-pressure conductivity cell.

tents by a 0.25-in. Teflon piston operating
tube attached to each cell compartment.
cross the glass wall was therefore zero.
in filling the cells so that no air bubbles
npartments, and working solutions were
akage past the Teflon piston was not a
tional problem arising in the system was
num to glass seals after several pressuriza-
ssures above 1364 atm. This behavior,
vas tolerated, and the cells simply were
vals. The ac conductivity bridge was of
specially constructed from high-precision
lement of this department. A sensitivity
tainable.
Because of the temperature sensitivity of
e, accurate control of this parameter is of
aining precision conductometric rate con-
tudies at atmospheric pressure such con-
accomplished by direct immersion of the
cision thermostat, the presence of the pres-
thermostating fluid and the reaction cell
eck of temperature control in this work.
ts due to pressurization further complicate
e control.
t capable of ±0.005° control at 50° in an
22° ambient temperature was used through-
mplete pressure vessel assembly was im-
and could be raised by a chain hoist suf-
removable head for cell loading. The
emoved from the thermostating fluid. In
me interval required for thermal equilibra-
ressurizing, the following procedures were

ing water at 0° and equipped with a ther-
"dummy" in the pressure vessel, and normal
wed. After 30 min no temperature dif-
ll contents and thermostat fluid at 50°
an additional check of the thermal equili-
luctivity cell of the type used in the rate
an aqueous solution of 5 × 10⁻⁴ mole/l.
ed into the pressure vessel in the normal
easurements were then taken at 1-min
that after 30 min the resistance changed by
n readings, indicating that the cell tempera-
uilibrium.

---

n, *Phil. Mag.*, (7) 2, 538 (1926).

Table I. Rate Constants for the Solvolysis of *t*-BuCl in 80% (v/v) Aqueous Ethanol at 30.00°

Pressure, atm	10^5k, sec^{-1} This work	10^5k, sec^{-1} Ref 19
1	1.90 ± 0.03	1.7 ± 0.5
681	3.14 ± 0.07	2.7 ± 0.7
1362	4.92 ± 0.05	4 ± 1
2042	6.7 ± 0.3	5 ± 2
ΔV_0^*,[a] ml/mole	−22.2 ± 0.9	−21 ± 4

[a] Throughout this series of papers, ΔV_0^* will be used to refer to the volume of activation evaluated at atmospheric pressure, while ΔV^* will refer to an activation volume of unspecified pressure.

Materials. Singly distilled water was passed through Illco-Way deionizing resin. It was then distilled in a Pyrex apparatus from which atmospheric carbon dioxide was excluded, and stored in polyethylene containers.

Standard hydrochloric acid was prepared by the method of Hulett and Bonner.[17]

The ethanol used was Reliance Chemicals absolute ethanol. It was dried over magnesium turnings by the method of Lund and Bjerrum.[18]

Eastman White Label *t*-butyl chloride was used without further purification.

Eastman White Label benzyl chloride was distilled in small quantities at 1 × 10⁻³ mm, as needed.

Kinetics. The mixtures of ethanol and water were prepared by weight to ±0.0002 mole fraction. Solutions of approximately 5 × 10⁻⁴ mole/l. of alkyl halide in the desired solvents were prepared by weight. These were filtered into a vial containing a stopcock and standard taper joint enabling the solutions to be degassed. The vial was then closed with a rubber septum, and the solutions were degassed by twice freezing, evacuating to a pressure of 10⁻³ mm, and thawing. They were then stored under vacuum in an ice–water bath.

New conductivity cells were initially cleaned with hot concentrated nitric acid and distilled water. Prior to a kinetic run each cell was aged with a solution of 5 × 10⁻⁴ mole/l. of HCl in the desired solvent for a minimum of 12 hr at the pressure and temperature to be used. The cell was then removed from the pressure vessel, emptied, and rinsed three times with acetone and three times with doubly distilled water (as above).

The vacuum in the vial containing the reaction mixture was released, after thorough agitation, and the desired amount of solution extracted through the rubber septum into a syringe. The reaction cell was rinsed twice with the solution and then filled to the top. The Teflon piston was inserted displacing some of the solution. This method prevented the entrapment of air bubbles. The cell was then placed in the high-pressure vessel which was lowered into the thermostat and connected to the pressurizing system. The vessel was brought up to the desired pressure, and sufficient time was allowed for thermal equilibrium to occur (30 min for those runs having half-lives of less than 2 hr and 60 min for the longer runs).

