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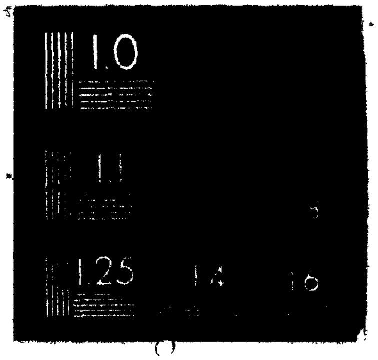

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STUDIES ON THE DECOMPOSITION OF SULFONIUM SALTS IN SOLUTION

BY

Md. Nurul Islam, B.Sc.(Hons), M.Sc.(Moncton)

A Thesis

Submitted to the Faculty of Graduate Studies

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ABSTRACT

The mechanism of the decomposition of benzyldimethylsulfonium salts has been studied in chloroform solvent. The reaction goes to completion; dimethyl sulfide and a benzyl compound, containing the anion of the salt, are the only products.

Conductivity measurements on diethylmethylsulfonium salts alone and on equimolar mixtures with n-tetrabutylammonium salts were carried out which allowed the calculation of the concentrations of the different ionic species present in chloroform solution. The addition of the ammonium salt dramatically increases the concentration of the triple ion of the type XSX^-, while drastically reducing that of SXS^+. The concentrations of the different ionic species were used in conjunction with the kinetic results, and product identities, to deduce the mechanism of the reaction.

The kinetic studies show that the reaction rate is proportional to the conductivity rather than molar concentration of the salt, and is controlled by the nucleophilicity of the anion. This is shown by the fact that benzyldimethylsulfonium perchlorate does not decompose alone, but does so in the presence of n-tetrabutylammonium bromide, producing dimethyl sulfide and benzyl bromide.

The addition of a small amount of ammonium salt causes a sharp decrease in the rate constant which then becomes gradual and linear

with subsequent additions of the ammonium salt. This negative salt effect is very insensitive to the identity of the ammonium salt anion.

The rate constant changes produced by variation of the concentration and anion of the salt, by the addition of other nucleophiles, and the secondary deuterium isotope effects, all suggest a mechanism which involves only the triple ion, consisting of two sulfonium cations and one anion, and no other ionic species.

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I. INTRODUCTION

INTRODUCTION

A. Nucleophilic substitution reactions, with especial reference to the sulfonium salt

(a) Terminology of nucleophilic reaction:

Of the various classes of organic reactions in solution, nucleophilic substitution reactions on carbon have probably been studied most intensively. In general, a nucleophile (i.e., an electron pair donating reagent), using a pair of its electrons, forms a new bond to the carbon atom under attack, while the leaving group departs with the pair of electrons from the bond that has been broken. A widely used classification of these reactions, largely through the pioneering investigations of Ingold, Hughes, and co-workers[1] is based on the molecularity of the reaction. The following schemes represent the two extremes of the nucleophilic reaction.

Scheme A $\quad Y + RX \longrightarrow Y\text{---}R\text{---}X \longrightarrow YR + X$

Scheme B $\quad RX \overset{\text{slow}}{\rightleftarrows} R^+ + X^- \xrightarrow[\text{fast}]{Y^-} RY$

In Scheme A (where no charges or partial charges are shown due to their variable nature) the synchronous bond making (between Y and R) and bond breaking (between R and X) are assumed, and inversion of configuration occurs in the product. The reaction is one step and passes through a transition state (or, activated complex) which contains both Y and RX and consequently second order kinetics are exhibited:

$$v = \frac{-d(RX)}{dt} = k(RX)(Y) \qquad (1)$$

Scheme A is generally abbreviated as the S_N2 (Substitution-Nucleophilic-Bimolecular).

Scheme B represents the two step S_N1 (Substitution-Nucleophilic-Unimolecular) mechanism, where the transition state does not contain any Y, but involves the formation of a metastable carbonium ion in the rate controlling step, which is rapidly converted to racemic products or reverts to reactants. Since the rate is independent of the nucleophile, and proportional only to the concentration of RX, first order kinetics are observed:

$$v = \frac{-d(RX)}{dt} = k(RX) \qquad (2)$$

(b) Modern theories of nucleophilic reactions: Sneen's theory:

However, in the case of solvolytic reactions, where the reaction media themselves are also the nucleophiles, the situation becomes more complicated[2] and Winstein[3] proposed an alternative nomenclature for these reactions where the transition state is being regarded as consisting of canonical structures I, II, and III (Scheme C).

Scheme C

$$\begin{array}{ccc} Y^{-}\ \ R{-}X & Y^{-}\ R^{+}\ X^{-} & Y - R\ \ X^{-} \\ \text{I} & \text{II} & \text{III} \end{array}$$

Only when all the three structures (I, II, and III) contribute significantly to the transition state, the mechanism is termed nucleophilic (N); otherwise, for the activated complex with insignificant role of structure III, the mechanism is said to be limiting (Lim.).

It was long felt that, although Ingold's theory was unique in explaining most of the reactions, it becomes less satisfactory in the mechanistic "border-line" region which appears to require two operative mechanisms, distinct S_N1 and S_N2 processes in competition[4-6]. The mechanisms developed by Winstein[7-9] and others[10-12] includes two intermediates: (1) an intimate ion pair ($R^{+}X^{-}$) formed by the intervention of the medium and (2) a solvent separated ion pair ($R^{+}||X^{-}$) as shown below (Scheme D):

Scheme D

$$\begin{tikzcd}
RX \arrow[r, shift left, "k_1"] \arrow[d] & R^{+}X^{-} \arrow[l, shift left, "k_2"] \arrow[r, shift left, "k_3"] \arrow[d] & R^{+}||X^{-} \arrow[l, shift left, "k_4"] \arrow[r, shift left, "k_5"] \arrow[d] & R^{+} + X^{-} \arrow[l, shift left, "k_6"] \arrow[d] \\
k_{1n}\ P & k_{2n}\ P & k_{3n}\ P & k_{4n}\ P
\end{tikzcd}$$

According to this scheme, the substrate as well as the other species (i.e., R^+X^-, $R^+||X^-$, and the free ions $R^+ + X^-$) derived from it may react with the nucleophile to form the product (P). The constants $k_{1n} \longrightarrow k_{4n}$ constitute the nucleophilic parts while the rate constants $k_1 \longrightarrow k_6$ form the ionic components of the overall reaction. The most distinctive feature of this mechanism (Scheme D) is the de-emphasis of the concerted processes, and recently Sneen and coworkers[13-16] have postulated that in nucleophilic media, the solvolysis goes exclusively by nucleophilic attack on an intimate ion-pair intermediate and thereby excludes the possibility of any reaction with the initial state of the reactant. In such media, for primary and secondary centres having good leaving group "a truncated" version of Scheme D can explain all the experimental facts, as shown in Scheme E[16]:

<u>Scheme E</u> $$RX \underset{k_2}{\overset{k_1}{\rightleftarrows}} R^+X^- \xrightarrow{k_{2n}} P$$

In Scheme E, the absence of k_{1n} shows that the Heitler-London mechanism[17-19] of the classical S_N2 reaction is kinetically insignificant[19].

(c) A survey of the reactions of sulfonium salts:

Sulfonium salts (R_3SX) have been found to decompose into thioether and alkyl halide, when X represents a halide ion. Since the formal charge is dispersed in the transition state in such a system, the reaction rate was found to be higher in a medium of lower dielectric constant[20-22]. Dimethyl-t-butylsulfonium chloride has been thoroughly studied and is believed to be S_N1 in a medium of high dielectric constant[22-25]. Similar results were obtained by others[26-28] for the decomposition of triethylsulfonium bromide and first order kinetics was observed in a variety of solvents. Gleave[29] and coworkers found trimethylsulfonium chloride, -bromide, and -carbonate in ethanol to give constant and identical first order rate constants, whereas, the second order rate constants varied by more than a factor of two in the course of a run. In addition, since the added carbonate ion (as tetraethylammonium carbonate) did not alter the reaction rate of triethylsulfonium carbonate, the conclusion was of a unimolecular reaction with

$$(CH_3)_3S^+ \longrightarrow CH_3^+ + (CH_3)_2S$$

as the rate determining step.

Later, Hughes and coworkers[30] investigated the decomposition of trimethylsulfonium chloride, -bromide, and -iodide in ethanol and found that the rate of decomposition followed the order $I^- > Br^- > Cl^-$ and concluded that the anion was involved in the rate-controlling step. Swain and Kaiser[31] considered the participation of ion-pairs in the rate-controlling step but have rejected the idea since in the reaction medium (D=25), good agreement was observed between the measured equivalent conductances and those calculated by the Onsager-Debye equation for strong electrolytes. While trimethylsulfonium perchlorate did not decompose in 90% acetone (D=25), the same reaction in the presence of added lithium chloride showed the consumption of chloride ion with good second-order kinetics, indicating that the anion was involved in the transition state. Pocker and Parker[32] not only found the decomposition of trimethylsulfonium salt in methanol and in ethanol to be S_N2, they showed that the Swain-Scott nucleophilicity of the anion was linearly related to the rate constants. Hyne's[33] studies of t-butyldimethylsulfonium iodide, -bromide, and -chloride in water, and in various water-ethanol mixtures indicate that the dependence of the rate on the anion character and on the concentration of the salt begins to develop as the dielectric constant of the medium is lowered. Unlike the explanation offered by Swain and Kaiser[31], he interpreted the results in terms of the increasing importance of an ion-pair mechanism as the dielectric constant of the medium is lowered[33,34]. Although, the kinetic effect of added common anion in the solvolysis in aqueous ethanol is analysed in terms of an ion pair mechanism, Hyne and Abrell[34] observed that the simple ion pair role fails to account for the kinetic behaviour with higher concentrations of the added common anion. An explanation consisting of a normal salt effect and further involvement of the ion pair in S_N2 attack by common anion has been cited as a possibility for the observed kinetic effects. Khim and Oae[35-36] studied the mechanism of the alkaline decomposition of triaryl sulfonium bromide with various bases. On the basis of the ratio of the products formed, they considered the reaction to proceed via three mechanistic routes, depending on the nature of the attacking agent; (1) a nucleophilic attack on the sulfur atom, (2) a nucleophilic attack on the aromatic carbon, and (3) a benzyne type mechanism. On the other hand, Lai and McEwen[37] isolated a mixture of aromatic hydrocarbons, alkyl aryl ether, diaryl sulfide, and aldol resin, together with a small amount of biaryl, from the reaction of triarylsulfonium halides with sodium alkoxide in corresponding alcohol. These authors proposed that the alkyl aryl ether is formed by a competing aromatic nucleophilic displacement, whereas, the other products are formed via a free radical mechanism.

More recently, the effect of dielectric constant of the medium on the rate of decomposition of trialkylsulfonium hydroxide[38] and the kinetics of the sulfonium ion decomposition in sodium hydroxide has been reinvestigated[39]. Thornton and his coworkers[40-42] studied the reaction of dimethyl-4-nitrobenzylsulfonium ion with sodium hydroxide, and obtained 4,4'-dinitrostilbene as the only product; and reported that the reaction was first order in both the hydroxide and the sulfonium ion. In their reinvestigation of this reaction, Closs and Goh[39] obtained 4,4'-dinitrostilbene oxide as a by-product besides trans-4,4'dinitrostilbene as the major product. Furthermore, they have found that the reaction was sensitive to the presence of oxygen, and overall third order kinetics (first order in hydroxide and second order in sulfonium ion) in nitrogen atmosphere, while an overall second order kinetics was observed in the presence of oxygen. In interpreting their experimental data, they preferred an S_N2, or a radical mechanism in such systems.

Darwish and Tourigny[43] reported that tert-butylethylmethylsulfonium bromide reacts more rapidly than the corresponding perchlorate in ethanol, acetic acid, and 50% acetic acid-acetic anhydride. A higher yield of olefin is obtained for the bromide than the corresponding perchlorate beside the substitution products from solvolysis of these salts. The addition of lithium chloride to the perchlorate salt yielded tert-butyl chloride as one of the products, indicating that the product of the solvolysis depends on the nature of the counter-ion. From the ratio of the products and other experimental data these authors have given an ion pair mechanism for the decomposition of these salts in such media.

The effects of isotopic substitution on the displaced group were first studied by Asperger and Saunders[44] for the decompositions of sulfonium ions, and observed that the sulfur isotope effect was larger for carbonium ion reactions than for bimolecular elimination where the carbon-sulfur bond is little stretched in the transition state. For the S_N2 reactions between hydroxide and benzyldimethylsulfonium ions the sulfur isotope effect is increased by electron supply to the reaction centre[45] suggesting that the amount of bond-breaking in the transition state is increased by electron donating substituents. However, Closs and Goh[39] have argued that the sulfur-isotope effect cannot provide unambiguous evidence for a particular mechanism of this reaction; because the observed isotope effect is an intermediate value between those which would be expected for S_N1 and S_N2 mechanisms. During the course of the writing of this thesis, Sneen and coworkers[46] have reported the decomposition of benzyldimethylsulfonium ion in water as competitive substitutions, by solvent water and added nucleophile; a unifying mechanism of nucleophilic substitution into sulfonium ions has been suggested by these authors to explain the borderline behaviour of these reactions.

B. Ionic compounds in non-aqueous solvents

(a) Incomplete dissociation of salts:

Walden's classical investigation on univalent electrolytes made it clear that so far as the behaviour of ionic compounds is concerned, the solvents fall into two distinct classes: (1) "differentiating" and (2) "levelling" solvents[47]. The latter class consists of the hydroxylic solvents in which the inorganic salts tend to be strong; even in ethanol, with a low dielectric constant, the pK's are surprisingly low, and similar to one another.

On the other hand, in the "differentiating" solvents the pK's are generally larger and cover a wide range of magnitude. Another characteristic feature of these solvents is that wherever a comparison amongst the alkali metal salts is possible, the lithium salt is the strongest and caesium salt the weakest in the "levelling" solvents unlike the case in the "differentiating" solvents. These differences between the two types of solvents have been assigned to differences in solvation energy. It is supposed that the cations are more strongly solvated in the hydroxylic solvents and that the donor properties of the hydroxylic solvents make them form solvates with the anions.

However, a somewhat different situation arises with salts of the larger cations, such as, quartenary ammonium ions[48]. In such cases, the main factor in determining the extent of ion association is the dielectric constant of the medium. This is in accordance with the assumption that these cations are too large to be strongly solvated. The order of strength of tetraethylammonium salts in non-hydroxylic solvents is: $Cl^{-}<Br^{-}$, $NO_3^{-}<I^{-}<ClO_4^{-}$ contrary to that in the hydroxylic solvents[49]. It would seem as if the strength of the solvation of the anion must be the deciding factor in such cases. The fact that the chloride and bromide are somewhat stronger in the nitro solvents than would be expected by comparison with acetonitrile indicates that minor solvation influences must be conceded even amongst the "differentiating" solvents.

Results of Kraus and coworkers[50-53] for ammonium salts indicate that these salts have much lower dissociation constants than the fully substituted ammonium salts, owing to hydrogen bonding between cation and anion or to solvolysis of the weakly acid and basic constituents (incomplete salt formation). Cations with central atoms other than nitrogen have also been studied. The pK value (in ethylene chloride, at 25°C) of methyl-tributyl-ammonium picrate is 3.921, of ethyl-triphenylphosphonium picrate

3.424, and of ethyl-triphenylarsonium picrate 3.465. The perchlorates and nitrates fall in the same fashion. Tetrabutylarsonium-, tributylsulfonium-, and diphenyliodonium picrate have pK value of 3.848, 4.348, and 5.633 respectively. The reason for this increasing weakness on passing from the tetrahedral cation through the planar sulfonium to the linear iodonium radical is supposed to be due to a closer approach of the picrate ion to the cation as the latter becomes more open.

(b) Concept of ion-pair:

The fact that the ionic compounds behave like weak electrolytes in non-aqueous medium of low polarity was first reported by Kraus[54]. The conductance of such a solution indicates that only a small fraction of the dissolved salt is dissociated into free ions. To account for these observations, Bjerrum[55] proposed that in non-aqueous solvents, the oppositely charged ions are associated into neutral ion-pairs which do not contribute to the electric conductance. He defined an ion-pair as two counter-ions at any separation whose electrostatic attraction is greater than their mean thermal energies. In solvents[56] of higher dielectric constant an ion-pair will be a more compact assembly compared to that in solvents of lower dielectric constant.

In 1954, Fouss[57,58] and Winstein[59] independently suggested that ion-pairs may exist in two distinct forms: the loose and the tight ion-pairs. The loose ion pairs may exist only in those solvents in which at least one of the ions is solvated; while a weak interaction of both the ions with the solvent gives rise to tight ion-pairs.

(c) Aggregation of ion-pairs:

Thorough studies of conductance of highly polar solutes in non-aqueous medium indicated that at higher salt concentrations simple ions will associate with ion-pairs to form triple ions[60]:

$$A^+, B^- + A^+ \rightleftarrows A^+, B^-, A^+ \qquad K_{+-+}$$

and $$A^+, B^- + B^- \rightleftarrows B^-, A^+, B^- \qquad K_{-+-}$$

The formation of triple ions increases the specific conductance, Λ, which is given by:

$$\Lambda = Ac^{-\frac{1}{2}} + Bc^{\frac{1}{2}} \qquad (3)$$

where c is the concentration of the salt. This dependence leads to a minimum in the Λ-c relation. In their original treatment of triple ion formation, Fuoss and Kraus[60] assumed that $K_{+-+} = K_{-+-}$. Although this generality holds very well in most cases, exceptions have also been cited by others[61,62].

The aggregation may proceed further with the formation quadrupoles, and these may associate into even larger aggregates[63,64] the binding energy being supplied mainly by the dipole-dipole interactions.

An extensive series of measurements on tetrabutylammonium salts in benzene is due to Fuoss and Kraus[60] as well as Hughes, Ingold, and their coworkers[56]. The latter group have shown that from below 10^{-5}M to 10^{-2}M, the salts are present mainly as ion-pairs; and at 10^{-5}M a few millionths of total salt concentration are dissociated into simple ions that carried most of the current. At 10^{-4}M, the simple ions add to ion-pairs producing ion triplets, to the extent of a few millionths of the total salt concentration, which now carry most of the current. At about 10^{-3}M, the triplets are being replaced by uncharged quadruplets. And finally around 10^{-2}M, charged aggregates higher than quadruplets are formed in greater amount, and simple kinetics in reactions of salts are not to be expected.

(d) Solvation of ion-pairs by external agents:

A suitable agent E added to solution of ion-pairs may form new species and equilibria such as

$$A^+, B^- + E \rightleftarrows A^+, B^-, E$$
$$A^+, B^-, E + E \rightleftarrows A^+, B^-, 2E \qquad \text{etc.,}$$

and

$$A^+ + E \rightleftarrows A^+, E$$
$$A^+, E + E \rightleftarrows A^+, 2E \qquad \text{etc.,}$$

may be established. The external agent, E may react with a tight ion-pair in two different ways: (1) it may form a tight A^+, B^- pair coordinated on its periphery with E, or (2) it may form a loose A^+, E, B^- pair in which E separates the ions. These ion-pairs, (1) and (2) may lead to an isomerization equilibrium,

$$A^+, B^-, E \rightleftarrows A^+, E, B^-,$$

and was first reported by Slates and Szwarc[65], while carrying out spectrophotometric studies of an equilibrium between an electron acceptor (biphenyl) and metallic sodium.

C. Effect of added salts in the reaction medium

(a) Ionic strength effect:

The rate of a reaction between two ionic components A and B, in which the activated complex A,B formed in the first step will be transformed into the final product, is governed by the Brønsted-Bjerrum theory[66-68] and is given by:

$$-dc/dt = kc_{A,B} \qquad (4)$$

$$f_A c_A \cdot f_B c_B / f_{A,B} c_{A,B} = K_{A,B} \qquad (5)$$

where the c's are concentrations, the f's the appropriate activity coefficients, k, rate constant, and K the dissociation constant of the activated complex. Combination of (4) and (5) gives,

$$-dc/dt = (k/K_{A,B}) c_A c_B (f_A f_B / f_{A,B}) \qquad (6)$$

$$= k_o \cdot c_A c_B \cdot F \qquad (7)$$

Calculation of the effect of the added salt on the activity coefficients should give a quantitative relation between rate and ionic strength. The activity coefficients can be calculated from the Debye-Hückel limiting equation. For aqueous solutions at room temperature, it reduces to[69],

$$\log F = z_A z_B I^{-\frac{1}{2}} \qquad (8)$$

where z's are the charges and I is the ionic strength of the medium.

The equation (8) was applied to interionic reactions as well as to reactions between ions and neutral molecules; and found satisfactory for only very dilute aqueous solutions.

It is now known that the electrolytes fall into two classes: (1) those in which the ratio $f_A f_B / f_{A,B}$ in equation (6) is independent of the nature of the salt, even though the individual activity coefficients vary widely. Many inorganic salts are of this type. These salts exert two-fold effects: one due to their interactions with the initial and transition states, and the other due to their ionic atmospheres. Since the interactions of these electrolytes with the initial and transition states cancel out in the Brønsted-Bjerrum rate equation, the only effect of the electrolyte is due to its ionic atmosphere, the magnitude of which agrees reasonably according to equation (8).

(2) But with the second type of electrolytes, their specific effects on the initial and transition states do not cancel out, and as a result the ionic atmosphere model does not apply to reactions carried out in the presence of this class of electrolytes which includes mineral acids, tetra-alkylammonium and carboxylate salts etc.

(b) Common ion retardation:

Although for many alkyl halides the specific rate of hydrolysis increases during the reaction, this is not common for S_N1 reactions. This increase is attributed to the increase in the ionic strength[70]. On the other hand the solvolysis of many halides shows a gradual decrease in the specific rate during the reaction: and added common halide ion retards the solvolysis[70,71]. This retardation can be explained by the fact that the intermediate carbonium ion is reconverted to reactant by the added halide ion:

$$R\text{-}X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R^+ + X^- \xrightarrow[k_2]{HOS} ROS + H^+$$

$$-\frac{d(RX)}{dt} = \frac{k_1 k_2 (RX)}{k_2 + k_{-1}(X^-)} = \frac{k_1 (RX)}{1+\alpha(X^-)} \qquad (9)$$

where α measures the relative reactivities of X^- and the solvent on the carbonium ion. When the carbonium ion is short-lived it is so reactive that it is largely captured by the species in excess, the solvent. Whereas, a more stable carbonium ion will be more selective towards a stronger nucleophile, and thus give a greater value for α and a greater retardation by the common ion.

The carbonium ion may be trapped by the addition of nucleophiles other than the solvent or the common anions, which thus lower the rate of solvolysis, but not of the overall reaction[72-74].

(c) Salt effects in solvents of low dielectric constant:

The simple electrostatic theory based on the concept of an ionic atmosphere suffers a complete break down when the salt effect is considered in non-polar solvents. Since ions are much less strongly solvated in such medium, they come together as ion-pairs, triple ions, or even as higher ionic aggregates, as already discussed. The retardation of the specific rate due to common ion addition will also be large, because the common ion will be weakly solvated and so more nucleophilic, in such solvents.

In aprotic solvents, salts can be very effective catalysts for S_N1 reactions. For example, the rate of decomposition of p-methoxyneophyltoluene-p-sulfonate in ether is increased about 10^5 times by the addition of M/10 lithium perchlorate. And the reaction in the presence of the salt is faster in ether than in acetic acid unlike the usual solvent effect for S_N1 reactions[75]. In non-polar ethyl ether medium the polar transition state will not be very stable, but the weakly solvated salt will react very strongly with the transition state. However, in such a medium, the reaction might be regarded as taking place on some ionic aggregation and not in the general body of the solution.

(d) Ion pairing and the reactivity of the nucleophilic anions:

Since the electrolytes affect the reaction rate due to their interactions with the initial and transition states, it is expected that the second order rate constants should decrease with increasing salt concentrations, when the anion of the salt itself is one of the reactants; and is associated in solution. This effect, which is actually observed, is explained assuming that the free anion is very much more reactive than the associated ion pair; and since the concentration of the former decreases with increasing concentration, the second order rate constant also decreases[76,77].

Generally, the ion pairing decreases with increasing size of the ions, and becomes less important for tetraalkylammonium salts, as mentioned earlier. The reactivities of the halide ions in acetone are found to be in the following sequence:

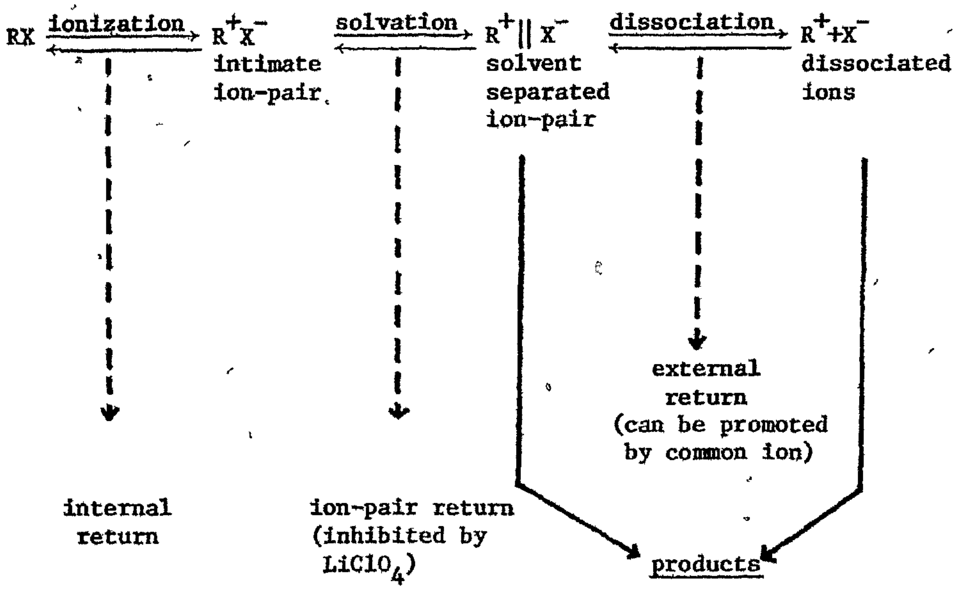
Cl > Br > I

Whereas, it is in the opposite order for reactions in hydroxylic solvents; and the reason is not only the solvation of anions by the hydroxylic solvents due to hydrogen bonding, but the small chloride ion will be much more effectively deactivated than the large iodide ion.

(e) "Special salt effect":

The studies of salt effects upon the rates of S_N1 reactions in solvents of low polarity have shown that salts can play an important role in converting the ion-pairs into free carbonium ions. Winstein and his coworkers[59,78] first reported this "special salt effect" in acetic acid when they observed that for some alkyl arenesulfonates there was a very sharp rate increase when small amounts ($<10^{-2}$M) of lithium perchlorate was added. Addition of larger amounts of the salt increases the rate in a way typical of a normal ionic strength effect. The explanation of this special salt effect is that the solvent separated ion-pair is a reaction intermediate that may collapse to reactant, or dissociate to give a free carbonium ion, and thence product. The special salt, e.g., lithium perchlorate is believed to intervene in this ion-pair scheme, converting the ion-pair $R^+\|X^-$ into another ion-pair $R^+\|ClO_4^-$. This change reduces the likelihood of the reversal to an intimate ion-pair, thus increasing the overall rate of solvolysis, as shown below:

Scheme F


RX
ionization
R+X−
intimate
ion-pair
solvation
R+|| X−
solvent
separated
ion-pair
dissociation
R++X−
dissociated
ions
internal
return
ion-pair return
(inhibited by
LiClO4)
external
return
(can be promoted
by common ion)
products

(f) Salt effects in non polar aprotic solvents

It is now an established fact that in such solvents reactions might have more than one intermediate. Swain and his coworkers[79,80], and Hughes, Ingold, and their coworkers[81,82] have carried out reactions in such non-polar aprotic medium as benzene, and came to the conclusion that ion-pairs are intermediates for nucleophilic substitution reactions in benzene. However, the latter group, places considerable importance on the great force range that would be exerted by the different components in benzene.

According to their postulation, when a substrate RX is ionized to an ion pair R^+X^- in a non-polar aprotic solvent containing a reactive salt M^+Y^- in moderate concentration, the carbonium ion will immediately react with the saline reagent which is already within its force range. The encounter probability being unity, an increase in reagent concentration cannot increase that, but if the reactants, after first contact, undergo an activated redisposition of the ions, before the latter can covalently react, then the rate may depend on the identity and not on the concentration of the reagent, because, the reagent is present in a kinetically significant second activation.

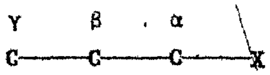
Hughes, Ingold, and their coworkers postulated that the consequence of the great force range in benzene is widespread electrostatic catalysis, of no fixed kinetic order. On a polar transition state polar ambient species will exert their kinetic effect in various numbers, from various contiguous and non-contiguous positions which need not be specifically prescribed. Such catalysis by ambient ion-pairs becomes important at about 10^{-2}M, and becomes more prominent with increasing concentrations.

D. The secondary kinetic isotope effect:

(a) Primary and secondary isotope effects:

The kinetic isotope effect, expressed as the ratio of the rate of the normal compound to that of the isotopically substituted analogue is termed 'primary' when the isotopically substituted bond(s) is(are) formed or broken in the rate-controlling step; otherwise, it is termed as the 'secondary' isotope effect. Primary isotope effects are generally large in magnitude and 'normal' in character, i.e., $k_H/k_D>1$, while the secondary effects can be extremely small and may be either 'normal' or 'inverse' i.e., $k_H/k_D<1$[83,84]. Since the isotope effects are largest when the ratio of the masses of heavy and light isotopes is maximized, deuterium isotope effects are studied to a greater extent than any other elements[85-87].

Secondary deuterium isotope effects can be classified as α, β, γ etc., effects depending on the position of the isotopic element relative to that of the leaving group X, as shown:



$\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-X$

Generally, the α-effect is considered as a probe of the S_N1-S_N2 axis and β-effect as a measure of the degree of the positive charge concentration at the reaction centre in the transition state.

(b) The Bigeleisen-Mayer formulation:

Bigeleisen and coworkers[88-90] have put forward a theory on the effect of isotopic substitution on the reaction rate. In this theory, the isotope effect is quantitatively related to the molecular vibrational frequencies of the initial and the transition states. From absolute rate theory, and statistical mechanics, they derived a relation, which written after Wolfsberg and Stern, gives[91]:

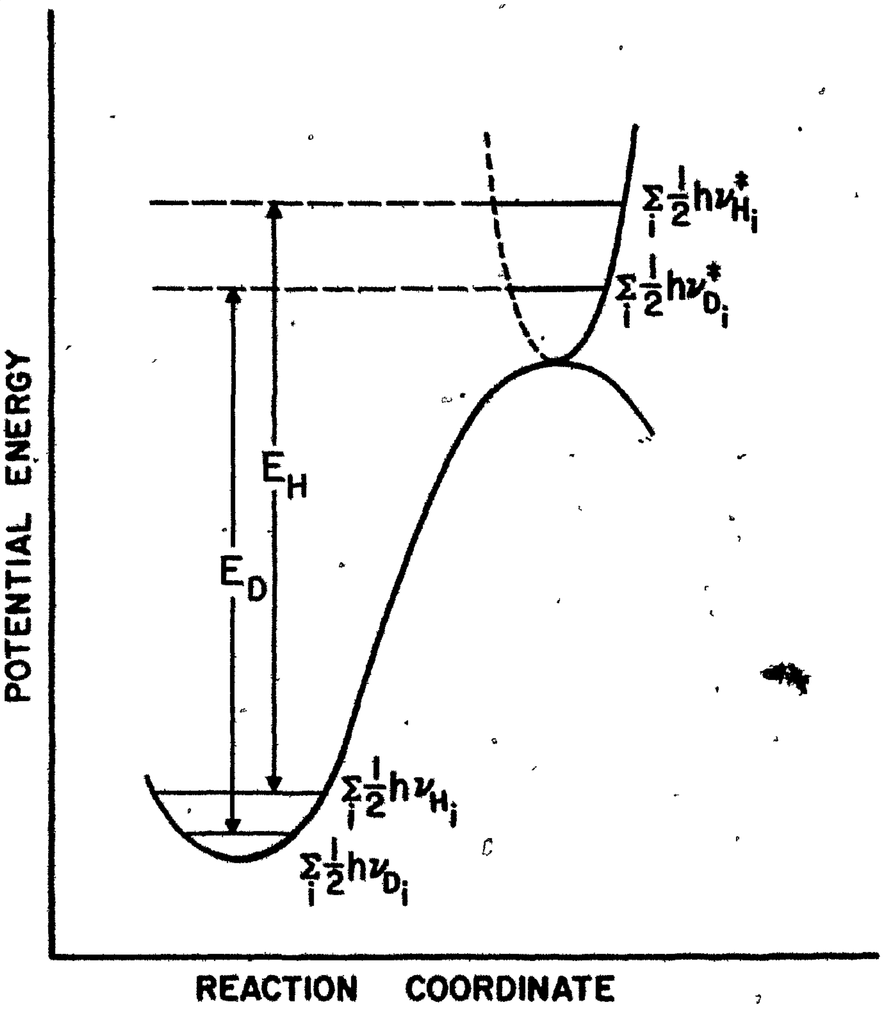
$$k_H/k_D = \left(\frac{\pi\ I_D}{\pi\ I_H}\right)^{1/2}\left(\frac{M_D}{M_H}\right)^{3/2} \Big/ \left(\frac{\pi\ I_D^{\ddagger}}{\pi\ I_H^{\ddagger}}\right)^{1/2}\left(\frac{M_D^{\ddagger}}{M_H^{\ddagger}}\right)^{3/2} \qquad (\equiv \mathrm{MMI})$$

$$\times \frac{\frac{3N-6}{\pi}\left(1-e^{-U_{Hi}}\right) \Big/ \frac{3N-6}{\pi}\left(1-e^{-U_{Di}}\right)}{\frac{3N^{\ddagger}-7}{\pi}\left(1-e^{-U_{Hi}^{\ddagger}}\right) \Big/ \frac{3N^{\ddagger}-7}{\pi}\left(1-e^{-U^{\ddagger}_{Di}}\right)} \qquad (\equiv \mathrm{EXC})$$

$$\times \frac{\exp.\left[\sum^{3N-6}\left\{1/2\ \left(U_{Hi} - U_{Di}\right)\right\}\right]}{\exp.\left[\sum^{3N^{\ddagger}-7}\left\{1/2\ \left(U^{\ddagger}_{Hi} - U^{\ddagger}_{Di}\right)\right\}\right]} \qquad (\equiv \mathrm{ZPE})$$

The simplest way to use this equation is to consider the ZPE factor, since each of the other two terms is approximately unity (assuming large molecules are involved, and all the isotopic vibrational frequencies are greater than 700 cm^{-1}). In the language of thermodynamics, this means that the isotope effect arises mainly from enthalpy of activation changes, $\Delta\Delta H^{\ddagger}(=\Delta H_D^{\ddagger} - \Delta H_H^{\ddagger})$, the entropy of activation changes, $\Delta\Delta S^{\ddagger}$ $(=\Delta S_D^{\ddagger} - \Delta S_H^{\ddagger})$, the latter being of less importance. So when the ZPE separation increases in the transition state compared to that in the initial state, $E_H > E_D$, an inverse effect, i.e. $(k_H/k_D) < 1$, is observed, as shown in the figure (1). A normal effect, $(k_H/k_D > 1)$ will be obtained when $E_H < E_D$.

Fig. I. THE ZERO-POINT ENERGY EFFECT

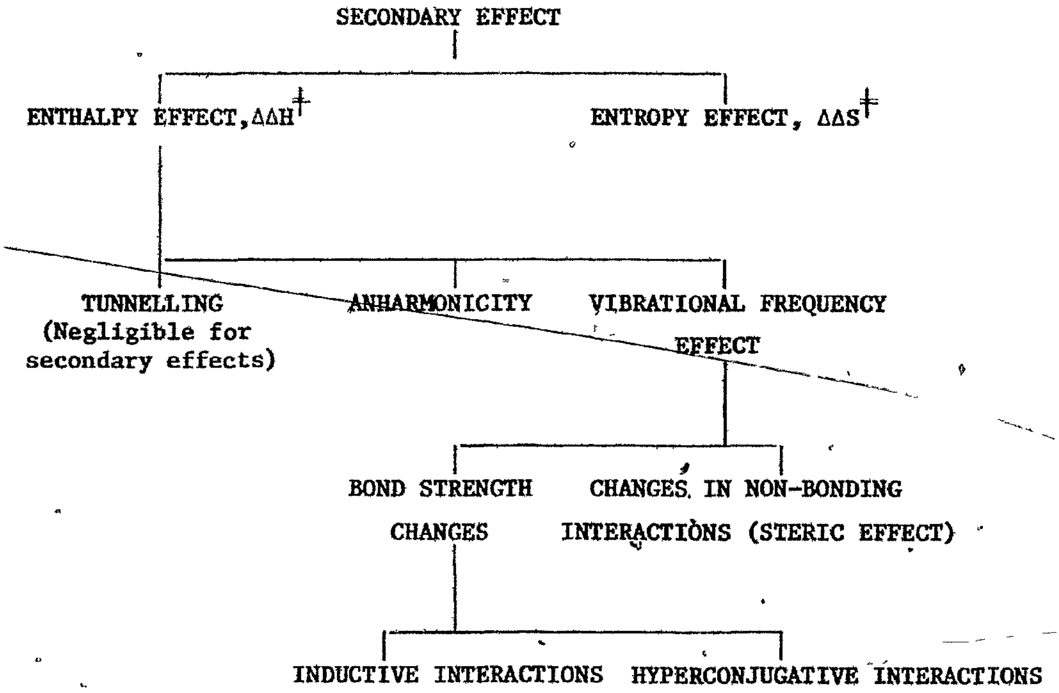


Shiner[92] has summarized the various sources of observed isotopic effects. From figure (2), due to him, it is apparent that the sources of isotope effects, usually cited, are, in fact $\Delta\Delta H^{\ddagger}$ effects; although, in certain cases $\Delta\Delta S^{\ddagger}$ effects may be important[93,94].

The secondary, kinetic, deuterium isotope effect together, with other experimental facts, can be very helpful in understanding the nature of the transition state, and thus provide support for the mechanism of the reaction.

FIGURE (2)

Sources of the Secondary Isotope Effects



E. The aims of the present studies:

From the survey of the chemical literature in the foregoing introduction, it is apparent that although the decomposition of the sulfonium salts has been a topic of active interest over the past seventy years, the mechanism and the order of the reaction could not be assigned with certainty; this is especially true when the reaction was performed in a medium of low polarity, where incomplete dissociation of the salt makes the situation more complicated. The purpose of the present work was to investigate the decomposition of the sulfonium salt by studying the nature of the different species present in the medium of low dielectric constant, such as chloroform. The nature and the concentration of the different species present, both in the presence and in the absence of added electrolytes should supply valuable information; and the knowledge obtained from the secondary, deuterium isotope effects, should be helpful in establishing the mechanism of the reaction. As far as the author is aware, the decomposition of the sulfonium salts has not previously been subjected to this type of investigation.

Another aim of this study was to make a comparison with the earlier project carried out in this laboratory on the decomposition of the ammonium salts in chloroform solution, and to gain support on the mechanism and the kinetics that have been proposed for such systems[95-98].

II ELECTROCHEMICAL RESULTS AND DISCUSSION

A. Introduction

Since the decomposition of the sulfonium salts was to be investigated, both alone and in the presence of added nucleophiles, the latter in the form of ammonium salts, we decided to study the electrochemistry of the pure salts, as well as of their equimolar mixtures, in chloroform solution.

It was hoped that such studies would supply information regarding what happens to this reaction, which depends on ions in polar solvents, when performed in a solvent of low polarity such as chloroform.