Twenty resistance measurements were taken at equally spaced intervals over approximately 1 half-life of the reaction. After 2 half-lives had elapsed a second set of 20 measurements was made at the same intervals.

Results

Rates. The conductance data was analyzed, according to the method of Guggenheim,[16] by eq 1 where Δt is an interval of about 2 half-lives of the reaction.

$$\ln\left(\frac{1}{R_{t+\Delta t}} - \frac{1}{R_t}\right) = -kt + \ln\left(\frac{1}{R_\infty} - \frac{1}{R_0}\right)(1 - e^{-k\Delta t}) \quad (1)$$

The method of least squares was used to solve eq 1 for k.

Table II. Rate Constants and Activation Parameters for the Solvolysis of Benzyl Chloride in Aqueous Ethanol at 50.25°

Pressure, atm	10^5k, sec^{-1} 0.000[a]	0.100[a]	0.200[a]	0.300[a]	0.400[a]
1	23.1 ± 0.4	6.690 ± 0.007	1.93 ± 0.01	0.80 ± 0.1	0.459 ± 0.007
341	24.42 ± 0.02	8.47 ± 0.01	2.46 ± 0.01	1.06 ± 0.01	
681	30.0 ± 0.2	10.25 ± 0.02	3.02 ± 0.07	1.29 ± 0.01	0.68 ± 0.03
1362	39.3 ± 0.3	13.68 ± 0.01	4.64 ± 0.01	2.04 ± 0.03	1.041 ± 0.002
2723		21 ± 2	7.7 ± 0.2	3.00 ± 0.02	1.81 ± 0.02
4084					2.6 ± 0.2
ΔV_0^*, ml/mole	−8 ± 1	−17 ± 1	−20.3 ± 0.2	−22.9 ± 0.2	−17.9 ± 0.9
$10^3(\partial\Delta V^*/\partial p)_T$, ml/atm mole	−3 ± 1	+4 ± 1	+4.9 ± 0.3	+7.2 ± 0.1	+3.2 ± 0.6

[a] Mole fraction of ethanol.

***t*-Butyl Chloride.** In order to check the apparatus and techniques, the rate of solvolysis of *t*-butyl chloride in 80% (v/v) aqueous ethanol at 30.00° as a function of pressure was studied. This system was studied previously by Buchanan and Hamann.[19] Our results for the first-order rate constant, together with those interpolated from the data of these authors, are given in Table I. The errors reported for our data are the average deviations of simultaneous, duplicate runs, whereas those for the interpolated data of Buchanan and Hamann are the 30% errors modestly claimed by Hamann.[20]

Benzyl Chloride. The first-order rate constants for the solvolysis of benzyl chloride in aqueous ethanol as a function of pressure are given in Table II. Most of these contants are the average of duplicate, simultaneous runs, while some are the average of three, nonsimultaneous determinations. The average deviations are also reported in Table II.

Activation Volumes. It was found that our data for the solvolysis of benzyl chloride are reliably described by eq 2 (see Appendix I).

$$\ln k = A + Bp + Cp^2 \quad (2)$$

Hence

$$\Delta V_0^* = -RTB \quad (3)$$

The parameters of eq 2 were calculated by the method of least squares, and those for benzyl chloride are pre-

---

(17) G. A. Hulett and W. D. Bonner, *J. Am. Chem. Soc.*, 31, 390 (1909).

(18) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., Ltd., London, 1961, p 167 ff.

(19) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, 49, 1425 (1953).

(20) S. D. Hamann, private communication.

sented in Table III, while the activation volumes at atmospheric pressure are given in Table II. It may be noted that the pressure dependence of the activation volume, as calculated by eq 2, is

$$\left(\frac{\partial \Delta V^*}{\partial p}\right)_T = -2RTC \qquad (4)$$

The values of this activation parameter are also given in Table II. All error limits shown for the activation parameters were calculated by the method described in Appendix I.