Although in the actual kinetic measurements benzyldimethylsulfonium salts were used, we have deliberately selected the diethylmethylsulfonium salts for electrochemical studies in the chloroform solvent, to avoid the difficulties arising from the decomposition of the benzyldimethylsulfonium salts, under the experimental conditions. This changeover will definitely produce some differences in the experimental results, but, nevertheless, will furnish information regarding the relative stability and concentration of the different species present in the actual reaction mixture.

The calculation of the concentration of different species requires a knowledge of the equilibrium constants for the ion-pair and for the triple ion dissociation. These constants are obtained when the limiting equiconductance for the particular salt is available, and it is in these calculations of the limiting equivalent conductance, that the greatest uncertainties remain.

B. Equivalent conductance at infinite dilution ($\Lambda°$)

(a) Single n-tetrabutylammonium salts

The equivalent conductance at infinite dilution for n-tetrabutylammonium bromide, -chloride, -iodide, and -perchlorate were evaluated by means of Walden's rule[59,100], which states that, for a given electrolyte, the product of its limiting equivalent conductance, and the viscosity of the solvent is approximately constant, and is independent of temperature, i.e.,

$$\Lambda°\eta° = \text{constant} \qquad \text{(11)}$$

where $\eta°$ is the viscosity of the solvent, in which $\Lambda°$ is the limiting equivalent conductance. The usual graphic method, such as the plotting of equivalent conductance against square root of concentration, was found to be unsatisfactory, as the equivalent conductance increased very sharply, with increasing dilution, making the extrapolation of $\Lambda°$, at zero-concentration, very difficult, and uncertain. Therefore, once the painstaking part of determining $\Lambda°$, of a compound in a particular solvent is obtained, Walden's rule becomes very convenient to determine the $\Lambda°$ of the same compound in a different solvent.

However, ions of small size, or of unsymmetrical shape, or charge distribution, show most serious departure from Walden's rule, especially when compared in solvents of widely differing polarizability and molecular volume. This break down of Walden's rule, is probably due to the solvation of the ions. Since the extent of solvation, as well as the size of the solvating molecules, varies with the nature of the solvent, the effective radius of the ion will not be constant, as required by Walden's rule. Walden's rule appears to be most closely obeyed by very large spherical ions of the type, NR_4^+, which are poorly solvated due to low charge density on their surfaces, and therefore the magnitude of their radii would be independent of the nature of the solvent.

The $\Lambda°$ values of n-tetrabutylammonium bromide, -chloride, -iodide and -perchlorate, have already been determined by Kraus[101,102], in acetone at 25°C. From these known values the corresponding value of $\Lambda°$ in chloroform at 25°C were computed, and are presented in Table 1.

Table 1. Limiting equivalent conductance of n-tetrabutylammonium salts in chloroform at 25°C.

Anion	Viscosity* $\eta°$(p)	Walden Constant $\eta° \times \Lambda°$	$\Lambda°$ $mho^{-1} cm^2 mole^{-1}$
Bromide	0.00524	0.578	110
Chloride	"	0.544	104
Iodide	"	0.567	108
Perchlorate	"	0.576	110

*Ref.103

(b) Single sulfonium salts

Unfortunately, for sulfonium salts, such as, diethylmethylsulfonium bromide, -chloride, -iodide, -perchlorate, and benzyldimethylsulfonium perchlorate, Walden's rule could not be applied due to the non-availability of Λ°-values for these salts in any solvent in the literature. The graphic methods, such as extrapolating the equivalent conductance to zero-concentration, were again found to be unsatisfactory, as was the case with the ammonium salts. Therefore the trial and error method formulated by Fuoss and Kraus[104], although time-consuming and laborious, was used to obtain the values of Λ° for the sulfonium salts. The derivation of the method in detail has been presented in Appendix A.

The values of Λ°, so obtained, have been tabulated below:

Table 2. Limiting equivalent conductance of the sulfonium salts in chloroform at 25°C.

Salt	Λ° $\text{mho}^{-1}\text{cm}^{2}\text{mole}^{-1}$
Diethylmethylsulfonium bromide	65
Diethylmethylsulfonium chloride	65
Diethylmethylsulfonium iodide	65
Diethylmethylsulfonium perchlorate	66
Benzyldimethylsulfonium perchlorate	65

C. Dissociation constants for single salts

The value of Λ°, having been determined for the simple 'onium salts, the limiting conductance of the triple ions was assumed to be one-third of that of simple ions[105]. Knowing the values of Λ° for the simple and triple ions, the equilibrium constant, K_2, for the ion-pair dissociation, and K_3 for the dissociation of triple ions into an ion-pair, and a simple ion, can be calculated from the curve of the logarithms of equivalent conductance, Λ, versus the logarithm of salt concentration; it has been assumed that K_3 is equal to the dissociation constant of both the triple ions,

$$[M^+X^-] \rightleftharpoons [M^+] + [X^-] \qquad K_2 = [M^+][X^-]/[M^+X^-]$$

$$[M^+X^-M^+] \rightleftharpoons [M^+X^-] + [M^+]$$

$$K_3 = \frac{[M^+X^-][M^+]}{[M^+X^-M^+]} = \frac{[X^-][M^+X^-]}{[X^-M^+X^-]}$$

$$[X^-M^+X^-] \rightleftharpoons [M^+X^-] + [X^-]$$

The plot of $\log_{10}\Lambda - \log_{10}c$ for the ammonium and sulfonium salts, passes through a minimum, C_{min}, around the concentration of 2x and 4×10^{-3}M respectively, Figs. 3 and 4. The experimental data are shown in Table 3A-3C and in Table 4A-4E for ammonium and sulfonium salts respectively. At these minima, simple and triple ions each carry one-half of the current. When the simple ions carry almost all the current, Ostwald's law for weak electrolytes should be obeyed. The broken line on the left-

Fig. 3 PLOT OF $LOG_{10}\Lambda - LOG_{10}c$ FOR n-TETRABUTYLAMMONIUM SALTS

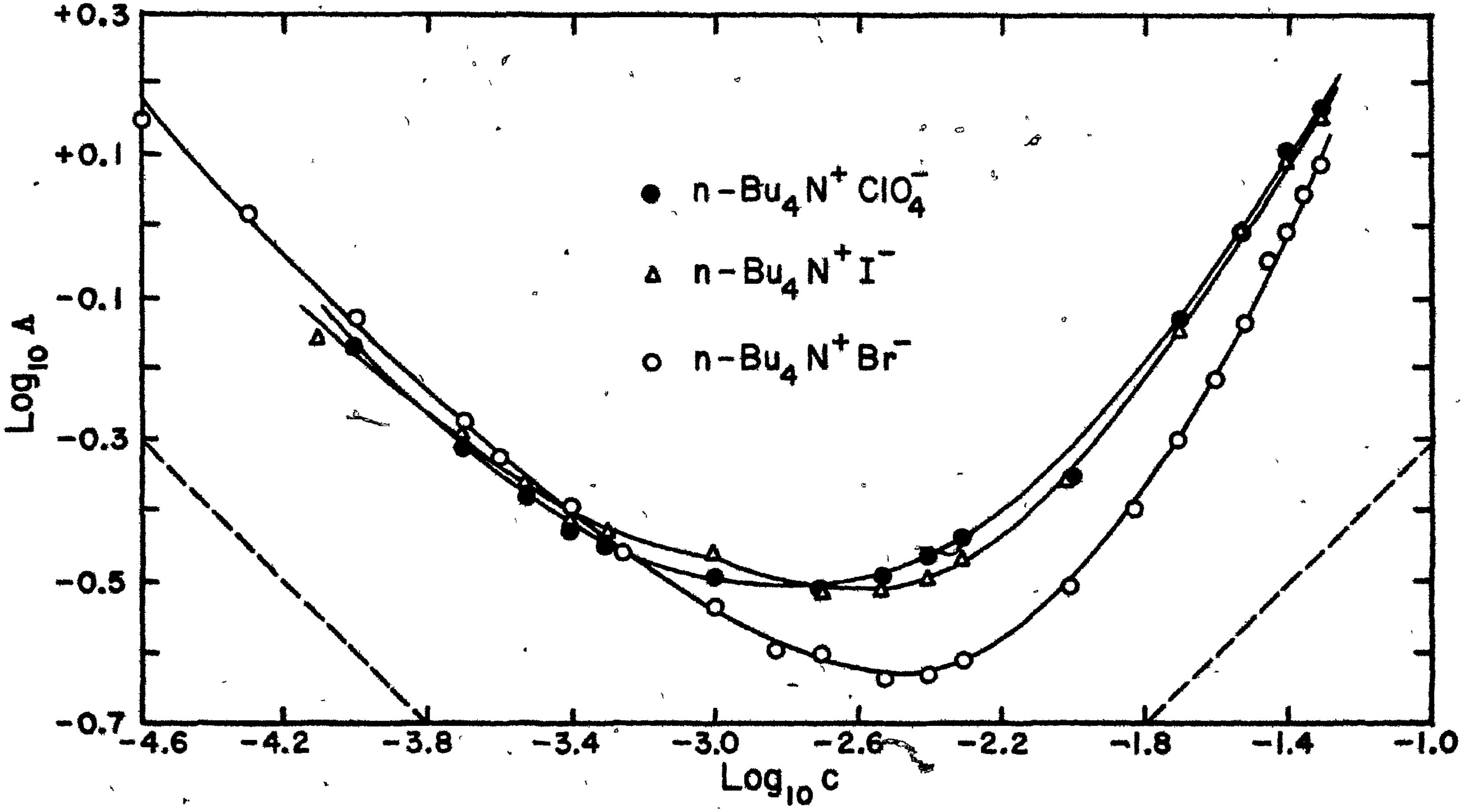


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Table 3A. Equivalent conductance of n-tetrabutylammonium bromide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}

Concentration (M/1)x10^3	$\log_{10}$ Conc.	Conductance (μ mho)	Equiv. Cond. (Λmho^{-1}cm^2)	$\log_{10}\Lambda$
50.0	-1.300	257.26	1.222	0.0871
45.0	-1.350	212.21	1.120	0.0492
40.0	-1.400	169.00	1.010	0.0043
35.0	-1.460	135.58	0.920	-0.0362
30.0	-1.520	92.98	0.736	-0.1331
25.0	-1.600	64.87	0.616	-0.2104
20.0	-1.700	42.58	0.506	-0.2958
15.0	-1.820	25.83	0.409	-0.3882
10.0	-2.000	13.40	0.318	-0.4975
5.0	-2.300	5.24	0.249	-0.6037
4.0	-2.400	4.00	0.237	-0.6251
3.0	-2.520	2.96	0.234	-0.6307
2.0	-2.700	2.09	0.249	-0.6037
1.5	-2.820	1.62	0.256	-0.5917
1.0	-3.000	1.24	0.294	-0.5316
0.5	-3.300	0.75	0.357	-0.4473
0.4	-3.400	0.68	0.404	-0.3935
0.25	-3.600	0.50	0.477	-0.3214
0.20	-3.700	0.45	0.532	-0.2740
0.10	-4.000	0.31_3	0.744	-0.1284
0.05	-4.300	0.22_1	1.050	0.0212
0.02_5	-4.600	0.14_8	1.403	0.1470

Table 3B. Equivalent conductance of n-tetrabutylammonium iodide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}

Concentration (M/1)x10^3	log_{10}Conc.	Conductance (μ mho)	Equiv. Cond. (Λmho^{-1}cm^2)	log_{10}Λ
50.0	-1.300	306.00	1.454	0.163
40.0	-1.400	210.00	1.247	0.096
30.0	-1.520	125.50	0.994	-0.003
20.0	-1.700	61.70	0.733	-0.135
10.0	-2.000	18.73	0.445	-0.352
5.0	-2.300	7.30	0.347	-0.460
4.0	-2.400	5.45	0.324	-0.490
3.0	-2.520	3.92	0.310	-0.508
2.0	-2.700	2.57	0.305	-0.515
1.0	-3.000	1.33	0.317	-0.460
0.5	-3.300	0.78_5	0.373	-0.429
0.4	-3.400	0.64_8	0.385	-0.415
0.3	-3.520	0.55_4	0.439	-0.357
0.2	-3.700	0.43	0.510	-0.292
0.1	-4.000	0.29_5	0.700	-0.155

Table 3C. Equivalent conductance of n-tetrabutylammonium perchlorate in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}.

Concentration (M/l)x10^3	log$_{10}$Conc.	Conductance (μ mho)	Equiv. Cond. (Λmho^{-1}cm^2)	log$_{10}\Lambda$
50.0	-1.300	312.00	1.482	0.171
40.0	-1.400	215.00	1.276	0.106
30.0	-1.520	128.40	1.016	0.007
20.0	-1.700	63.75	0.754	-0.121
10.0	-2.000	18.90	0.449	-0.348
5.0	-2.300	7.58_7	0.360	-0.444
4.0	-2.400	5.81_1	0.345	-0.462
3.0	-2.520	4.08	0.323	-0.491
2.0	-2.700	2.62	0.311	-0.507
1.0	-3.000	1.35_8	0.323	-0.491
0.5	-3.300	0.75_8	0.360	-0.444
0.4	-3.400	0.62_6	0.372	-0.430
0.3	-3.520	0.52_6	0.416	-0.381
0.2	-3.700	0.41_1	0.488	-0.312
0.1	-4.000	0.29	0.680	-0.167

Fig. 4 PLOT OF $\mathrm{LOG}_{10}\Lambda - \mathrm{LOG}_{10}c$ FOR DIMETHYLSULFONIUM SALTS

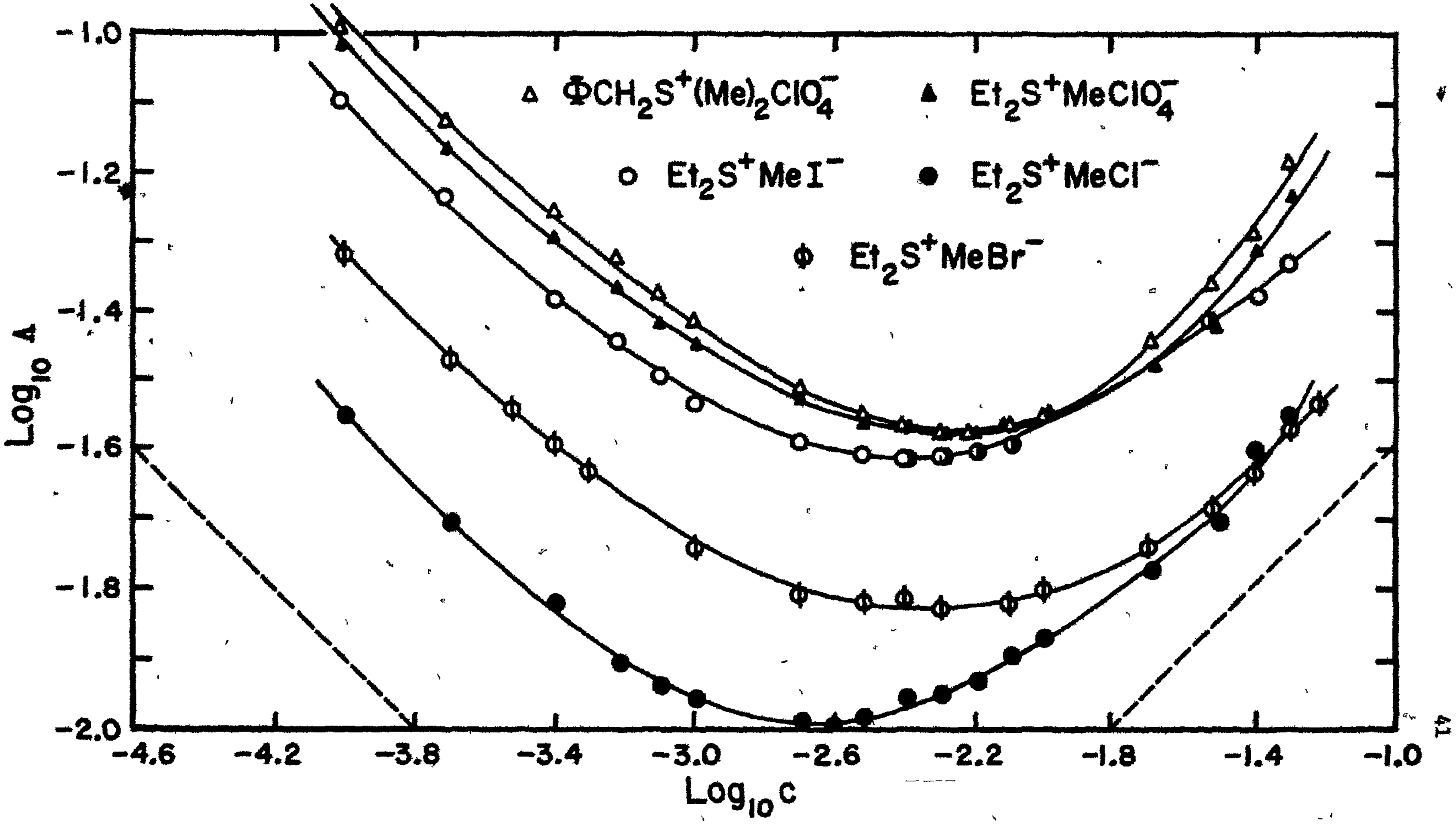

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Table 4A. Equivalent conductance of diethylmethylsulfonium bromide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}.

Concentration $(M/l)x10^3$	log_{10}Conc.	Conductance (μ mho)	Equiv. Cond. $(\Lambda mho^{-1}cm^2)$	$log_{10}\Lambda$
60.0	-1.222	7.200	0.0285	-1.5452
50.0	-1.300	5.718	0.0272	-1.5655
40.0	-1.400	3.887	0.0231	-1.6364
30.0	-1.520	2.564	0.0203	-1.6926
20.0	-1.700	1.536	0.0182	-1.7400
10.0	-2.000	0.668	0.0159	-1.7987
8.0	-2.100	0.512	0.0152	-1.8181
5.0	-2.300	0.310	0.0147	-1.8327
4.0	-2.400	0.255	0.0151	-1.8211
3.0	-2.520	0.189	0.0150	-1.8239
2.0	-2.700	0.132	0.0156	-1.8069
1.0	-3.000	0.080	0.0185	-1.7382
0.5	-3.300	0.049	0.0233	-1.6326
0.4	-3.400	0.043	0.0255	-1.5934
0.3	-3.520	0.037	0.0289	-1.5390
0.2	-3.700	0.027	0.0340	-1.4685
0.1	-4.000	0.020	0.0480	-1.3188

Table 4B. Equivalent conductance of diethylmethylsulfonium chloride in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}.

Concentration $(M/l)x10^3$	log_{10}Conc.	Conductance (μ mho)	Equiv. Cond. ($\Lambda mho^{-1}cm^2$)	$log_{10}\Lambda$
50.0	-1.300	5.910	0.0281	-1.551
40.0	-1.400	4.227	0.0251	-1.600
30.0	-1.520	2.400	0.0190	-1.699
20.0	-1.700	1.432	0.0170	-1.769
10.0	-2.000	0.568	0.0135	-1.869
8.0	-2.100	0.429	0.0127	-1.894
6.0	-2.220	0.296	0.0117	-1.930
5.0	-2.300	0.238	0.0113	-1.948
4.0	-2.400	0.189	0.0112	-1.949
3.0	-2.520	0.133	0.0105	-1.976
2.0	-2.700	0.084	0.0103	-1.986
1.0	-3.000	0.047	0.0112	-1.950
0.8	-3.100	0.038	0.0113	-1.946
0.6	-3.220	0.031	0.0122	-1.912
0.4	-3.400	0.025	0.0150	-1.824
0.2	-3.700	0.017	0.0199	-1.702
0.1	-4.000	0.012	0.0280	-1.553

Table 4C. Equivalent conductance of diethylmethylsulfonium iodide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}.

Concentration (M/1)x10^3	$\log_{10}$Conc.	Conductance (μ mho)	Equiv. Cond. ($\Lambda mho^{-1}cm^2$)	$\log_{10}\Lambda$
50.0	-1.300	9.650	0.0458	-1.338
40.0	-1.400	6.874	0.0408	-1.389
30.0	-1.520	4.721	0.0374	-1.447
20.0	-1.700	3.010	0.0357	-1.446
10.0	-2.000	1.300	0.0309	-1.510
8.0	-2.100	0.855	0.0254	-1.595
6.0	-2.220	0.619	0.0245	-1.610
5.0	-2.300	0.514	0.0244	-1.612
4.0	-2.400	0.406	0.0241	-1.618
3.0	-2.520	0.309	0.0243	-1.614
2.0	-2.700	0.216	0.0257	-1.590
1.0	-3.000	0.122	0.0290	-1.540
0.8	-3.100	0.109	0.0325	-1.488
0.6	-3.220	0.092	0.0363	-1.440
0.4	-3.400	0.070	0.0416	-1.381
0.2	-3.700	0.050	0.0589	-1.230
0.1	-4.000	0.034	0.0800	-1.090

Table 4D. Equivalent conductance of diethylmethylsulfonium perchlorate in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}.

Concentration (M/l)x10^3	$\log_{10}$Conc.	Conductance (μ mho)	Equiv. Cond. ($\Lambda mho^{-1} cm^2$)	$\log_{10}\Lambda$
50.0	-1.300	11.458	0.0544	-1.264
40.0	-1.400	7.854	0.0466	-1.330
30.0	-1.520	4.450	0.0352	-1.453
20.0	-1.700	2.675	0.0318	-1.498
10.0	-2.000	1.171	0.0278	-1.556
8.0	-2.100	0.876	0.0260	-1.585
6.0	-2.220	0.647	0.0256	-1.591
5.0	-2.300	0.539	0.0256	-1.591
4.0	-2.400	0.431	0.0256	-1.591
3.0	-2.520	0.333	0.0264	-1.578
2.0	-2.700	0.241	0.0286	-1.543
1.0	-3.000	0.147	0.0348	-1.458
0.8	-3.100	0.126	0.0375	-1.426
0.6	-3.220	0.106	0.0420	-1.377
0.4	-3.400	0.084	0.0500	-1.300
0.2	-3.700	0.057	0.0673	-1.172
0.1	-4.000	0.040	0.0950	-1.022

Table 4E. Equivalent conductance of benzyldimethylsulfonium perchlorate in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}.

Concentration (M/l)x10^3	log$_{10}$Conc.	Conductance (μ mho)	Equiv. Cond. (Λmho^{-1}cm^2)	log$_{10}$Λ
50.0	-1.300	13.221	0.0628	-1.202
40.0	-1.400	8.421	0.0500	-1.300
30.0	-1.520	5.547	0.0432	-1.365
20.0	-1.700	2.989	0.0355	-1.450
10.0	-2.000	1.170	0.0278	-1.556
8.0	-2.100	0.904	0.0268	-1.572
6.0	-2.220	0.664	0.0262	-1.582
5.0	-2.300	0.560	0.0266	-1.575
4.0	-2.400	0.453	0.0269	-1.570
3.0	-2.520	0.355	0.0281	-1.551
2.0	-2.700	0.256	0.0304	-1.517
1.0	-3.000	0.157	0.0373	-1.428
0.8	-3.100	0.136$_7$	0.0406	-1.375
0.6	-3.220	0.115$_5$	0.0457	-1.332
0.4	-3.400	0.093$_5$	0.0552	-1.258
0.2	-3.700	0.063	0.0750	-1.125
0.1	-4.000	0.043	0.1020	-0.991

bottom of $\log_{10}\Lambda$-$\log_{10}c$, has the Ostwald-law slope $-\frac{1}{2}$, when simple ions carry the current, while the one on the right-bottom with a slope of $\frac{1}{2}$ is obtained if triple ions carried all the current. These theoretical slopes are shown to compare with those obtained in the present study. Immediately on the high concentration side of the minimum, of these $\log_{10}\Lambda$-$\log_{10}c$ plots, the main carriers of the current are the triple ions. With still higher concentrations, quadrupoles, and other charged complexes are formed. The equation that takes account of all species up to quadrupoles, mentioned before, is given by[60] (shown in Appendix B)

$$\Lambda = Ac^{-\frac{1}{2}} + Bc^{\frac{1}{2}} \qquad (3)$$

where $A = \sqrt{K_2}\Lambda^\circ{}_1$, and $B = \sqrt{K_2}\Lambda^\circ{}_3/K_3$; $\Lambda^\circ{}_1$ and $\Lambda^\circ{}_3$ being the limiting conductances of the single and triple ions respectively.

Differentiating eqn (3), we see that the condition for a minimum in Λ as a function of concentration, c, is,

$$-\tfrac{1}{2}Ac^{-3/2} + \tfrac{1}{2}Bc^{-\frac{1}{2}} = 0 \qquad (12)$$

$$\text{or,}\quad Bc^{-\frac{1}{2}} = Ac^{-3/2}$$

$$\text{or,}\quad C_{min} = A/B \qquad (13)$$

With this value of C_{min} in eqn (3),

$$\Lambda_{min} = A(B/A)^{\frac{1}{2}} + B(A/B)^{\frac{1}{2}}$$

$$= (AB)^{\frac{1}{2}} + (AB)^{\frac{1}{2}}$$

$$= 2(AB)^{\frac{1}{2}} \qquad (14)$$

From eqns (13) and (14), the equilibrium constants K_2 and K_3 can be obtained in the following way:

<u>Calculation of K_3</u>

$$C_{min} = \frac{A}{B} = \frac{\sqrt{K_2}\Lambda^\circ_1}{\frac{\sqrt{K_2}\Lambda^\circ_3}{K_3}} = K_3\,\frac{\Lambda^\circ_1}{\Lambda^\circ_3}$$

$$K_3 = C_{min}\,\frac{\Lambda^\circ_3}{\Lambda^\circ_1} \qquad (15)$$

<u>Calculation of K_2</u>

$$\Lambda_{min} = 2\sqrt{AB}$$

$$= 2\sqrt{(K_2)^{\frac{1}{2}}\Lambda^\circ_1 \times \frac{(K_2)^{\frac{1}{2}}}{K_3}\,\Lambda^\circ_3}$$

$$= 2\sqrt{\frac{K_2\Lambda^\circ_1\Lambda^\circ_3}{K_3}}$$

$$(\Lambda_{min})^2 = 4\,\frac{K_2\Lambda^\circ_1\Lambda^\circ_3}{K_3}$$

$$\text{or,} \quad K_2 = \frac{(\Lambda_{min})^2 K_3}{4\Lambda^\circ_1 \Lambda^\circ_3}$$

$$= \frac{(\Lambda_{min})^2 \cdot C_{min} \Lambda^\circ_3}{4\Lambda^{\circ 2}_1 \cdot \Lambda^\circ_3} \qquad \left[\quad K_3 = C_{min} \frac{\Lambda^\circ_3}{\Lambda^\circ_1} \right]$$

$$K_2 = C_{min} \left(\frac{\Lambda_{min}}{2\Lambda^\circ_1} \right)^2 \qquad (16)$$

From eqn. (3), a plot of $\Lambda(c)^{\frac{1}{2}}$ against (c) will give initially a straight line, the intercept of which is 'A', while 'B' equals the slope. Such plots together with the Tables, are given on pp.50-60. The values of A, and B being known, K_2, and K_3 can be calculated from eqn. (16) and (15). The values of A, B, Λ_{min}, C_{min}, and K_2 and K_3 obtained for the single ammonium and sulfonium salts have been collated in Table 8 on p.61.

Fig. 5 PLOT OF $\Lambda\sqrt{c}$ AGAINST c FOR n-TETRABUTYLAMMONIUM SALTS

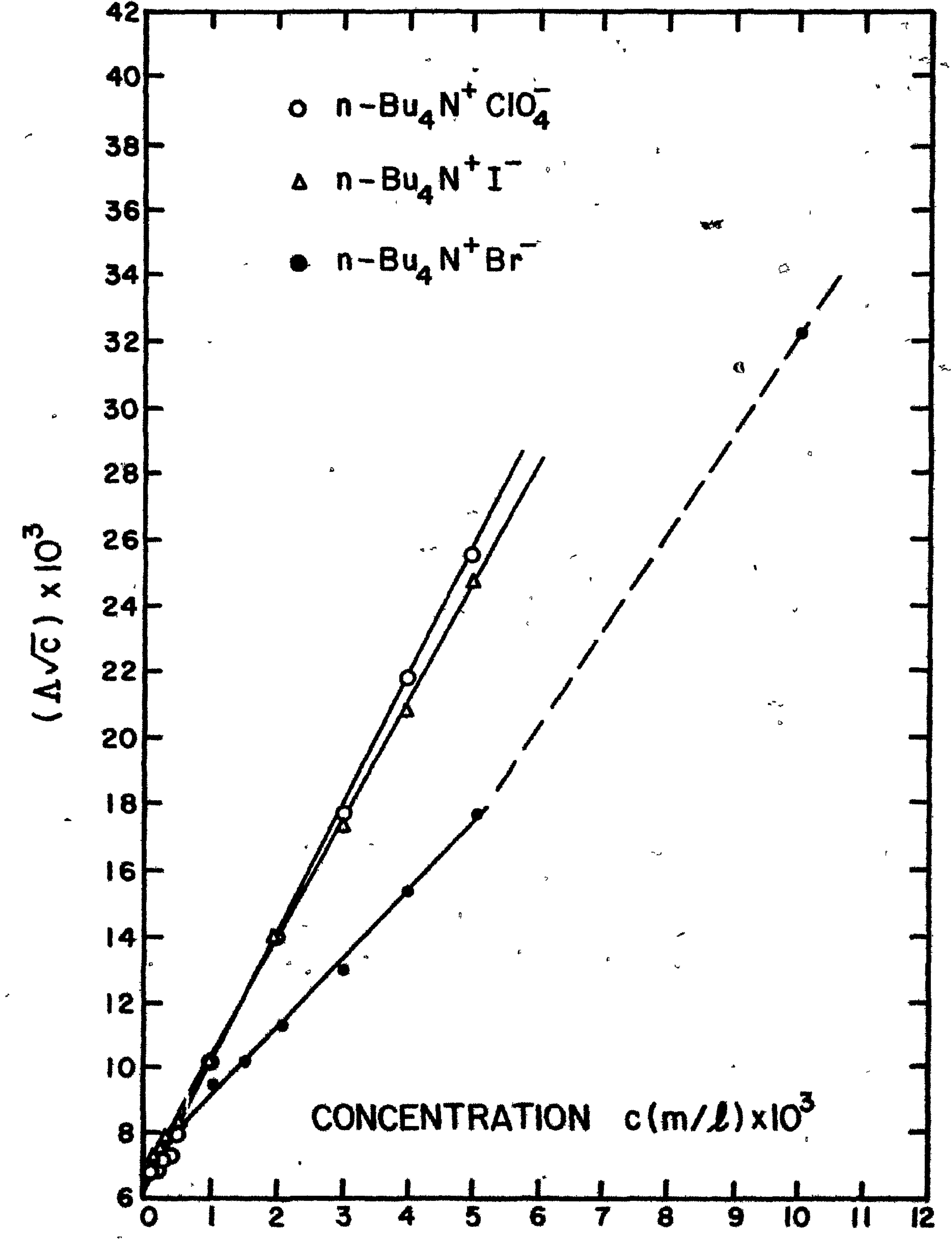

Table 5A. Values of $\Lambda(c)^{\frac{1}{2}}$ at different concentrations of n-tetrabutylammonium bromide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}.

Concentration $(c)\times10^3$	$(c)^{\frac{1}{2}}$	Equiv. Cond. $(\Lambda mho^{-1}cm^2)$	$\Lambda(c)^{\frac{1}{2}}$
10.00	0.1000	0.318	0.0320
5.00	0.0707	0.249	0.0176
4.00	0.0632	0.237	0.0150
3.00	0.0548	0.234	0.0128
2.00	0.0447	0.249	0.0111
1.50	0.0387	0.256	0.0099
1.00	0.0316	0.294	0.0093
0.50	0.0223	0.357	0.0080
0.40	0.0200	0.404	0.0080
0.25	0.0158	0.477	0.0075
0.20	0.0141	0.532	0.0075
0.10	0.0100	0.744	0.0074
0.05	0.0071	1.050	0.0074
0.02_5	0.0050	1.403	0.0070

Table 5B. Values of $\Lambda(c)^{\frac{1}{2}}$ at different concentrations of n-tetrabutylammonium iodide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}.

Concentration (c)x10^3	$(c)^{\frac{1}{2}}$	Equiv. Cond. (Λmho^{-1}cm^2)	$\Lambda(c)^{\frac{1}{2}}$
5.00	0.071	0.347	0.0245
4.00	0.063	0.324	0.0205
3.00	0.055	0.310	0.0170
2.00	0.045	0.305	0.0136
1.00	0.032	0.317	0.0100
0.50	0.022	0.373	0.0082
0.40	0.020	0.385	0.0077
0.30	0.017_3	0.439	0.0076
0.20	0.014_1	0.510	0.0072
0.10	0.010	0.700	0.0070

Table 5C. Values of $\Lambda(c)^{\frac{1}{2}}$ at different concentrations of n-tetrabutylammonium perchlorate in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}.

Concentration $(c)x10^3$	$(c)^{\frac{1}{2}}$	Equiv. Cond. $(\Lambda mho^{-1}cm^2)$	$\Lambda(c)^{\frac{1}{2}}$
5.00	0.071	0.360	0.0255
4.00	0.063	0.345	0.0218
3.00	0.055	0.323	0.0177
2.00	0.045	0.311	0.0139
1.00	0.032	0.323	0.0102
0.50	0.022	0.360	0.0080
0.40	0.020	0.372	0.0074
0.30	0.017_3	0.416	0.0072
0.20	0.014_1	0.488	0.0069
0.10	0.010	0.680	0.0068

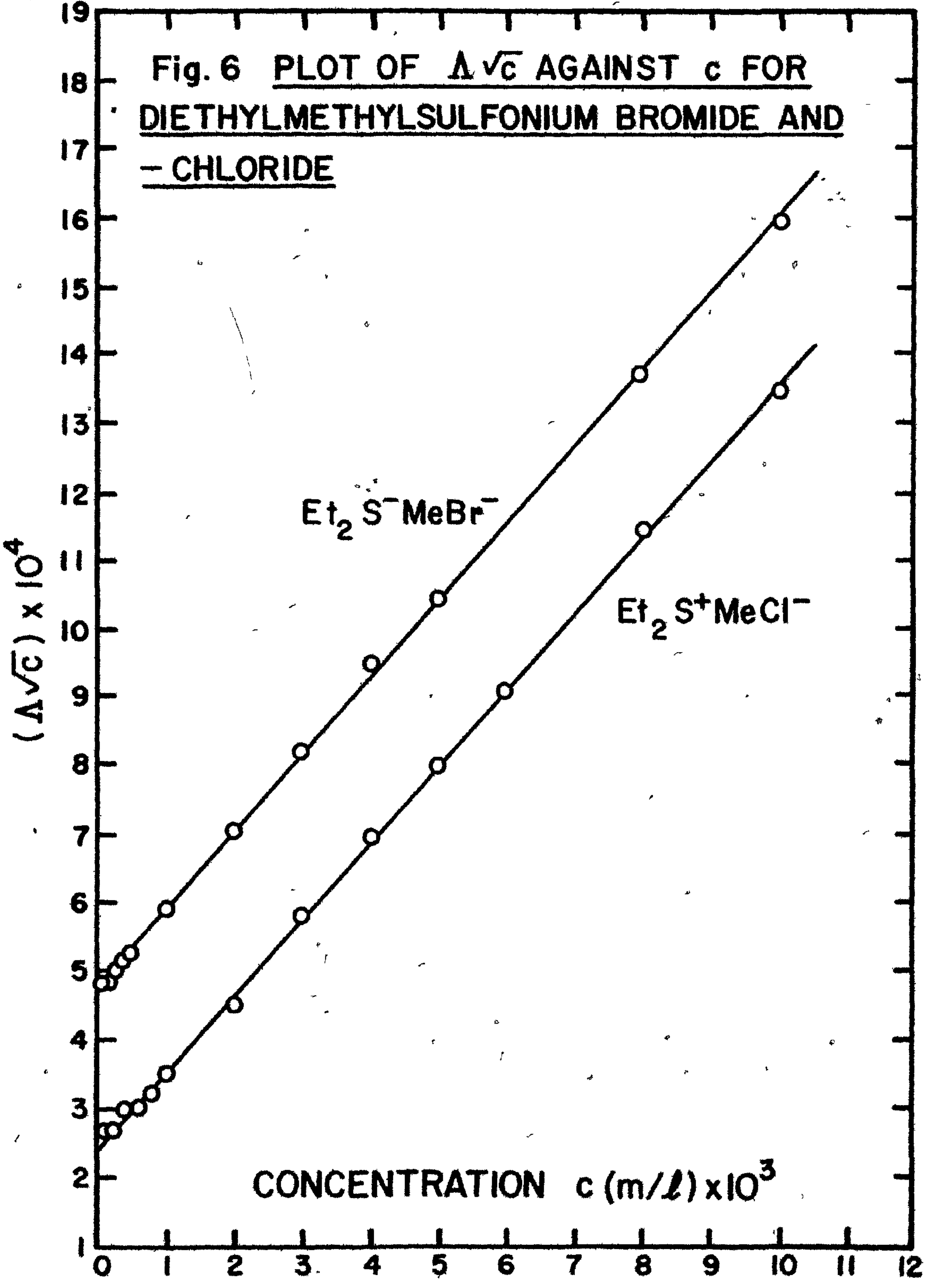

Fig. 6 PLOT OF $\Lambda\sqrt{c}$ AGAINST c FOR DIETHYLMETHYLSULFONIUM BROMIDE AND – CHLORIDE

Table 6A. Values of $\Lambda(c)^{\frac{1}{2}}$ at different concentrations of diethylmethylsulfonium bromide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}.

Concentration (c)x10^3	(c)$^{\frac{1}{2}}$	Equiv. Cond. (Λmho^{-1}cm^2)	Λ(c)$^{\frac{1}{2}}$
10.00	0.100	0.0159	0.00160
8.00	0.089_4	0.0152	0.00136
5.00	0.071	0.0147	0.00104
4.00	0.063_2	0.0151	0.00095
3.00	0.055	0.0150	0.00082
2.00	0.044_7	0.0156	0.00070
1.00	0.031_6	0.0185	0.00059
0.50	0.022_3	0.0233	0.00052
0.40	0.0200	0.0255	0.00051
0.30	0.017_3	0.0289	0.00050
0.20	0.014_1	0.0340	0.00048
0.10	0.010	0.0480	0.00048

Table 6B. Values of $\Lambda(c)^{\frac{1}{2}}$ at different concentrations of diethylmethylsulfonium chloride in chloroform at 25°C.

Cell #3, const.: 0.2375 cm^{-1}.