Table III. The Values of the Parameters of Eq 2

Mole fraction of ethanol	A	10^5B, atm^{-1}	10^8C, atm^{-2}
0.000	−8.39 ± 0.02	31 ± 4	+6 ± 2
0.100	−9.599 ± 0.002	65 ± 3	−9 ± 2
0.200	−10.864 ± 0.005	76.4 ± 0.9	−9.3 ± 0.4
0.300	−11.744 ± 0.007	86.1 ± 0.7	−13.6 ± 0.2
0.400	−12.30 ± 0.03	68 ± 3	−6 ± 1

Discussion

Solvolysis of *t*-Butyl Chloride. The main purpose of studying the pressure dependence of rate of solvolysis of *t*-butyl chloride in 80% (v/v) ethanol–water was to compare the results obtainable using the apparatus described with those previously published by Buchanan and Hamann.[19] This comparison is presented in Table I. Our results are well within the error range reported by these authors;[20] of greater significance is the fact that the higher precision of our rate determination permits the evaluation of an activation parameter with considerably smaller uncertainty. This increase in confidence is necessary for the meaningful study of ΔV_0^* variation with solvent composition, and essential if the pressure dependence of ΔV_0^* is a desired parameter.

Solvolysis of Benzyl Chloride. The values of ΔV_0^* for benzyl chloride solvolysis in ethanol–water mixtures shown in Table II are all negative. This observation is consistent with previous claims that the major contribution to changes in volume on activation for ionogenic reactions is in the structure of the immediate solvent environment rather than in the substrate itself.[19,21]

The dependence of ΔV_0^* on solvent composition is characterized by behavior of the type previously reported[13b] for the behavior of ΔH^* and ΔS^*. A comparative presentation of the behavior of these three activation parameters is demonstrated in Figure 2, the ΔH^* and ΔS^* values having been calculated from the data of ref 13b. In a recent report, Whalley and coworkers[22] comment on the apparent compensatory behavior between enthalpy and entropy or volume changes on activation. In their interpretation of the effect of pressure on the hydrolysis of methyl acetate and ethylene oxide in acetone–water mixtures, these authors state that for these systems "the existence of the minimum is therefore best considered as a trivial fact, not related to mechanism except insofar as changes in $T\alpha\Delta V^*/\kappa$ are related to mechanism."[22] Supporting evidence for this statement consists primarily of the observation that no extremum behavior is noted in the activation energy at constant volume, $\Delta U_v^* = \Delta H_p^* - T\alpha\Delta V^*/\kappa$. Whalley and co-workers further state that most of the change in the term $T\alpha\Delta V^*/\kappa$, which results in compensation of the extremum behavior of ΔH_p^*, is "due to changes in the thermal expansivity α of the solvent. . .[while] changes of the volume of activation contribute to a smaller extent, and changes of the compressibility [κ] are of little consequence."

The results plotted in Figure 2 clearly establish that the compensating extremum behavior characteristic of ΔH^* and ΔS^* is also a feature of ΔH^* and ΔV_0^*. Consequently at least some scepticism arises regarding the "trivial" nature of such extrema although the possible semantic nature of any disagreement on this point must not be overlooked.

One immediately obvious feature of the ΔV_0^* dependence on solvent composition is the higher ethanol concentration at which the extremum occurs compared with ΔH^* and ΔS^*. If the fundamental reason for the existence of these extrema is the same for all three activation parameters, it must be concluded that the factors leading to the extremum in ΔV_0^* have a different dependence on solvent composition from those responsible for the extremum in ΔH^* and ΔS^*. The existence of such a situation is not hard to envision since ΔV_0^* behavior is probably *more directly* related to solvent structure than either ΔH^* or ΔS^*. It is interesting to note at this point that the excess thermodynamic parameters of mixing of ethanol with water[23] show extremum behavior between 0.2 and 0.4 mole fraction of ethanol rather than at the lower ethanol concentration characteristic of ΔH^* and ΔS^*.

Turning to the question of the source of the extremum in ΔV_0^*, the ever present question of "which end of the differential is responsible" arises. Like ΔH^* and ΔS^*, ΔV_0^* is a difference between the partial molal volume of the kinetically effective initial state (including solute and associated solvent) and that of the transition state. As the solvent composition is varied, either or both of these volumes can be altered, leading to variation of ΔV_0^*. The recent, elegant work of Arnett and co-workers[14,15] has been directed toward answering this question as it relates to the behavior of ΔH^*. As yet, no similar breakdown of ΔV_0^* for the benzyl chloride system under study here is possible since the partial molal volume of benzyl chloride in the various solvent mixtures is not available. Such work is currently underway in these laboratories on various systems. In this regard, however, it is interesting to note the work of Bateman on the apparent molal volume of barium chloride in ethanol–water mixtures,[24] which shows the molal volume to have a maximum value at 0.3 mole fraction of ethanol. If the crude assumption is made that barium chloride, as an ionic species, bears some resemblance to the transition state of benzyl chloride solvolysis, then the suggestion may be advanced that

---

(21) (a) H. G. David and S. D. Hamann, *Trans. Faraday Soc.*, **50**, 1188 (1954); (b) A. H. Ewald and S. D. Hamann, *Australian J. Chem.*, **9**, 54 (1956); (c) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955); (d) S. D. Hamann and W. Strauss, *Discussions Faraday Soc.*, **22**, 70, (1956).

(22) B. T. Baliga, R. J. Withey, D. Poulton, and E. Whalley, *Trans. Faraday Soc.*, **61**, 517 (1965).

(23) A. G. Mitchell and W. F. K. Wynne-Jones, *Discussions Faraday Soc.*, **15**, 161, (1953).

(24) R. L. Bateman, *J. Am. Chem. Soc.*, **74**, 5516 (1952).

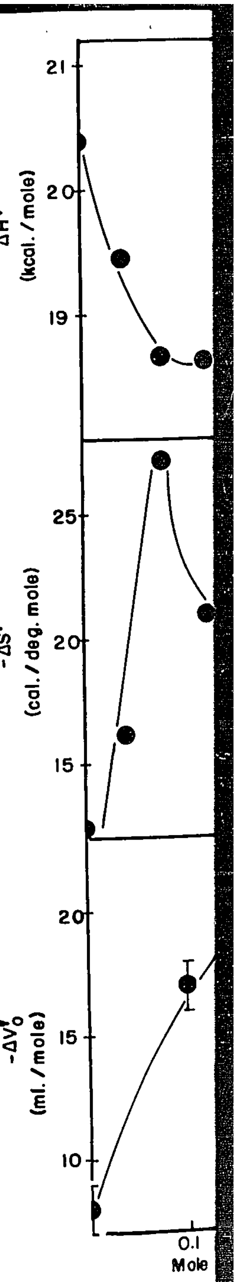


Figure 2. Solvent composit
eters for benzyl chloride solv

the extremum behavior
in transition state solva

Pressure Dependence
previous rate determina
usually has been inadeq
pressure dependence o
problems of determining
for $(\partial\Delta H^*/\partial T)_p$ or ΔC_p^*.
rate with respect to en
responsile for the nonli
type plots of log k va
function (eq 2) permits
and the error analysis
vides a measure of con

ater mixtures, these authors
ns "the existence of the mini-
nsidered as a trivial fact, not
xcept insofar as changes in
mechanism."[22] Supporting
ent consists primarily of the
mum behavior is noted in the
tant volume, $\Delta U_v^* = \Delta H_p^* -$
co-workers further state that
e term $T\alpha\Delta V^*/\kappa$, which results
xtremum behavior of ΔH_p^*, is
thermal expansivity α of the
s of the volume of activation
xtent, and changes of the com-
e consequence."
Figure 2 clearly establish that
num behavior characteristic of
ature of ΔH^* and ΔV_0^*. Con-
scepticism arises regarding the
extrema although the possible
isagreement on this point must

ious feature of the ΔV_0^* de-
nposition is the higher ethanol
he extremum occurs compared
the fundamental reason for the
na is the same for all three ac-
must be concluded that the
xtremum in ΔV_0^* have a dif-
olvent composition from those
emum in ΔH^* and ΔS^*. The
ion is not hard to envision since
bly *more directly* related to sol-
r ΔH^* or ΔS^*. It is interesting
hat the excess thermodynamic
f ethanol with water[23] show ex-
en 0.2 and 0.4 mole fraction of
he lower ethanol concentration
d ΔS^*.
ion of the source of the extre-
present question of "which end
onsible" arises. Like ΔH^* and
nce between the partial molal
y effective initial state (including
lvent) and that of the transition
composition is varied, either or
can be altered, leading to varia-
ent, elegant work of Arnett and
en directed toward answering
es to the behavior of ΔH^*. As
wn of ΔV_0^* for the benzyl chlo-
here is possible since the partial
l chloride in the various solvent
e. Such work is currently under-
ies on various systems. In this
interesting to note the work of
arent molal volume of barium
ter mixtures,[24] which shows the
maximum value at 0.3 mole frac-
e crude assumption is made that
n ionic species, bears some re-
nsition state of benzyl chloride
ggestion may be advanced that

. F. K. Wynne-Jones, *Discussions F raday*

. *Chem. Soc.*, **74**, 5516 (1952).