Concentration (c)x10^{3}	$(c)^{\frac{1}{2}}$	Equiv. Cond. (Λmho^{-1}cm^{2})	$\Lambda(c)^{\frac{1}{2}}$
10.00	0.100	0.0135	0.00135
8.00	0.089_4	0.0127	0.00114
6.00	0.077_6	0.0117	0.00091
5.00	0.071	0.0113	0.0080
4.00	0.063_2	0.0112	0.00071
3.00	0.055	0.0105	0.00058
2.00	0.044_7	0.0103	0.00045
1.00	0.031_6	0.0112	0.00035
0.80	0.028_3	0.0113	0.00032
0.60	0.024_5	0.0122	0.00030
0.40	0.020	0.0150	0.00030
0.20	0.014_1	0.0199	0.00028
0.10	0.010	0.0280	0.00028

Fig. 7. PLOT OF $\Lambda\sqrt{c}$ AGAINST c FOR DIMETHYLSULFONIUM SALTS

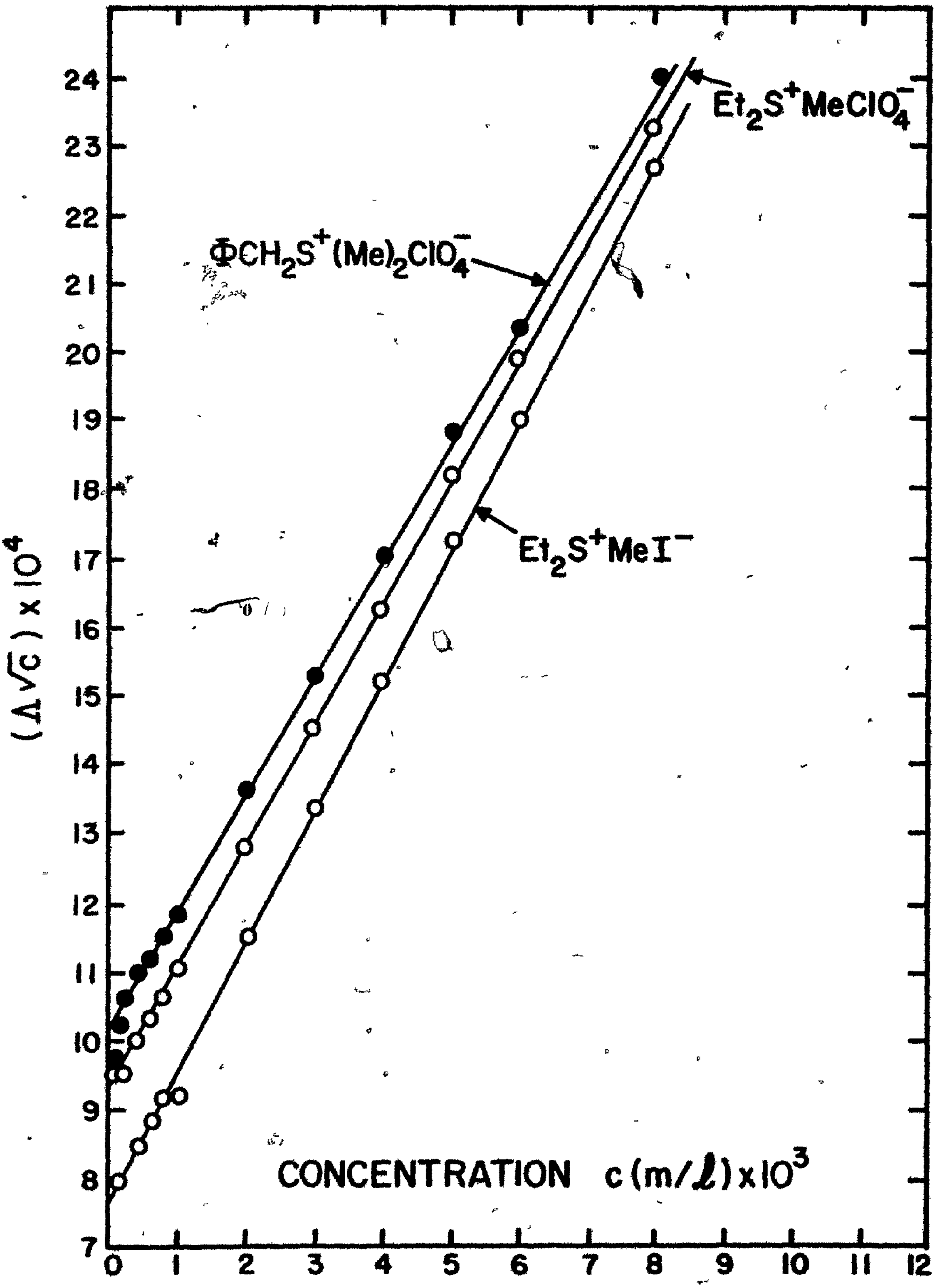

Table 7A. Values of $\Lambda(c)^{\frac{1}{2}}$ at different concentrations of diethylmethylsulfonium iodide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}.

Concentration $(c)\times10^3$	$(c)^{\frac{1}{2}}$	Equiv. Cond. (Λmho^{-1}cm^2)	$\Lambda(c)^{\frac{1}{2}}$
8.00	0.089_4	0.0254	0.00227
6.00	0.077_6	0.0245	0.00190
5.00	0.071	0.0244	0.00173
4.00	0.063_2	0.0241	0.00152
3.00	0.055	0.0243	0.00134
2.00	0.044_7	0.0257	0.00115
1.00	0.031_6	0.0290	0.00092
0.80	0.0283	0.0325	0.00092
0.60	0.0245	0.0363	0.00089
0.40	0.020	0.0415	0.00085
0.20	0.0141	0.0589	0.00083
0.10	0.010	0.0800	0.00080

Table 7B. Values of $\Lambda(c)^{\frac{1}{2}}$ at different concentrations of diethylmethylsulfonium perchlorate in chloroform at 25.0°C. Cell #3, const.: 0.2375 cm^{-1}.

Concentration (c)x10^3	$(c)^{\frac{1}{2}}$	Equiv. Cond. (Λmho^{-1}cm^2)	$\Lambda(c)^{\frac{1}{2}}$
8.00	0.089_4	0.0260	0.00232
6.00	0.077_6	0.0256	0.00199
5.00	0.071	0.0256	0.00182
4.00	0.063_2	0.0256	0.00162
3.00	0.055	0.0264	0.00145
2.00	0.044_7	0.0286	0.00128
1.00	0.031_6	0.0348	0.00110
0.80	0.028_3	0.0375	0.00106
0.60	0.024_5	0.0420	0.00103
0.40	0.020	0.0500	0.00100
0.20	0.014_1	0.0673	0.00095
0.10	0.010	0.0950	0.00095

Table 7C. Values of $\Lambda(c)^{\frac{1}{2}}$ at different concentrations of benzyldimethylsulfonium perchlorate in chloroform at 25.0°C.

Cell #3, const. 0.2375 cm^{-1}

Concentration (c)x10^3	$(c)^{\frac{1}{2}}$	Equiv. Cond. (Λmho^{-1}cm^2)	$\Lambda(c)^{\frac{1}{2}}$
8.00	0.089_4	0.0268	0.00240
6.00	0.077_6	0.0262	0.00203
5.00	0.071	0.0266	0.00188
4.00	0.063_2	0.0269	0.00170
3.00	0.055	0.0281	0.00154
2.00	0.044_7	0.0304	0.00136
1.00	0.031_6	0.0373	0.00118
0.80	0.028_3	0.0406	0.00115
0.60	0.024_5	0.0457	0.00112
0.40	0.020	0.0552	0.00110
0.20	0.014_1	0.0750	0.00106
0.10	0.0100	0.1020	0.00102

Table 8A. Electrolytic constants of single ammonium and sulfonium salts in chloroform at 25.0°C.

n-Tetrabutylammonium salts	Br^-	I^-	ClO_4^-
$10^3 \times A(ohm^{-1}cm^2mole^{-0.5}l.^{-0.5})$	7.2	6.4	6.2
$B(ohm^{-1}cm^2mole^{-1.5}l.^{-0.5})$	1.98	3.52	3.88
$\Lambda min(ohm^{-1}cm^2mole^{-1})$	0.239	0.300	0.310
$Cmin(mole^{-1})$	0.0036	0.0018	0.0016
$10^{10} \times K_2$ (mole $l.^{-1}$)	45.66	35.20	34.00
$10^3 \times K_3$ (mole $l.^{-1}$)	1.21	1.21	0.54

Diethylmethylsulfonium salts	Br^-	Cl^-	I^-	ClO_4^-	$\emptyset CH_2S(Me)_2ClO_4$
$10^4 \times A(ohm^{-1}cm^2mole^{-0.5}l.^{-0.5})$	4.7	2.4	7.8	9.3	10.2
$B(ohm^{-1}cm^2mole^{-1.5}l.^{-0.5})$	0.113	0.111	0.186	0.175	0.170
$\Lambda min(ohm^{-1}cm^2mole^{-1})$	0.0146	0.010	0.024	0.025_4	0.026
Cmin(mole $l.^{-1}$)	0.0042	0.002	0.004	0.005	0.006
$10^{10} \times K_2$(mole $l.^{-1}$)	0.510	0.14	1.45	1.98	2.38
$10^3 \times K_3$(mole $l.^{-1}$)	1.39	0.72	1.40	1.77	2.00

D. Dissociation constants for mixed salts

(a) Salts with one common ion:

In order to study the mechanistic problem, it was thought to be instructive to calculate the actual fractions of the salts which are present as simple ions, and as triple ions. Furthermore, to gain information of the extent to which the ion-pair form of one salt could provide a stable seat for the simple anion of another, conductimetric studies of the mixed salts were undertaken whereby, dissociation constants of the unsymmetrical triple ions could be obtained. The method of deriving the new equilibrium constants for the equimolar mixtures of the ammonium and sulfonium salts, from conductance data, that was followed in the present investigation is due to Ingold and co-workers[6]. According to this procedure, the following eight equilibria are to be considered:

$$S^+Br^- \rightleftharpoons S^+ + Br^- \quad \ldots\ldots\ K_{2x} = [S^+][Br^-]/[S^+Br^-]$$

$$N^+Br^- \rightleftharpoons N^+ + Br^- \quad \ldots\ldots\ K_{2y} = [N^+][Br^-]/[N^+Br^-]$$

$$Br^-S^+Br^- \rightleftharpoons Br^-S^+ + Br^- \quad \ldots\ldots\ K_{3x} = [S^+Br^-][Br^-]/[Br^-S^+Br^-]$$

$$S^+Br^-S^+ \rightleftharpoons S^+Br^- + S^+ \quad \ldots\ldots\ K_{3x} = [S^+Br^-][S^+]/[S^+Br^-S^+]$$

$$Br^-N^+Br^- \rightleftharpoons Br^-N^+ + Br^- \quad \ldots\ldots\ K_{3y} = [N^+Br^-][Br^-]/[Br^-N^+Br^-]$$

$$N^+Br^-N^+ \rightleftharpoons N^+Br^- + N^+ \quad \ldots\ldots\ K_{3y} = [N^+Br^-][N^+]/[N^+Br^-N^+]$$

$$S^+Br^-N^+ \rightleftharpoons S^+Br^- + N^+ \quad \ldots\ldots\ K_{3xy} = [S^+Br^-][N^+]/[S^+Br^-N^+]$$

$$N^+Br^-S^+ \rightleftharpoons N^+Br^- + S^+ \quad \ldots\ldots\ K_{3yx} = [N^+Br^-][S^+]/[N^+Br^-S^+]$$

Also, $K_{3yx}/K_{2x} = K_{3xy}/K_{2y}$

So, there are actually five independent equilibrium constants, four of which can be evaluated from the conductances of the pure salts; the remaining equilibrium constant can be derived from the conductance of the mixture. Besides these, charge balance provides the relation,

$$[Br^-]+[Br^-S^+Br^-]+[Br^-N^+Br^-] = [S^+]+[N^+]+[S^+Br^-S^+]+[N^+Br^-N^+]+[S^+Br^-N^+] \quad (17)$$

and material balance two more relations, which can be simplified to,

$$[S^+Br^-] = [N^+Br^-] = c/2 \quad (18)$$

because only a very small fraction of the ions carries the current.

However, by introducing some auxiliary quantities, the concentrations of the different species can be more conveniently expressed. Let the arithmetic K_2 mean, a harmonic K_3 mean, and three K_2/K_3 ratios, and their sum be defined as:

$$K_{2m} = \tfrac{1}{2}(K_{2x}+K_{2y}); \quad K_{3M}^{-1} = \tfrac{1}{2}(K_{3x}^{-1}+K_{3y}^{-1}) \quad (19)$$

$$\rho_x = K_{2x}/K_{3x}; \quad \rho_y = K_{2y}/K_{3y}; \quad \rho_{xy} = K_{2x}/K_{3yx} = K_{2y}/K_{3xy}; \quad (20)$$

$$s = \rho_x+\rho_y+\rho_{xy}$$

In terms of the above K combinations, and of the concentration c, a pure number F is defined as:

$$F = \left[1 + \frac{cS}{K_{2m}}\right]^{\frac{1}{2}} \cdot \left[1 + \frac{c}{K_{3M}}\right]^{-\frac{1}{2}} \qquad (22)$$

Finally, a concentration R is related to F, by:

$$R = (cK_{2m})^{\frac{1}{2}}. F \qquad (23)$$

The simple and triple ion concentrations can now be expressed as follows, the first expression being shown in Appendix C:

$$[Br^-] = R$$
$$[S^+] = cK_{2x}/2R$$
$$[N^+] = cK_{2y}/2R$$
$$[Br^-S^+Br^-] = cR/2K_{3x}$$
$$[Br^-N^+Br^-] = cR/2K_{3y}$$
$$[S^+Br^-S^+] = c^2K_{2x}/4RK_{3x}$$
$$[N^+Br^-N^+] = c^2K_{2y}/4RK_{3y}$$
$$[S^+Br^-N^+] = c^2K_{2x}/4K_{3yx} = c^2K_{2y}/4K_{3xy}$$

The results of these calculations allow one to derive the equation for the equivalent conductance of the mixed salts, the equation being,

$$\bar{\Lambda} = \Lambda^\circ{}_1\phi_1 + \frac{1}{3}\Lambda^\circ{}_3\phi_3 \qquad (24)$$

where ϕ_1 and ϕ_3 are the fractions of total salts present as single and triple ions respectively. Here again, ϕ_1 and ϕ_2 can simply be expressed with the help of the function F:

$$\phi_1 = \left(\frac{K_{2m}}{c}\right)^{\frac{1}{2}} \left(\frac{F^2+1}{2F}\right) \tag{25}$$

$$1/3\ \phi_3 = \left(\frac{cK_{2m}}{K_3}\right)^{\frac{1}{2}} F + \left(\frac{K_{2m}}{c}\right)^{\frac{1}{2}} \left(\frac{F^2-1}{2F}\right) \tag{26}$$

The equation for $\bar{\Lambda}$ can be expanded in ascending powers of c, and it can be shown that:

$\Lambda_1^\circ \phi_1$ contains terms in $c^{-\frac{1}{2}}$, –, $c^{3/2}$, $c^{5/2}$ ....

and $\frac{1}{3}$ $\Lambda_3^\circ \phi_3$ contains terms in –, $c^{\frac{1}{2}}$, $c^{3/2}$, $c^{5/2}$ ....

Since both $c^{-\frac{1}{2}}$ and $c^{\frac{1}{2}}$ are present in the equation for $\bar{\Lambda}$, the $\log_{10}\bar{\Lambda} - \log_{10}c$ curves for mixtures, like the $\log_{10}\bar{\Lambda} - \log_{10}c$ curves for the single salts, pass through the minimum, Fig.8. Neglecting the terms in $c^{3/2}$ and higher powers, the practically useful equation for $\bar{\Lambda}$ is given by,

$$\bar{\Lambda} = \bar{A}c^{-\frac{1}{2}} + \bar{B}c^{\frac{1}{2}} + \ldots\ldots \tag{27}$$

$$\text{where } \bar{\Lambda} = \Lambda_1^\circ\sqrt{K_{2m}}; \quad \bar{B} = \Lambda_3^\circ \frac{\sqrt{K_{2m}}}{2K_{3M}} + \frac{S}{8\sqrt{K_{2m}}} \tag{28}$$

When from the experimental data, $\Lambda(c)^{\frac{1}{2}}$ is plotted against c_1 for the mixed salts, we get an initial straight line, having an intercept $\bar{A}$, and a slope $\bar{B}$, Fig.9, K_{2m} and K_{3M} being known from the studies of single salts, $\bar{B}$ permits one to calculate the sum of ratios, S. Since ρ_x, and ρ_y are similarly known, the remaining one can be deduced, and therefrom, the equilibrium constants, K_{3xy} and K_{3yx} for the mixed triple anion, can be worked out.

Fig. 8 PLOT OF LOG$_{10}\Lambda$ − LOG$_{10}$c FOR EQUIMOLAR MIXTURES OF AMMONIUM AND SULFONIUM SALTS

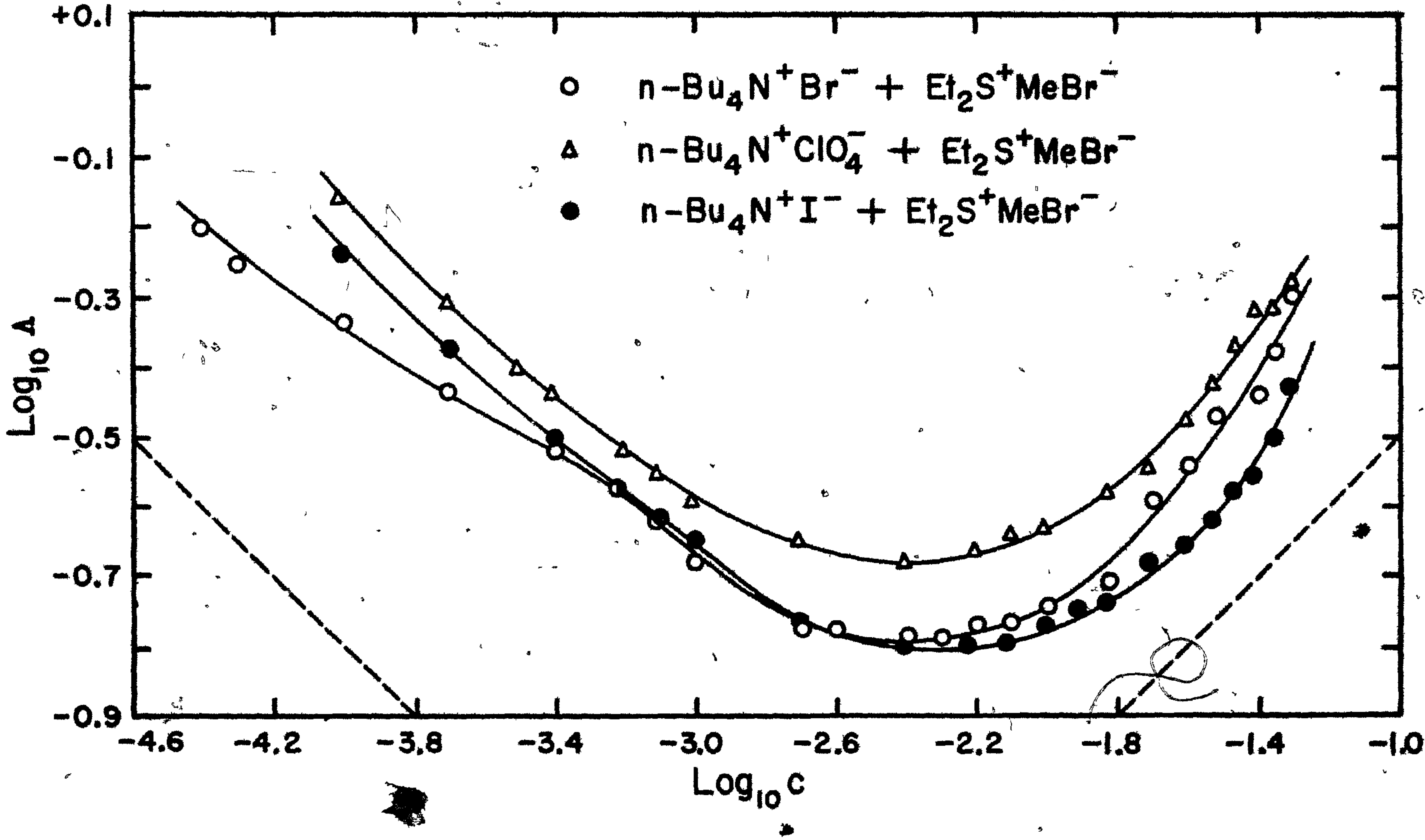

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Table 8B. Equivalent conductance of equimolar mixture of diethylmethylsulfonium bromide and n-tetrabutylammonium bromide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}

Concentration (M/l)x10^3	log_{10}Conc.	Conductance (μ mho)	Equiv. Cond. (Λmho^{-1}cm^2)	log_{10}Λ
50.0	-1.300	104.70	0.4974	-0.3034
45.0	-1.350	79.41	0.4191	-0.3777
40.0	-1.400	61.00	0.3621	-0.4411
30.0	-1.520	42.60	0.3372	-0.4720
25.0	-1.600	30.26	0.2875	-0.5414
20.0	-1.700	21.60	0.2565	-0.5909
15.0	-1.820	12.40	0.1963	-0.7070
10.0	-2.000	7.70	0.1829	-0.7378
8.0	-2.100	5.88	0.1745	-0.7582
6.0	-2.220	4.23	0.1675	-0.7532
5.0	-2.300	3.40	0.1615	-0.7918
4.0	-2.400	2.77	0.1645	-0.7833
2.5	-2.600	1.79	0.1701	-0.7692
2.0	-2.700	1.43	0.1701	-0.7692
1.0	-3.000	0.88_8	0.2104	-0.6759
0.80	-3.100	0.814	0.2416	-0.6168
0.60	-3.220	0.680	0.2679	-0.5720
0.40	-3.400	0.508	0.3016	-0.5206
0.20	-3.700	0.282	0.3288	-0.4831
0.10	-4.000	0.188	0.4466	-0.3501
0.05	-4.300	0.118	0.5622	-0.2501
0.02_5	-4.400	0.066	0.6283	-0.2107

Table 8C. Equivalent conductance of equimolar mixture of diethylmethylsulfonium bromide and n-tetrabutylammonium iodide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}

Concentration (M/l)x10^3	log_{10}Conc.	Conductance (μ mho)	Equiv. Cond. ($\Lambda mho^{-1}cm^2$)	$log_{10}\Lambda$
50.0	-1.300	79.10	0.3752	-0.426
45.0	-1.350	58.43	0.3084	-0.511
40.0	-1.400	46.21	0.2744	-0.562
35.0	-1.460	39.10	0.2653	-0.576
30.0	-1.520	30.51	0.2415	-0.617
25.0	-1.600	23.30	0.2210	-0.655
20.0	-1.700	17.65	0.2400	-0.678
15.0	-1.820	11.41	0.1800	-0.743
10.0	-2.000	7.10	0.1680	-0.773
8.0	-2.100	5.36	0.1590	-0.798
6.0	-2.220	3.98	0.1575	-0.803
4.0	-2.400	2.68	0.1590	-0.800
2.0	-2.700	1.44	0.1710	-0.767
1.0	-3.000	0.94	0.2230	-0.651
0.8	-3.100	0.80	0.2375	-0.624
0.6	-3.220	0.66	0.2610	-0.583
0.4	-3.400	0.53	0.3110	-0.507
0.2	-3.700	0.35	0.4200	-0.377
0.1	-4.000	0.24	0.5800	-0.237

Table 8D. Equivalent conductance of equimolar mixture of diethylmethylsulfonium bromide and n-tetrabutylammonium perchlorate in chloroform at 25.0°C.