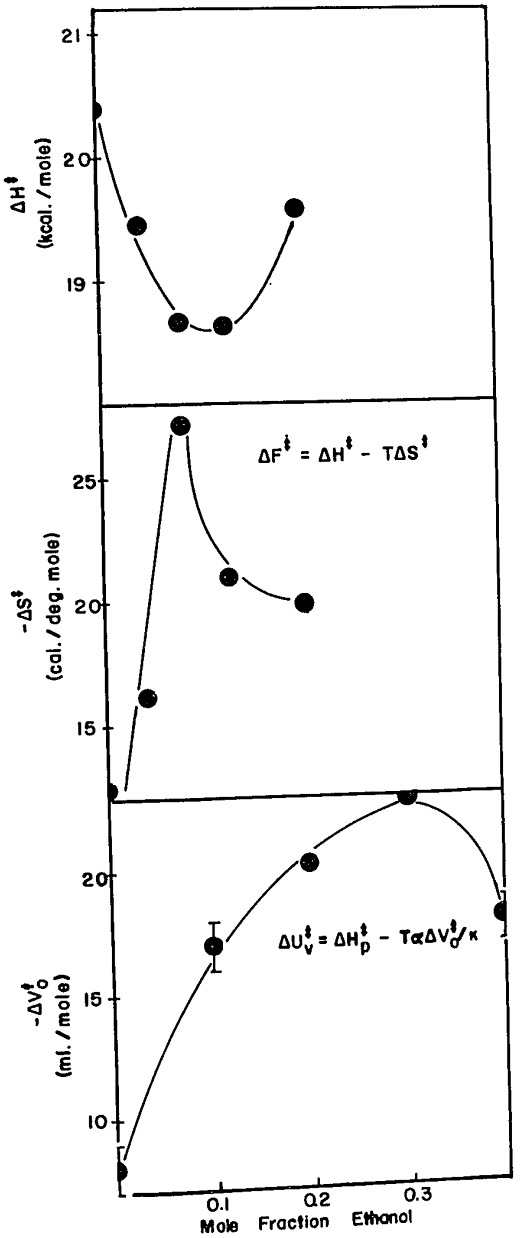


Figure 2. Solvent composition dependence of activation parameters for benzyl chloride solvolysis in ethanol-water mixtures.

the extremum behavior of ΔV_0^* may be due to changes in transition state solvation.

Pressure Dependence of ΔV^*. The precision of previous rate determinations as a function of pressure usually has been inadequate to permit evaluation of the pressure dependence of ΔV^*. In many respects the problems of determining $(\partial\Delta V^*/\partial p)_T$ are similar to those for $(\partial\Delta H^*/\partial T)_p$ or ΔC_p^*. Both are second derivatives of rate with respect to environmental variables, and are responsible for the nonlinearity of the simple van't Hoff type plots of log k variation. Use of the quadratic function (eq 2) permits direct evaluation of $(\partial\Delta V^*/\partial p)_T$, and the error analysis described in the Appendix provides a measure of confidence for the values obtained. The values of $(\partial\Delta V^*/\partial p)_T$ shown in Table II, together with the corresponding error limits, leave little doubt as to the reality of this additional activation parameter. As in the case of ΔC_p^* for benzyl chloride solvolysis in ethanol-water, calculated from ref 13b, $(\partial\Delta V^*/\partial p)_T$ appears to show extremum behavior. It would be premature at this stage to attempt to give a physical picture accounting for this term, but it appears that modern kinetic techniques are capable of extending the range of measurable activation parameters to include this additional term.

Acknowledgments. Financial assistance by the National Research Council of Canada to H. S. G. is gratefully acknowledged. The authors wish to thank the staff of the University of Alberta, Calgary, Computing Centre, for writing the FORTRAN programs used in this study.

Appendix I

The question of obtaining a volume of activation from a set of rate constants at various pressures is one which has not been answered unambiguously. It is known that the relation between the activation volume and the pressure dependence of the rate constant is given by eq 5.[25] The difficulty lies in determining the func-

$$\Delta V^* = -RT(\partial \ln k/\partial p)_T \qquad (5)$$

tional dependence of ln k upon p so that $(\partial \ln k/\partial p)_T$ can be evaluated. Since we are interested in the variation of ΔV^* for reactions in solution as the composition of the binary solvent medium is changed, we must be concerned with obtaining as reliable a set of activation volumes and precision measurements as our data permit. This position has led us to a study of various functional representations of the dependence of k upon p.

Walling and Peisach,[26] Benson and Berson,[27] Burris and Laidler,[28] and Whalley, *et al.*,[29] have all used different methods for extracting the value of this derivative. We have examined each of these in turn and have found that the quadratic function (eq 2) best represents our data. The quantitative comparison of these various methods will be published elsewhere.

Having established the functional dependence of the rate of benzyl chloride solvolysis on pressure, the next step is to establish the precision of the derivatives. This is readily accomplished by determining the maximum deviations of the constants in eq 2. These in turn are conveniently determined by differentiation.[30] The least-squares functional forms of these constants were differentiated, and the values of dA, dB, and dC were calculated using an IBM 1620 computer. The average deviation of the rate constants were used for the dk_i's, and the pressure fluctuation limits were used for the dp_j's.

---

(25) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).

(26) C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958).

(27) S. W. Benson and J. A. Berson, *ibid.*, **84**, 152 (1962).

(28) C. T. Burris and K. J. Laidler, *Trans. Faraday Soc.*, **51**, 1497 (1955).

(29) B. T. Baliga, R. J. Withey, D. Poulton, and E. Whalley, *ibid.* **61**, 517 (1965); E. Whalley, *Advan. Phys. Org. Chem.*, **2**, 100 (1964). Note that these references contain an error in the method of extracting the pressure dependence of ln k. The corrected version, as used here, is given in B. T. Baliga and E. Whalley, *Can. J. Chem.*, **43**, 2453 (1965).

(30) F. Daniels, *et al.*, "Experimental Physical Chemistry," 5th ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 326.

THE EFFECT OF ALKYL GROUP VARIATION ON THE RATES OF SOLVOLYSIS OF ALKYL SULPHONIUM HALIDES

J. B. HYNE AND H. S. GOLINKIN

Tertiary butyl and amyl dimethylsulphonium salts have been the standard examples of the sulphonium salt series used in neutral solvolytic rate studies of this type of compound in the past (1). Apart from these cases the apparent hygroscopic nature of the sulphonium salts has limited the study of their solvolytic behavior. In the course of our studies of sulphonium salt solvolysis we have prepared and characterized α-phenethyldimethylsulphonium and benzyldimethylsulphonium bromides. The solvolytic rate behavior of these two compounds together with comparative data on the *t*-butyldimethylsulphonium salt are reported here.

RESULTS

Approximately 10^{-3} *M* solutions of the various sulphonium salts in the desired solvent media were prepared by weight. Solvolytic kinetics were followed using the conductimetric technique described previously (2) and due to Robertson (3). While the iodide salt was used in the *t*-butyl case the bromides of both the α-phenethyl and benzyl sulphonium ions were employed. Since 0.325 mole fraction ethanol in water was the lowest polarity solvent used the anion does not enter the rate determining step as was shown previously (2, 4). Consequently the change from iodide to bromide does not invalidate the comparison of rates. In both the α-phenethyl and benzyl cases difficulty was encountered in obtaining reproducible results in pure water. In the benzyl case only those rates measured in higher ethanolic compositions were of satisfactory reproducibility. In Table I the rates for the

Canadian Journal of Chemistry. Volume 41 (1963)

TABLE I

Rates of solvolysis of sulphonium salts in EtOH–H$_2$O mixtures

Mole fraction EtOH	$k \times 10^5$ sec^{-1}				
	t-Bu$\overset{+}{S}$Me$_2$I$^-$		PhCHCH$_3$$\overset{+}{S}Me_2Br^-$		PhCH$_2$$\overset{+}{S}Me_2Br^-$
	50.3°	78.4°	50.3°	78.4°	78.4°
0.000	0.62_9	$36._1$		$23._5$	
0.125	0.66_4	$39._4$	0.45_4	$26._5$	
0.204	0.73_0	$44._2$	0.47_9	$27._2$	0.10
0.325	0.85_0	$49._8$	0.53_2	$29._6$	0.26

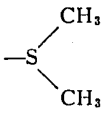
three sulphonium salts studied under various solvent and temperature conditions are recorded.

DISCUSSION

The availability of the rates of solvolysis for the three sulphonium salts in Table I enables a comparison to be made with the rate behavior of the corresponding alkyl chlorides. Using the date of Winstein and Fainberg (5) and Hyne, Wills, and Wonkka (6) the relative rates of solvolysis of the t-butyl, α-phenethyl, and benzyl chlorides and dimethylsulphonium salts may be compared. Conditions chosen for the comparison were 0.204 mole fraction ethanol (approx. 45% ethanol by volume in water) at 50° C for the chloride and 78.4° C for the sulphonium salts. These conditions were dictated largely by the availability of results. The temperature difference is unlikely to have a significant effect since the comparisons are internal within a given set at the same temperature. Use of a mixed solvent medium is perhaps not the best condition in view of the established selective solvation effects (6, 7). Since free energies of activation are being compared, however, the likelihood of gross errors being introduced by such effects is minimized. The rate comparisons are shown in Table II.