Cell #3; const.: 0.2375 cm^{-1}

Concentration (M/l)x10^3	$\log_{10}$Conc.	Conductance (μ mho)	Equiv. Cond. ($\Lambda mho^{-1}cm^2$)	$\log_{10}\Lambda$
50.0	-1.300	108.50	0.515	-0.288
45.0	-1.350	90.21	0.476	-0.322
40.0	-1.400	79.95	0.475	-0.324
35.0	-1.460	62.34	0.423	-0.374
30.0	-1.520	47.32	0.375	-0.426
25.0	-1.600	35.25	0.334	-0.476
20.0	-1.700	24.00	0.285	-0.545
15.0	-1.820	16.54	0.262	-0.582
10.0	-2.000	9.80	0.233	-0.633
8.0	-2.100	7.64	0.227	-0.644
6.0	-2.220	5.51	0.218	-0.661
4.0	-2.400	3.51	0.208	-0.681
2.0	-2.700	1.87	0.222	-0.654
1.0	-3.000	1.07	0.254	-0.595
0.8	-3.100	0.93	0.276	-0.559
0.6	-3.220	0.76	0.303	-0.518
0.4	-3.400	0.61	0.365	-0.438
0.2	-3.700	0.42	0.495	-0.305
0.1	-4.000	0.29	0.680	-0.162

Fig. 9 PLOT OF $\Lambda\sqrt{c}$ AGAINST c FOR EQUIMOLAR MIXTURES OF AMMONIUM AND SULFONIUM SALTS

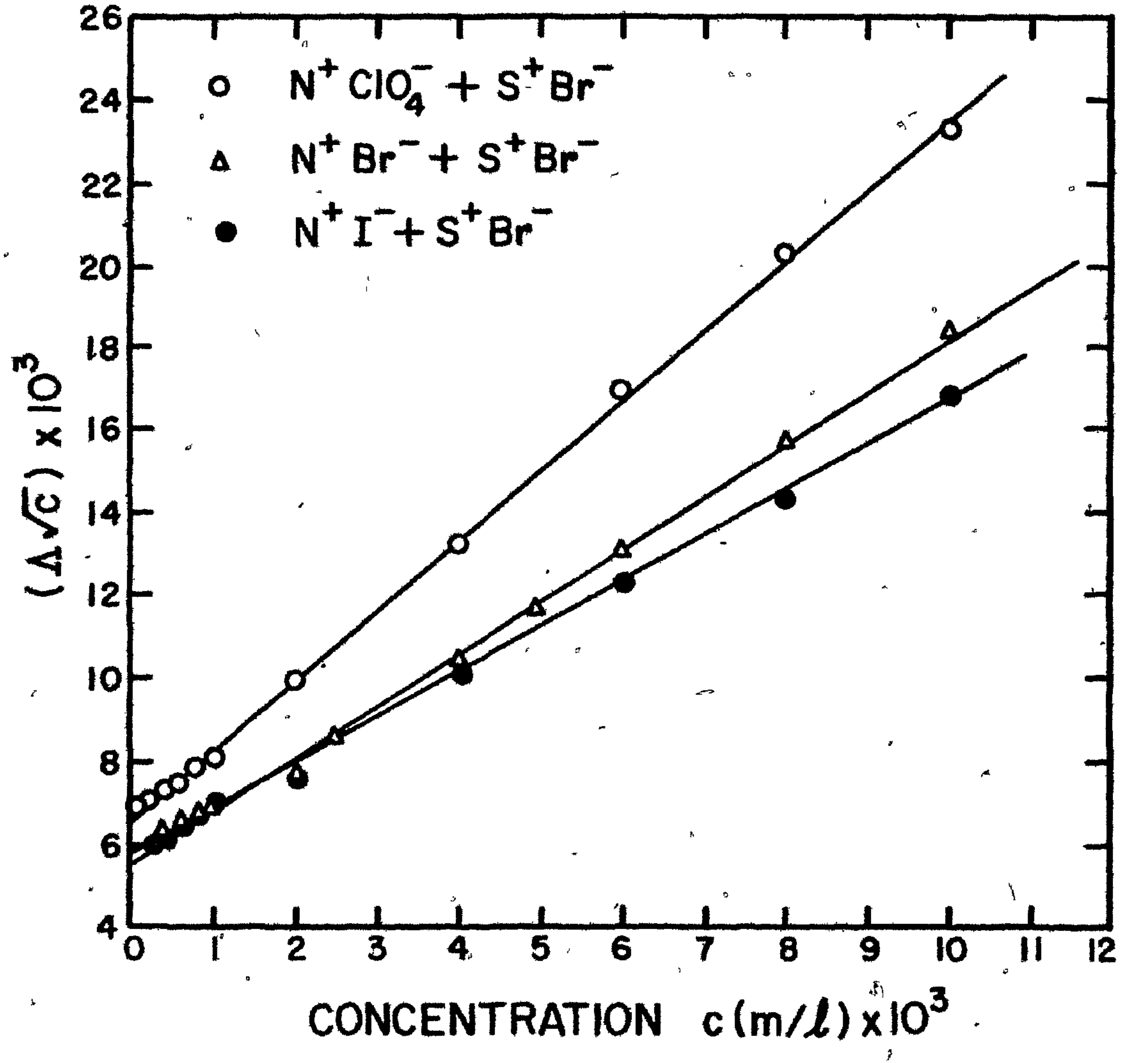


Table 9A. Values of $\Lambda(c)^{\frac{1}{2}}$ at different concentrations of equimolar mixtures of n-tetrabutylammonium bromide and diethylmethylsulfonium bromide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}

Concentration $(c)\times10^3$	$(c)^{\frac{1}{2}}$	Equiv. Cond. $(\Lambda mho^{-1}cm^2)$	$\Lambda(c)^{\frac{1}{2}}$
10.00	0.100	0.1829	0.0183
8.00	0.099_4	0.1745	0.0156
6.00	0.077_6	0.1675	0.0130
5.00	0.071	0.1615	0.0115
4.00	0.063_2	0.1645	0.0104
2.50	0.050	0.1701	0.0085
2.00	0.044_7	0.1701	0.0076
1.00	0.031_6	0.2104	0.0067
0.80	0.028_3	0.2416	0.0068
0.60	0.024_5	0.2679	0.0066
0.40	0.020	0.3016	0.0063

Table 9B. Values of $\Lambda(c)^{\frac{1}{2}}$ at different concentrations of equimolar mixtures of n-tetrabutylammonium iodide and diethylmethylsulfonium bromide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}

Concentration (c)x10^3	$(c)^{\frac{1}{2}}$	Equiv. Cond. (Λmho^{-1}cm^2)	$\Lambda(c)^{\frac{1}{2}}$
10.00	0.100	0.1680	0.0168
8.00	0.089_4	0.1590	0.0142
6.00	0.077_6	0.1575	0.0122
4.00	0.063_2	0.1590	0.0100
2.00	0.044_7	0.1710	0.0076
1.00	0.31_6	0.2230	0.0070
0.80	0.028_3	0.2375	0.0067
0.60	0.024_5	0.2610	0.0064
0.40	0.020	0.3110	0.0062
0.20	0.014_1	0.4200	0.0059
0.10	0.010	0.5800	0.0058

Table 9C. Values of $\Lambda(c)^{\frac{1}{2}}$ at different concentrations of equimolar mixtures of n-tetrabutylammonium perchlorate and diethylmethylsulfonium bromide in chloroform at 25.0°C.

Cell #3, const.: 0.2375 cm^{-1}

Concentration $(c)\times 10^3$	$(c)^{\frac{1}{2}}$	Equiv. Cond. (Λmho^{-1}cm^2)	$\Lambda(c)^{\frac{1}{2}}$
10.00	0.100	0.233	0.0233
8.00	0.089_4	0.227	0.0203
6.00	0.077_6	0.218	0.0169
4.00	0.063_2	0.208	0.0132
2.00	0.044_7	0.222	0.0099
1.00	0.031_6	0.254	0.0080
0.80	0.028_3	0.276	0.0078
0.60	0.024_5	0.303	0.0074
0.40	0.020	0.365	0.0073
0.20	0.014_1	0.495	0.0070
0.10	0.010	0.680	0.0068

(b) Salts with no common ions

The situation becomes very complex due to a large number of equilibria constants, when the mixed salts do not contain any common ion. In this case, instead of two ion-pairs, and six triple ions, as is the case of the mixed salts with one common ion, four ion-pairs and sixteen triple ion dissociations are obtained, as shown below for S^+Br^- and N^+I^-, as an example,

$$\begin{array}{rcll}
S^+Br^- & \rightleftharpoons & S^+ + Br^- \;\ldots\ldots & K_{2x} = [S^+][Br^-]/[S^+Br^-] \\
N^+I^- & \rightleftharpoons & N^+ + I^- \;\ldots\ldots & K_{2y} = [N^+][I^-]/[N^+I^-] \\
S^+I^- & \rightleftharpoons & S^+ + I^- \;\ldots\ldots & K'_{2x} = [S^+][I^-]/[S^+I^-] \\
N^+Br^- & \rightleftharpoons & N^+ + Br^- \;\ldots\ldots & K'_{2y} = [N^+][Br^-]/[N^+Br^-] \\
Br^-S^+Br^- & \rightleftharpoons & S^+Br^- + Br^- \;\ldots & K_{3x} = [S^+Br^-][Br^-]/[Br^-S^+Br^-] \\
S^+Br^-S^+ & \rightleftharpoons & S^+Br^- + S^+ \;\ldots. & K_{3x} = [S^+Br^-][S^+]/[S^+Br^-S^+] \\
I^-N^+I^- & \rightleftharpoons & N^+I^- + I^- \;\ldots\ldots & K_{3y} = [N^+I^-][I^-]/[I^-N^+I^-] \\
N^+I^-N^+ & \rightleftharpoons & N^+I^- + N^+ \;\ldots\ldots & K_{3y} = [N^+I^-][N^+]/[N^+I^-N^+] \\
I^-S^+I^- & \rightleftharpoons & S^+I^- + I^- \;\ldots\ldots & K'_{3y} = [S^+I^-][I^-]/[I^-S^+I^-] \\
S^+I^-S^+ & \rightleftharpoons & S^+I^- + S^+ \;\ldots\ldots & K'_{3y} = [S^+I^-][S^+]/[S^+I^-S^+] \\
Br^-N^+Br^- & \rightleftharpoons & N^+Br^- + Br^- \;\ldots & K'_{3x} = [N^+Br^-][Br^-]/[Br^-N^+Br^-] \\
N^+Br^-N^+ & \rightleftharpoons & N^+Br^- + N^+ \;\ldots. & K'_{3x} = [N^+Br^-][N^+]/[N^+Br^-N^+] \\
N^+Br^-S^+ & \rightleftharpoons & S^+Br^- + N^+ \;\ldots. & K_{3xy} = [S^+Br^-][N^+]/[N^+Br^-S^+] \\
Br^-S^+I^- & \rightleftharpoons & S^+Br^- + I^- \;\ldots. & K_{3xy} = [S^+Br^-][I^-]/[I^-S^+Br^-] \\
N^+I^-S^+ & \rightleftharpoons & N^+I^- + S^+ \;\ldots\ldots & K_{3yx} = [N^+I^-][S^+]/[N^+I^-S^+] \\
Br^-N^+I^- & \rightleftharpoons & N^+I^- + Br^- \;\ldots & K_{3yx} = [N^+I^-][Br^-]/[Br^-N^+I^-]
\end{array}$$

$$Br^-S^+I^- \rightleftharpoons S^+I^- + Br^- \text{ .... } K'_{3xy} = [S^+I^-][Br^-]/[I^-S^+Br^-]$$
$$S^+I^-N^+ \rightleftharpoons S^+I^- + N^+ \text{ .... } K'_{3xy} = [S^+I^-][N^+]/[S^+I^-N^+]$$
$$I^-N^+Br^- \rightleftharpoons N^+Br^- + I^- \text{ .... } K'_{3yx} = [N^+Br^-][I^-]/[I^-N^+Br^-]$$
$$N^+Br^-S^+ \rightleftharpoons N^+Br^- + S^+ \text{ .... } K'_{3yx} = [N^+Br^-][S^+]/[N^+Br^-S^+]$$

Besides these, from charge and material balance, the following two relations are obtained respectively,

$$[S^+]+[N^+]+[S^+Br^-S^+]+[N^+I^-N^+]+[S^+Br^-N^+]+[N^+I^-S^+]+[S^+I^-S^+]+[N^+Br^-N^+]$$

$$= [Br^-]+[I^-]+[Br^-S^+Br^-]+[I^-N^+I^-]+[I^-S^+Br^-]+[Br^-N^+I^-]+[I^-S^+I^-]+[Br^-N^+Br^-]$$

and, $[S^+Br^-]+[N^+Br^-] = [S^+I^-]+[N^+I^-] = c/2$ (29a)

$[S^+Br^-]+[S^+I^-] = [N^+Br^-]+[N^+I^-] = c/2$ (29b)

For mixed salts having no common ion, we define the following terms in the analogous manner, as was done for the previous example:

$$K_{2m} = \tfrac{1}{4}(K_{2x}+K_{2y}+K'_{2x}+K'_{2y}) \tag{30}$$

$$K_{3M}^{-1} = \tfrac{1}{4}(K_{3x}^{-1}+K_{3y}^{-1}+K'^{-1}_{3x}+K'^{-1}_{3y}) \tag{31}$$

$$\rho_x = K_{2x}/K_{3x}; \quad \rho_y = K_{2y}/K_{3y}; \quad \rho'_x = K'_{2x}/K'_{3x}; \quad \rho'_y = K'_{2y}/K'_{3y}; \tag{32}$$

$$\rho_{xy} = K_{2x}/K_{3yx}=K_{2y}/K_{3xy}=K'_{2x}/K'_{3yx}=K'_{2y}/K'_{3xy} \tag{33}$$

and also $S = \rho_x+\rho'_x+\rho_y+\rho'_y+\rho_{xy}$ (34)

In contrast to the salt mixtures with a common ion, in this case, we have calculated the concentrations of (S^+) and (N^+) from two different sets of reactions, and then followed a 'successive approximation procedure' until the concentration of each of the simple ions was constant. The reason for following this procedure is to calculate the concentrations of the four different ion-pairs, which are used to obtain the concentrations of the triple ions. In the case of salt mixtures, with a common ion, the number of ion-pairs is only two, the concentration of each must be equal to c/2. However, with 4 different ion-pairs the individual concentrations cannot be assumed to be c/4.

As an example of the 'successive approximation procedure', ($S+Br^-+N^+I^-$) system is chosen, and the following equilibria are considered:

$$S^+Br^- \longrightarrow S^+ + Br^- \quad : \quad K_{2x} = \frac{[S^+][Br^-]}{[S^+Br^-]}$$

$$S^+I^- \longrightarrow S^+ + I^- \quad : \quad K'_{2x} = \frac{[S^+][I^-]}{[S^+I^-]}$$

$$N^+I^- \longrightarrow N^+ + I^- \quad : \quad K_{2y} = \frac{[N^+][I^-]}{[N^+I^-]}$$

$$N^+Br^- \longrightarrow N^+ + Br^- \quad : \quad K'_{2y} = \frac{[N^+][Br^-]}{[N^+Br^-]}$$

The equilibrium constants for ion-pair dissociation were obtained from the experiments with the single salts and are shown in Table 8A

Step 1

The concentrations of (S^+), (N^+), and (Br^-) ions are obtained from the following reactions:

$$S^+Br^- \longrightarrow S^+ + Br^-$$

$$N^+Br^- \longrightarrow N^+ + Br^-$$

From these reactions,

$$[Br^-] = R \doteq (cK_{2m})^{\frac{1}{2}} \text{ x } F \qquad (35)$$

$$\text{where } c = 0.025 \text{ M/l}$$

$$K_{2m} = \tfrac{1}{2}(K_{2x} + K'_{2y})$$

$$\text{and } F = 0.37$$

$$[S^+] = \frac{cK_{2x}}{2[R]} \qquad (36)$$

$$\text{and} \quad [N^+] = \frac{cK'_{2y}}{2[R]} \qquad (37)$$

Similarly from the reactions

$$N^+I^- \longrightarrow N^+ + I^-$$

$$S^+I^- \longrightarrow S^+ + I^-$$

$$[I^-] = R = (cK_{2m})^{\frac{1}{2}} F \qquad (38)$$

where $K_{2m} = \frac{1}{2}(K_{2y} + K'_{2x})$

$$[S^+] = \frac{cK'_{2x}}{2[R]} \qquad (39)$$

and
$$[N^+] = \frac{cK_{2y}}{2[R]} \qquad (40)$$

Step 2.

The average value of $[S^+]$ from (36) and (39) and that of $[N^+]$ from (37) and (40) are obtained.

Step 3.

This average value of $[S^+]$ (Step 2) is put in eqns. (36) and (39) to get new values of $[Br^-]$ and $[I^-]$ respectively. From the average value of $[N^+]$ in step 2, another set of $[Br^-]$ and $[I^-]$ are calculated from (37) and (40).

Step 4.

The values of $[Br^-]$ and $[I^-]$ of step 3 are averaged, and used in eqns. (36), (37), (39) and (40) to get a new set of $[S^+]$ and $[N^+]$.

Step 2 is then repeated and the cycle followed until the values of different ions are constant as shown below.