TABLE II

Relative rates of solvolysis of alkyl halides and sulphonium salts in 0.204 mole fraction EtOH–H$_2$O

Leaving group		Alkyl group		
		t-Bu	PhCHCH$_3$	PhCH$_2$
	$k_{78.4°}$ sec^{-1}	4.42×10^{-4}	2.72×10^{-4}	1×10^{-6}
	Relative log k (ΔF^*)	1	1.07	1.79
—Cl	$k_{50.0°}$ sec^{-1} [a]	1.32×10^{-2}	9.80×10^{-3}	1.89×10^{-5}
	Relative log k (ΔF^*)	1	1.07	2.51

[a] NOTE: Rates in this row interpolated from data of refs. 5 and 6.

Comparison of the free energies of activation (ratio of log k) for the two types of solvolysis shows immediately that structural changes in the alkyl group have the same effect on the solvolysis rates of both the halide and the sulphonium salts. Although the two reactions have opposite charge character on activation—one involving charge delocalization while the other requires charge creation—in both cases an incipient alkyl carbonium ion develops on activation.

The similar effects of str
of the incipient carboni
rate as a function of th
that we are dealing her
character. Clearly the st
case—brought about by
as the nature of the alk
the alkyl group variatio
be very much different

The data in Table I
considerably less for th
This should be compare
the two corresponding
sulphoniums is in the o
the charge character of
case probably reflects a
this is due to a lowerin
polarity of the transiti
character of the initial st
ties of the t-butyl and α

The data recorded in
of activation for the t-
insensitive to structural
kcal/mole for both salt
range of +15 to +18 e.u
in "desolvation" of the

Synthesis of Sulphonium

The following refers
t-butyl salt is readily sy
in nitromethane. The m
Dimethyl sulphide and
The reaction vessel was
covered with aluminum
temperature until the b
was deep red in color p
50 ml anhydrous ethe
decanted, but enough w
5 to 10 ml absolute etha
times necessary for sol
was then treated with n
on a sintered glass funn
filtrate was placed in a

mixtures

hCH$_2\overset{+}{S}$Me$_2$Br$^-$
78.4°
0.10 0.26

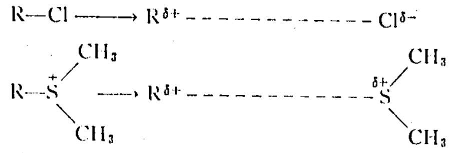
nperature conditions are

honium salts in Table I
the corresponding alkyl
e, Wills, and Wonkka (6)
benzyl chlorides and di-
for the comparison were
water) at 50° C for the
were dictated largely by
ely to have a significant
e same temperature. Use
view of the established
ion are being compared,
ch effects is minimized.

ium salts

PhCH$_2$
1×10^{-6}
1.79
1.89×10^{-5}
2.51

for the two types of sol-
yl group have the same
ium salts. Although the
—one involving charge
cases an incipient alkyl



$R{-}Cl \longrightarrow R^{\delta+} \text{- - - - - - - - - -} Cl^{\delta-}$

$R{-}\overset{+}{S}(CH_3)_2 \longrightarrow R^{\delta+} \text{- - - - - - - - - -} \overset{\delta+}{S}(CH_3)_2$

The similar effects of structural change in the alkyl group must imply that the stabilization of the incipient carbonium ion in the transition state is the dominant factor affecting the rate as a function of the alkyl group. This is particularly interesting in view of the fact that we are dealing here with two reactions having leaving groups of entirely different character. Clearly the stabilization of the transition state—or lack of it in the sulphonium case—brought about by solvation of the leaving group does not appear to vary significantly as the nature of the alkyl group is varied. If it did one would imagine that the effect of the alkyl group variation in the case where leaving group solvation was important would be very much different from that in the case where leaving group solvation was minimal.

The data in Table I also shows that the rate dependence on solvent composition is considerably less for the α-phenethylsulphonium salt than for the *t*-butyl compound. This should be compared with the very similar rate dependence on solvent exhibited by the two corresponding alkyl chlorides (5). While the solvent dependence for all three sulphoniums is in the opposite sense from the alkyl halides, as would be expected from the charge character of the activation process, the smaller dependence in the α-phenethyl case probably reflects a smaller change in polarity of the solute on activation. Whether this is due to a lowering of the polarity of the ionic initial state thus approaching the polarity of the transition state or to a more polar transition state closer to the ionic character of the initial state can only be resolved by studies of the relative physical properties of the *t*-butyl and α-phenethyl initial states.

The data recorded in Table I permits the calculation of both enthalpies and entropies of activation for the *t*-butyl and α-phenethyl cases. These parameters are remarkedly insensitive to structural changes. Values of activation energy vary between 32.4 and 33.0 kcal/mole for both salts over the range of solvents used. The entropy values lie in the range of +15 to +18 e.u. in keeping with the charge delocalization on activation resulting in "desolvation" of the transition state compared with the ionic initial state.

Synthesis of Sulphonium Halides

The following refers particularly to the α-phenethyl and benzyl sulphonium salts; the *t*-butyl salt is readily synthesized and isolated from *t*-butyl iodide and dimethyl sulphide in nitromethane. The method is a modified form of that reported by Siegel and Graefe (8). Dimethyl sulphide and the corresponding alkyl halide were mixed in a 1:1 mole ratio. The reaction vessel was stoppered with an aluminum foil covered rubber stopper, and was covered with aluminum foil to omit light. The mixture was allowed to stand at room temperature until the bottom of the flask was covered with crystals. The remaining liquid was deep red in color possibly due to bromine formation. The mixture was washed with 50 ml anhydrous ether to remove any unreacted starting materials. The ether was decanted, but enough was left so that the crystals were not exposed to the atmosphere; 5 to 10 ml absolute ethanol was added to dissolve the crystals. Gentle heating was sometimes necessary for solution to occur. Warm tap water generally sufficed. The solution was then treated with norite A to decolorize it, after which it was filtered over a celite bed on a sintered glass funnel to remove the norite and any undissolved residue. The clear filtrate was placed in a 50-ml standard taper flask, equipped with a vacuum adapter, which was previously evacuated and weighed. The flask was then filled with dry ether to precipitate the salt and placed in the refrigerator overnight. The liquor was decanted using an aspirator, but enough was left behind to keep the crystals covered. The remaining liquid was removed under vacuum. The white salt was then dried over phosphorous pentoxide under vacuum. α-Phenethyldimethylsulphonium bromide—reaction time 96 hours; yield 10.1%; m.p. 91.7–92.8° C (lit. m.p. 76–80° C ref. (8)); analysis % C calc. 48.58%, obs. 48.50%; % H calc. 6.12%, obs. 6.09%; % S calc. 12.97%, obs. 12.94%; % Br calc. 32.33%, obs. 32.24%. Benzyldimethylsulphonium bromide—reaction time 120 hours; yield 22.7%; m.p. 100.5–101.5° C; analysis % C calc. 46.36%, obs. 46.69%; % H calc. 5.62%, obs. 5.73%; % S calc. 13.76%, obs. 13.92%; % Br calc. 34.27%, obs. 34.08%.

Copies of infrared potassium bromide pellet spectra of the above salts are available on request.

ACKNOWLEDGMENTS

The authors acknowledge the assistance of Mr. R. E. Wonkka in making certain of the rate measurements and the National Research Council of Canada for financial support.

1. K. A. Cooper, E. D. Hughes, C. K. Ingold, and B. J. MacNulty. J. Chem. Soc. 2038–42 (1948).
2. J. B. Hyne. Can. J. Chem. **39**, 1207 (1961).
3. R. E. Robertson. Can. J. Chem. **33**, 1536 (1955).
4. J. B. Hyne and J. W. Abrell. Can. J. Chem. **39**, 1657 (1961).
5. S. Winstein and A. H. Fainberg. J. Am. Chem. Soc. **79**, 1597, 5937 (1957).
6. J. B. Hyne, R. Wills, and R. E. Wonkka. J. Am. Chem. Soc. **84**, 2194 (1962).
7. E. McC. Arnett, P. McC. Duggleby, and J. J. Burke. J. Am. Chem. Soc. **85**, 1350 (1963).
8. S. Siegel and A. F. Graefe. J. Am. Chem. Soc. **75**, 4519 (1953).

RECEIVED JULY 31, 1963.
DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, CALGARY,
CALGARY, ALBERTA.