Concentration of simple ions $c \times 10^5$

cycle	S^+	N^+	Br^-	I^-
1st	0.0460	1.880	0.219	0.314
2nd	0.0435	2.004	0.216	0.318_4
3rd	0.0432	2.012	0.215_7	0.319
4th	0.0432	2.012	0.215_7	0.319

As a further test of internal consistency, these simple ion concentrations are used to calculate the ion-pair concentrations which should add to 0.050 M/1. The ion-pair concentrations obtained from the simple ion concentrations are:

$$[S^+Br^-] = 0.0183 \text{ M/1}$$
$$[S^+I^-] = 0.0095 \text{ M/1}$$
$$[N^+I^-] = 0.018_2 \text{ M/1}$$
$$[N^+Br^-] = 0.009_5 \text{ M/1}$$

The results show an approximate 10% discrepancy from the actual value of the ion-pair concentrations. As a further test, we use these ion-pair concentrations to verify the relations (29a) and (29b) on p. 76.

$$[S^+Br^-] + [N^+Br^-] = 0.027_8 \text{ M/1}$$
$$[S^+I^-] + [N^+I^-] = 0.027_2 \text{ M/1}$$
$$[S^+Br^-] + [S^+I^-] = 0.0278 \text{ M/1}$$
$$[N^+Br^-] + [N^+I^-] = 0.027_7 \text{ M/1}$$

Here again we find the results approximately 10% more than the actual value of 0.025 M/1 in each case.

This 10% discrepancy in the value of the ion-pair concentration is probably accumulated experimental and other errors. One of these is the limitations to which the eight equilibrium constants, used in this calculation, are obtained. They are calculated by graphic methods and the graphs could be read only to two significant figures. An error in each equilibrium constant of about 1.5% will account for the 10% discrepancy. In fact the error in the equilibrium constants is probably significantly greater than this.

Because of the approximations which have to be made in assuming that the equilibrium constants of different dissociation processes listed on pages 75 and 76, it is not possible to calculate the concentrations of the unsymmetrical triple ions except in a semi-quantitative manner.

All the electrolytic constants, obtained for the mixed salts, are shown in Table 10. From these equilibrium constants, we can calculate the concentrations of the different ionic species for mixed salts. A similar calculation can also be done for single salts. Concentrations of the different species, up to triple ions, of single and mixed salts are collated in Table 12. For those triple ions whose concentrations can be obtained only semi-quantitatively, an error range is shown which represents an estimate of the limits within which the concentration of the particular ion probably falls.

Table 10. Electrolyte constants of equimolar binary mixtures of sulfonium and ammonium salts in chloroform at 25.0°C.

Diethylmethylsulfonium salts:	Br^-	Br^-	Br^-
n-Tetrabutylammonium salts:	Br^-	I^-	ClO_4^-
Observed results for mixed salts			
$10^3 x \bar{A}$ (ohm^{-1}cm^{2}mole$^{-0.5}$l$^{-0.5}$)	5.6	5.8	6.5
$\bar{B}$ (ohm^{-1}cm^{2}mole$^{-0.5}$l$^{-0.5}$)	1.25	1.07	1.69
Calculated from data on pure salts			
$10^{10} x K_{2m}$ (mole l^{-1})	23.09	20.45	20.54
$10^3 x K_{3M}$ (mole l^{-1})	1.29	1.30	1.01
Calculated from data on mixed salts			
$10^7 x S$	54.2	29.0	46.4
$10^3 x K_{3xy}$ (mole l^{-1})	3.22	0.09	0.61
$10^3 x K_{3yx}$ (mole l^{-1})	0.04	0.01	0.01
$10^3 x K'_{3xy}$ (mole l^{-1})	---	1.17	0.81
$10^3 x K'_{3yx}$ (mole l^{-1})	---	0.04	0.03

Table 11. Concentrations of simple and triple ions of pure sulfonium and ammonium salts in chloroform at 25.0°C.

Sulfonium salts, 0.05M/l soln.

$(c)\times 10^5$	S^+Br^-	S^+Cl^-	S^+I^-	$S^+ClO_4^-$	$\phi CH_2\overset{+}{S}(Me)_2ClO_4^-$
$[X^-]$	0.160	0.082	0.269	0.314	0.345
$[S^+]$	0.160	0.082	0.269	0.314	0.345
$[X^-S^+X^-]$	5.770	5.690	9.600	8.870	8.620
$[S^+X^-S^+]$	5.770	5.690	9.600	8.870	8.620

Ammonium salts, 0.05M/l soln.

$(c)\times 10^5$	N^+Br^-	N^+I^-	$N^+ClO_4^-$
$[X^-]$	1.511	1.327	1.304
$[N^+]$	1.511	1.327	1.304
$[X^-N^+X^-]$	62.30	54.80	122.3
$[N^+X^-N^+]$	62.30	54.80	122.3

X^- = anion of the salt

S = $Et_2S(Me)$

N = $n\text{-}Bu_4N$

Table 12. Concentration of different ionic species of diethylmethylsulfonium bromide and that of its equimolar mixture with ammonium salts in chloroform at 25.0°C.

Concentration: 0.05 M/1

$(c)\times10^5$	(S^+Br^-)	$\frac{1}{2}(S^+Br^-+N^+Br^-)$	$\frac{1}{2}(S^+Br^-+N^+I^-)$	$\frac{1}{2}(S^+Br^-+N^+ClO_4^-)$*
$[Br^-]$	0.16	0.94	0.21_6	0.21
$[S^+]$	0.16	0.01_4	0.04_3	0.05
$[N^+]$	—	1.21	2.01	1.95
$[I^-]$	—	—	0.32	—
$[ClO_4^-]$	—	—	—	0.36
$[S^+Br^-]$	ca.5000	ca.2500	1830	2000
$[S^+I^-]$	—	—	950	—
$[S^+ClO_4^-]$	—	—	—	800
$[N^+Br^-]$	—	ca.2500	950	900
$[N^+I^-]$	—	—	1820	—
$[N^+ClO_4^-]$	—	—	—	2000
$[Br^-S^+Br^-]$	5.77	16.9	2.84	3.00
$[S^+Br^-S^+]$	5.77	0.25	0.56	0.72
$[S^+Br^-N^+]$	—	9.0	25±15	39±24
$[Br^-N^+Br^-]$	—	19.2	1.7	1.56
$[N^+Br^-N^+]$	—	25.00	15.8	14.50
$[Br^-S^+I^-]$	—	—	12±5	—
$[N^+I^-S^+]$	—	—	38±20	—
$[I^-N^+I^-]$	—	—	4.8	—
$[N^+I^-N^+]$	—	—	30.2	—
$[Br^-N^+I^-]$	—	—	190±100	—
$[I^-S^+I^-]$	—	—	2.17	—
$[S^+I^-S^+]$	—	—	0.29	—
$[Br^-S^+ClO_4^-]$	—	—	—	7±5
$[N^+ClO_4^-S^+]$	—	—	—	60±40
$[ClO_4^-N^+ClO_4^-]$	—	—	—	13.33
$[N^+ClO_4^-N^+]$	—	—	—	72±22
$[ClO_4^-N^+Br^-]$	—	—	—	264±156
$[ClO_4^-S^+ClO_4^-]$	—	—	—	1.63
$[S^+ClO_4^-S^+]$	—	—	—	0.23

* S = Et_2SMe; N = n-Bu_4N

As mentioned earlier, we studied the diethylmethylsulfonium salts instead of benzyldimethylsulfonium salts, in order to avoid the difficulties, arising from the decomposition of the latter, under the experimental conditions. However, this replacement is justified only if both the salts had similar electrochemical properties. In order to check this similarity, we studied both diethylmethylsulfonium- and benzyldimethylsulfonium perchlorate, in addition to other sulfonium salts.

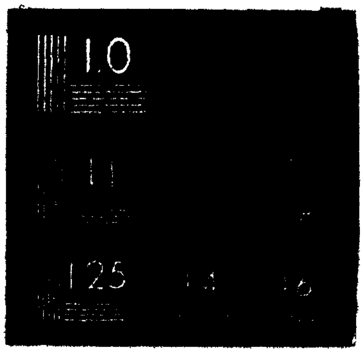
If we compare the experimental results of the two sulfonium perchlorates, in Table 8A, we at once find some striking similarities in them. For example, the similar Λ_{min} and C_{min} values of the salts suggest that both these salts start to form the triple ion at about the same concentration. The values of A and B are also similar for both the salts. All these similar values, together with the closeness of the respective K_2 and K_3 values, suggest that the concentration of simple and triple ions of the two perchlorates should be similar. That this is actually so, can be easily seen from the concentrations of these species, presented in Table 11.

Therefore, the results of these two perchlorates suggest that the electrochemical properties of diethylmethylsulfonium salts very reasonably represent those of the benzyldimethylsulfonium analogues; and thus justify the validity of replacing the latter by the diethylmethylsulfonium salts in this electrochemical study.

All the experimental data obtained in this electrochemical study of the pure sulfonium and ammonium salts, and of their equimolar mixtures, are presented in Tables 8-11. If we compare the results of pure sulfonium and ammonium salts, it is seen that in all cases the concentrations of different ionic species of the ammonium salt is several-fold greater than the concentration of those of the sulfonium salt. Table 8A shows that except for the chloride, the sulfonium salts start forming the triple ion, beyond a concentration of about 0.004M/l, compared to around 0.002M/l for the ammonium salts. Since only a small fraction of both the ammonium and sulfonium salts is present as simple and triple ion, in a 0.05M/l solution, these salts undoubtedly remain mainly as ion-pairs in such a system.

In the case of mixed salts, the ions which are common to all mixtures are the following: Br^-, S^+, $Br^-S^+Br^-$, $S^+Br^-S^+$, N^+, and $N^+Br^-S^+$. Only the first four species have been considered in the case of pure sulfonium salts; and it is seen from Table 12 that the addition of ammonium salts drastically changes the concentration of these species. For example, irrespective of the nature of the anion of the ammonium salt, the concentration of $Br^-S^+Br^-$ goes up, while the concentration of $S^+Br^-S^+$ goes down dramatically. The concentrations of the different ionic species will be further discussed in conjunction with the kinetic results to propose the reaction mechanism.

2 OF/DE 3



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III. KINETIC RESULTS AND DISCUSSION

In order to study the mechanism of the decomposition of the sulfonium salts in chloroform, we decided to study the reaction of benzyldimethylsulfonium bromide in detail, starting with the analysis of the reaction products.

A. Product analysis of the decomposition of benzyldimethylsulfonium bromide in chloroform.

The reaction products of the decomposition of this sulfonium salt were analysed by (a) vapour phase chromatography, and (b) nuclear magnetic resonance spectroscopy, as described in the experimental section.

(a) The gas chromatographic analysis, in Fig. 10, showed only three peaks which were identified as (1) dimethyl sulfide, (2) chloroform solvent, and (3) benzyl bromide, by comparing their retention times with those of the authentic samples, under exactly the same experimental conditions.

(b) In the case of the NMR spectroscopic analysis of the decomposition products of benzyldimethylsulfonium bromide, five peaks were obtained of which peak '1' was due to methyl proton of TMS; which was used as the internal reference. Peak '2' is due to methyl proton of $(C\underline{H}_3)_2S$ (δ=2.1; lit. (2.1)[106]); peak '3' is for the methylene proton of $\phi C\underline{H}_2Br$ (δ=4.42: lit. (4.41)[107]). Two more peaks (not shown in the

Fig. 10 GAS CHROMATOGRAPHIC ANALYSIS OF REACTION PRODUCTS

$\Phi CH_2S^+(Me)_2Br^- \rightarrow \Phi CH_2Br + Me_2S$

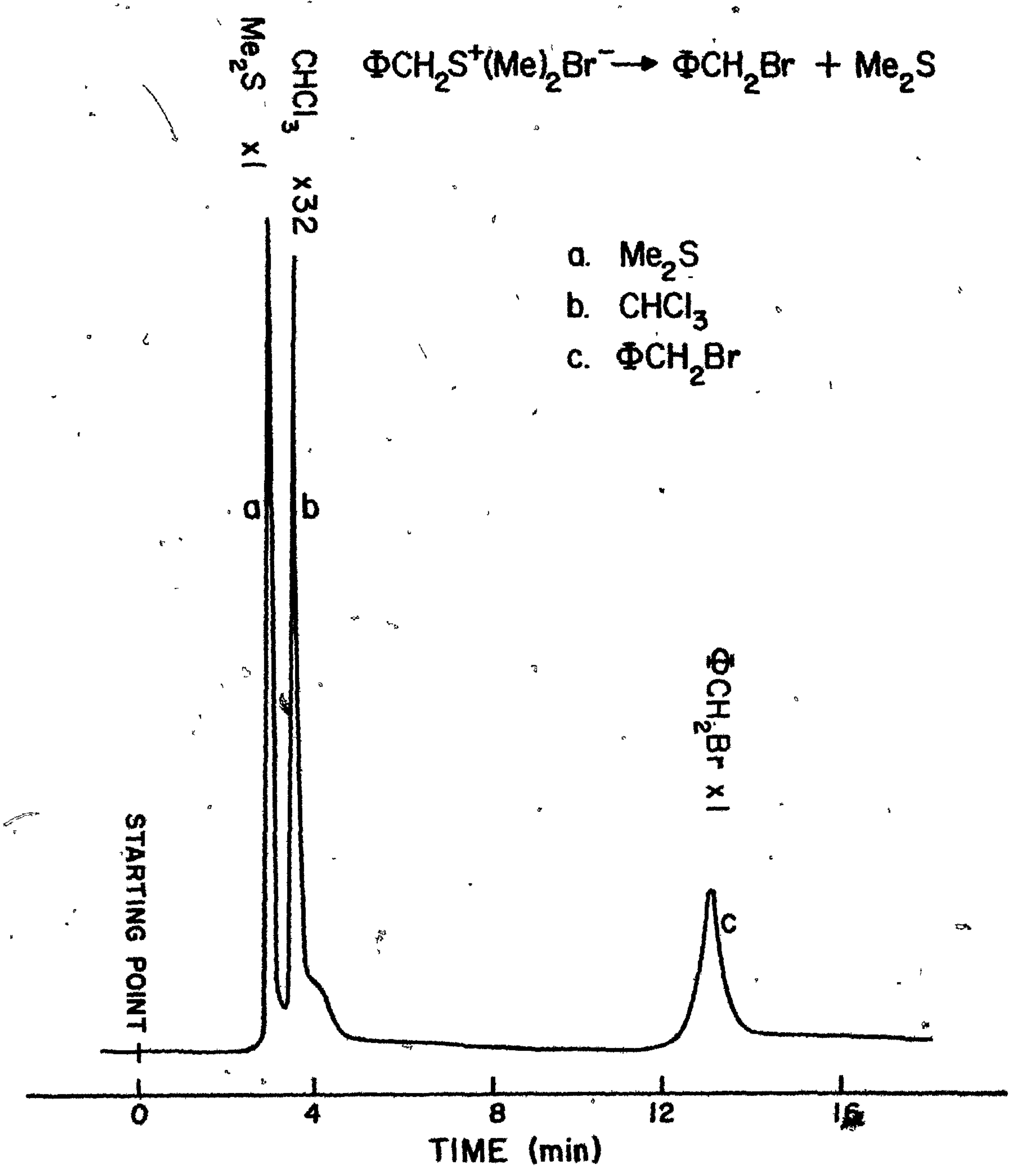


figure) are due to the proton of chloroform (δ = 7.3: lit. (7.28)[108]) and protons of the benzene ring (δ = 7.4: lit. (6-9)[109]) respectively. The analysis shown in Fig.11, indicates that the reaction goes to completion and benzyl bromide and dimethyl sulfide are the only products.

B. Kinetic measurements of the decomposition of sulfonium salts

The decomposition reaction was not followed by titrating the remaining bromide ion of the reactant against silver nitrate solution, because benzyl bromide, which is one of the reaction products, easily hydrolizes during the titration and regenerates the bromide ion. Since the decomposition of benzyldimethylsulfonium bromide gives electrically neutral species, i.e., benzyl bromide and dimethyl sulfide, it was decided that the conductimetric method to follow the reaction would be much more convenient and precise. Attempts were also made to follow the reaction by NMR spectroscopy by following the disappearance of the signal due to methyl proton of $(C\underline{H}_3)_2S^+$, present as ion-pairs mainly; these peak-heights were then converted to concentration and to conductance by means of the calibration curve (Figs. 30, 31). When the Guggenheim method was applied to these concentration and conductance data, the points were scattered, Fig. 12, 13, indicating that the NMR technique is not a good method to follow this reaction. However, a

Fig.11. Products analysis of benzyldimethylsulfonium bromide decomposition by NMR spectroscopy.

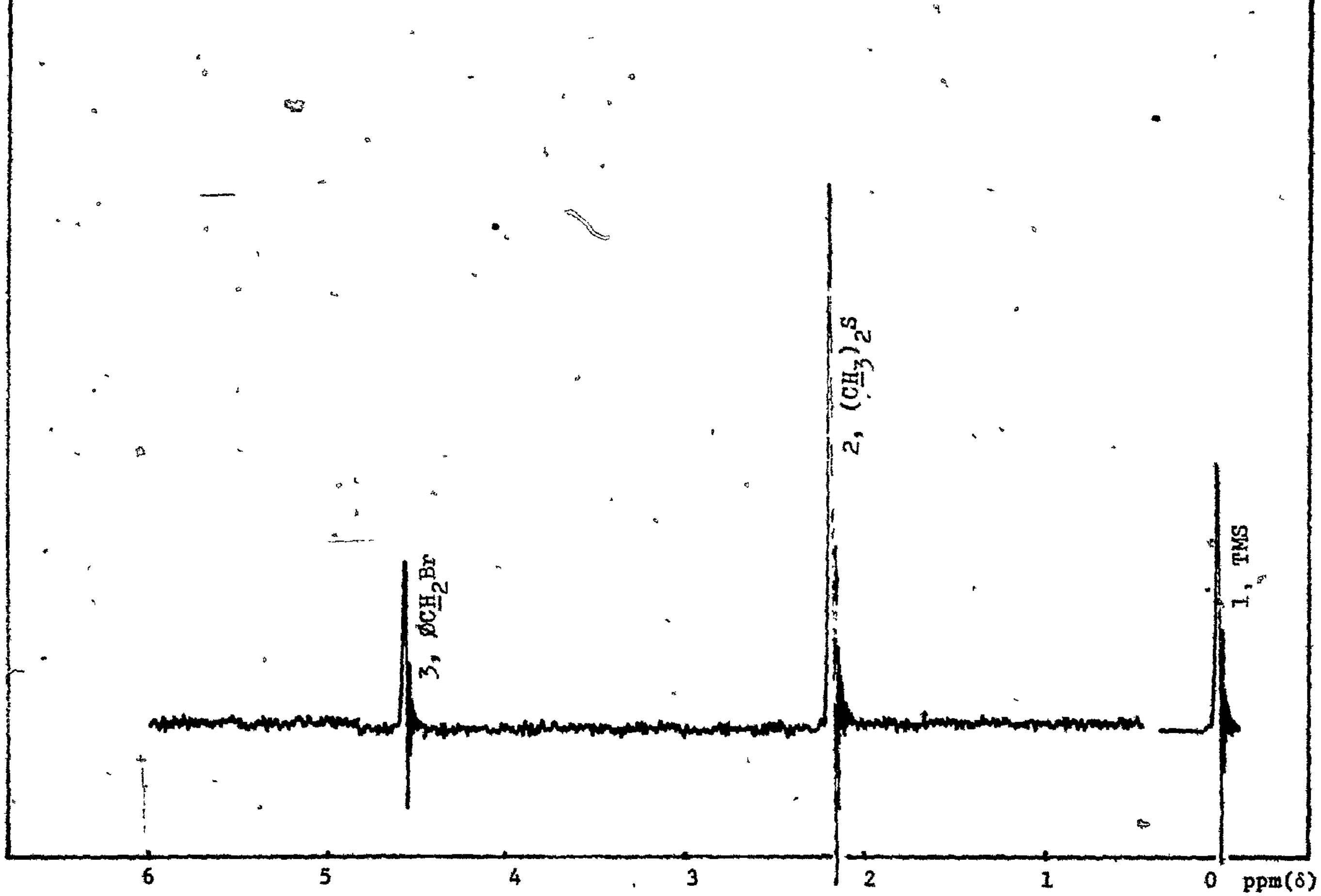


Fig. 12 PLOT OF LOG(c−c') AGAINST 't' FOR THE DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM BROMIDE IN CHLOROFORM

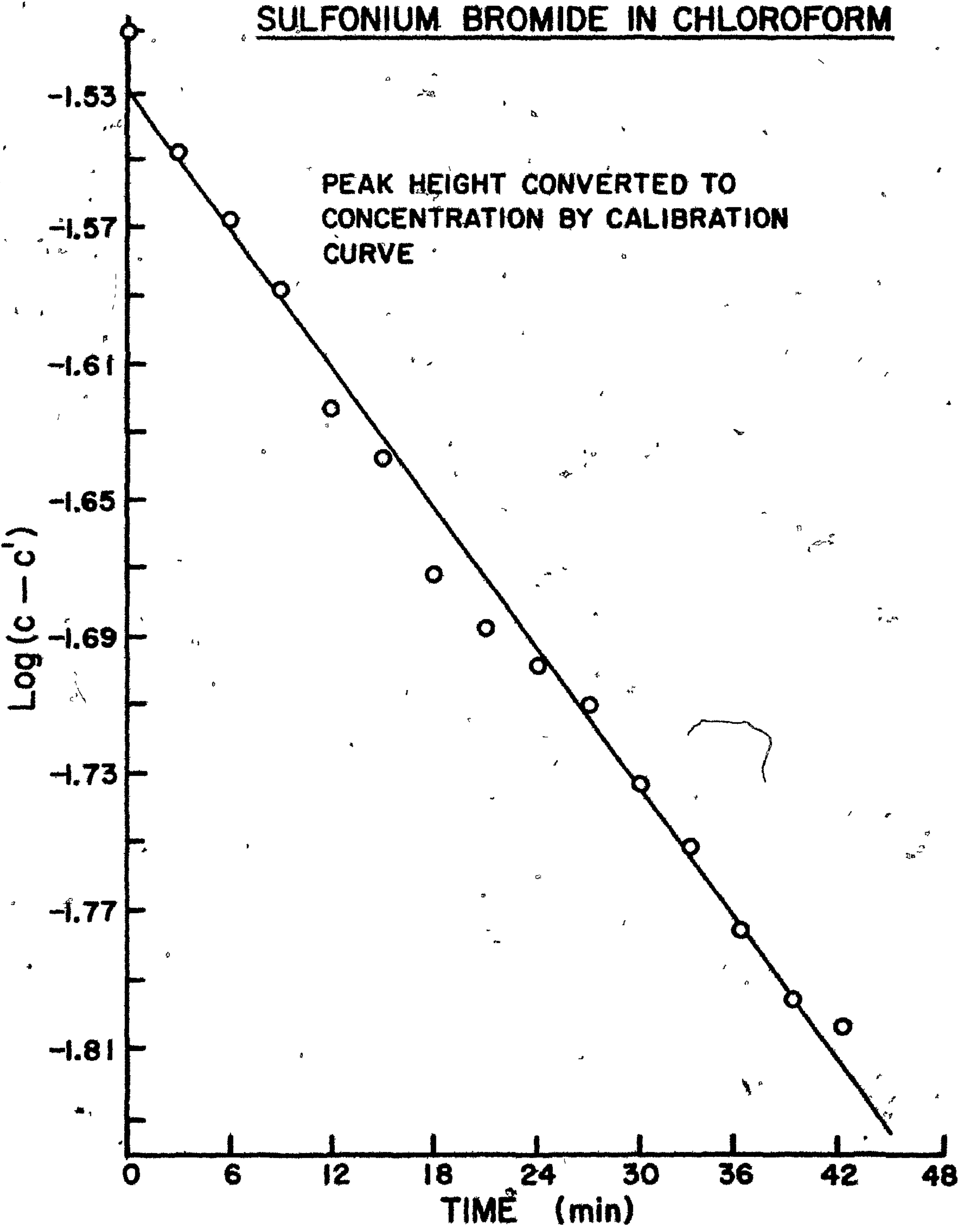


Table 12A. Decomposition of benzyldimethylsulfonium bromide (0.05M/1) in chloroform at ∿33°C.

Time	Concentration (M/1)*			
(t,min)	(c, at t)	(c',at 84+t)	(c - c')	$\log_{10}(c-c')$
0	0.0432	0.0125	0.0307	-1.5134
3	0.0423	0.0120	0.0303	-1.5489
6	0.0385	0.0115	0.0270	-1.5686
9	0.0368	0.0110	0.0258	-1.5892
12	0.0343	0.0105	0.0238	-1.6244
15	0.0330	0.0100	0.0230	-1.6383
18	0.0303	0.0090	0.0213	-1.6727
21	0.0285	0.0080	0.0205	-1.6882
24	0.0275	0.0075	0.0200	-1.6990
27	0.0268	0.0072_5	0.0195_5	-1.7100
30	0.0255	0.0070	0.0185	-1.7328
33	0.0245	0.0067_5	0.0177_5	-1.7508
36	0.0230	0.0062_5	0.0167_5	-1.7760
39	0.0220	0.0060	0.0160	-1.7959
42	0.0215	0.0057_5	0.0157_5	-1.8027

*Concentration data were obtained from NMR peak-heights by the calibration curve on p.168.

Fig. 13 PLOT OF LOG(c−c') AGAINST 't' FOR THE DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM BROMIDE IN CHLOROFORM

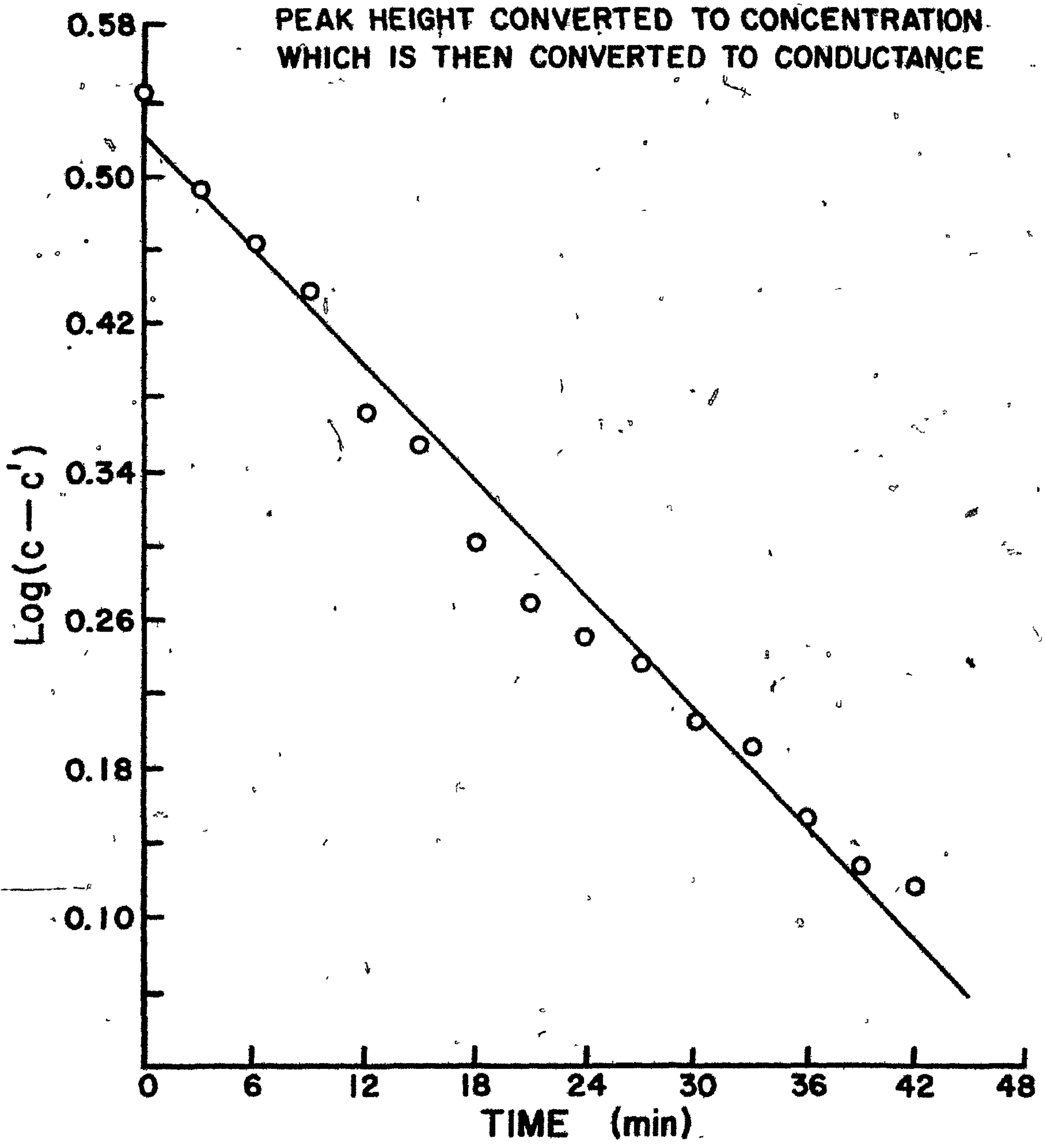


Table 13A. Decomposition of benzyldimethylsulfonium bromide (0.05M/l) in chloroform at 33°C.

Time	Conductance (μ mho)*			
(t,min)	(C,at t)	(C',at 84+t)	(C - C')	$\log_{10}$(C-C')
0	4.44	0.95	3.49	0.5428
3	4.00	0.90	3.10	0.4914
6	3.76	0.86	2.90	0.4624
9	3.56	0.83	2.73	0.4362
12	3.14	0.80	2.34	0.3692
15	3.02	0.76	2.26	0.3541
18	2.68	0.68	2.00	0.3010
21	2.46	0.61	1.85	0.2672
24	2.36	0.58	1.78	0.2504
27	2.28	0.56	1.72	0.2355
30	2.14	0.54	1.60	0.2041
33	2.08	0.52	1.56	0.1931
36	1.90	0.48	1.42	0.1523
39	1.80	0.46	1.34	0.1271
42	1.74	0.43	1.31	0.1173

*Conductance data were obtained from the concentration data of Table 12A by the calibration curve on p. 166.

comparison of the rate constant obtained at ~33°C from the concentration (k_1 = $27x10^{-5}sec^{-1}$) and conductance data (k_1 = $40x10^{-5}sec^{-1}$) with that measured by the conductimetric method (k_1 = $60x10^{-5}sec^{-1}$, at 40°C) shows that they are all of the same magnitude. This agreement in the magnitude of the rate constants by two independent techniques suggests that the same reaction is being followed by the NMR and conductimetric methods.

In the conductimetric method in order to convert the observed conductance to molar concentration, a conductance-concentration calibration curve was made (p.166) which reveals that the observed conductance is not directly proportional to the molar concentration. This is expected from the results of the electrochemical studies which showed that in a 0.05M solution, the sulfonium salt is mainly present as ion-pairs and the observed conductance is largely due to triple ions.

A very significant result was obtained when both the conductance data, and the molar concentrations obtained from them by the calibration curve, were treated by the Guggenheim method (p.170), to evaluate the rate constant. It was observed that, in a conductimetric run, when the rate constant was calculated from the molar concentration, the Guggenheim plot was curved. On the other hand a straight line was obtained from the observed conductance, as seen in Fig.14. While the correlation coefficient of the line obtained from the concentration

Fig. 14 PLOT OF LOG(C−C') AND LOG(c−c') Vs. TIME FOR THE DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM BROMIDE IN CHLOROFORM AT 25.0° C.

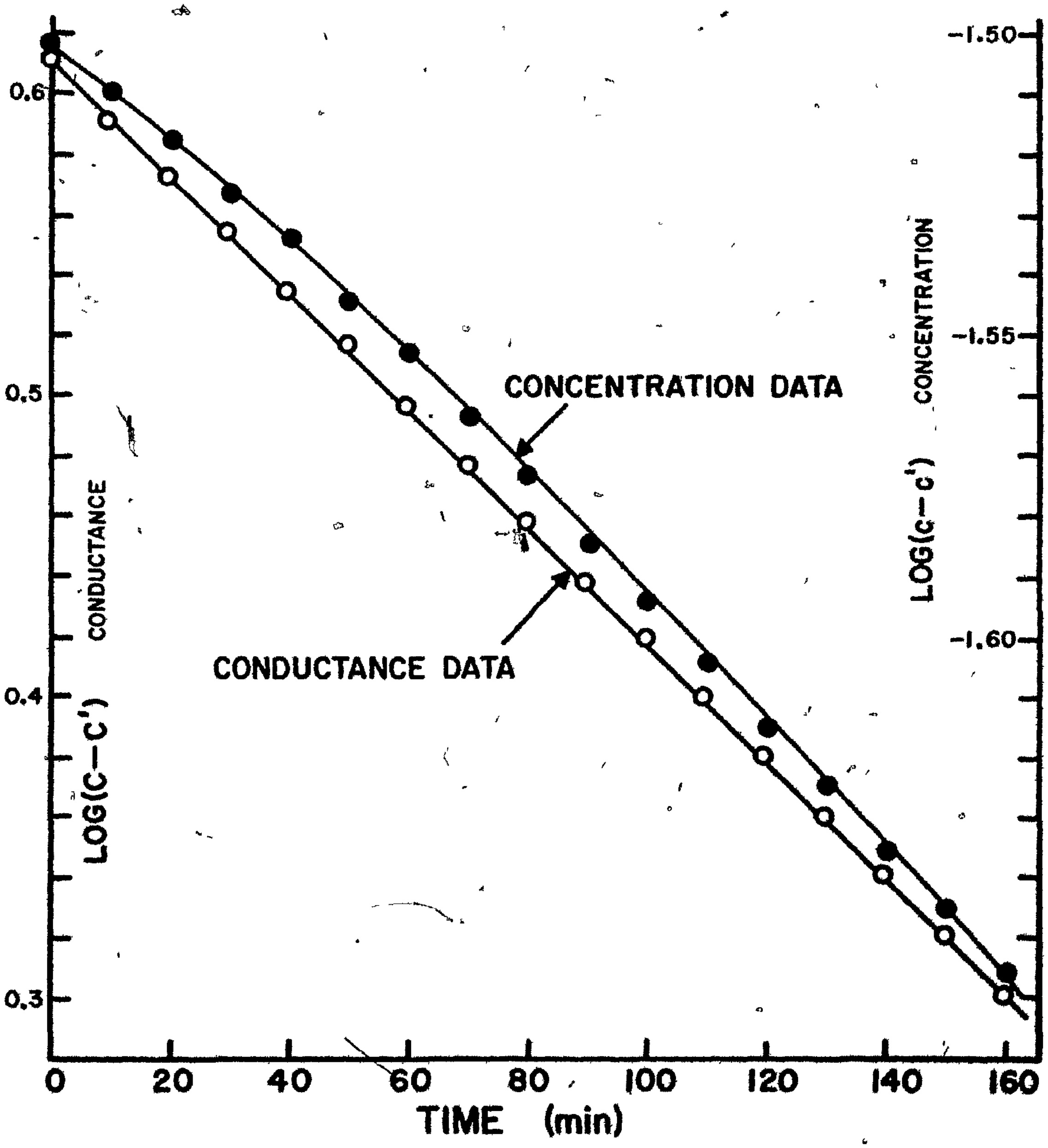


Table 14A. Decomposition of benzyldimethylsulfonium bromide (0.05M/1) in chloroform at 25°C.

Cell #3, constant: 0.2375 cm^{-1}

Time	Conductance (μ mho)			
(t,min)	(C,at t)	(C',at 320+t)	(C − C')	$\log_{10}$(C−C')
—	5.286	1.200	4.086	0.6113
10	5.036	1.137	3.899	0.5909
20	4.816	1.074	3.742	0.5731
30	4.596	1.018	3.578	0.5536
40	4.384	0.958	3.426	0.5348
50	4.184	0.930	3.254	0.5124
60	3.987	0.855	3.132	0.4958
70	3.803	0.806	2.997	0.4767
80	3.626	0.760	2.866	0.4573
90	3.459	0.715	2.744	0.4384
100	3.297	0.674	2.623	0.4188
110	3.143	0.634	2.509	0.3995
120	2.990	0.596	2.394	0.3791
130	2.850	0.559	2.291	0.3600
140	2.715	0.523	2.192	0.3408
150	2.586	0.491	2.095	0.3212
160	2.454	0.460	1.994	0.2997

Table 14B: Decomposition of benzyldimethylsulfonium bromide (0.05M/1) in chloroform at 25.0°C.

Cell #3, constant: 0.2375 cm^{-1}

Time	Concentration (M/1)*			
(t,min)	(c,at t)	(c',at 320+t)	(c – c')	$\log_{10}(c-c')$
–	0.0475	0.0160	0.0315	-1.5014
10	0.0463	0.0154	0.0309	-1.5098
20	0.0450	0.0147	0.0303	-1.5183
30	0.0438	0.0140	0.0298	-1.5255
40	0.0425	0.0133	0.0292	-1.5343
50	0.0413	0.0128	0.0285	-1.5449
60	0.0398	0.0118	0.0280	-1.5525
70	0.0386	0.0113	0.0273	-1.5636
80	0.0373	0.0106	0.0267	-1.5732
90	0.0360	0.0100	0.0260	-1.5847
100	0.0348	0.0094	0.0254	-1.5949
110	0.0336	0.0088	0.0248	-1.6053
120	0.0326	0.0084	0.0242	-1.6159
130	0.0314	0.0077	0.0237	-1.6250
140	0.0304	0.0073	0.0231	-1.6361
150	0.0294	0.0068	0.0226	-1.6456
160	0.0283	0.0063	0.0220	-1.6573

*Concentrations obtained by converting the conductance data of Table 14A by means of the calibration curve on p. 166.

data is only 0.99642, it is 0.99996 for the graph obtained from the conductance data. Although the former correlation coefficient may be acceptable in certain instances, it is obvious that in the present case the reaction is first order with respect to conductance, rather than concentration. The rate constant, k, was then measured from the slope, -k/2.303, of the straight line, obtained from logarithm of the conductance versus time. In all cases, very good straight lines (correlation coefficient, 0.9999+) were obtained from the observed conductance data. In this reaction, the rate is proportional not to the molar concentration, but to ionic concentration.

From the foregoing observation, the following cases may be considered.

(a) Suppose the reaction is a unimolecular decomposition of the ion-pair, it may be expressed by equation (41), in which for simplicity, the sulfonium salt is given the symbol $R_3S^+X^-$,

$$R_3S^+X^- \xrightarrow[\text{slow}]{k_a} R_2S + R^+ + X^- \xrightarrow[\text{fast}]{} R_2S + RX \qquad (41)$$

then the rate is given by,

$$-d[R_3S^+X^-]/dt = k_a[R_3S^+X^-] \qquad (42)$$

Ignoring the activity coefficients, the association constant, K, for the sulfonium salt is given by,

$$R_3S^+ + X^- \underset{}{\overset{K}{\rightleftarrows}} R_3S^+X^- \qquad (43)$$

$$\alpha c \quad \alpha c \qquad (1-\alpha)c$$

where α is the degree of ionization at molar concentration 'c'

$$K = [R_3S^+X^-]/[R_3S^+][X^-] \qquad (44)$$

$$= (1-\alpha)c/\alpha^2c^2 \qquad (45)$$

Substitution in equation (42) yields

$$-d[R_3S^+X^-]/dt = k_aK[R_3S^+][X^-] \qquad (46)$$

$$= k_a(1-\alpha)c \qquad (47)$$

Since this compound is a weak electrolyte in chloroform solvent, α is negligible compared to unity; and hence the rate becomes,

$$-d[R_3S^+X^-]/dt = k_ac \qquad (48)$$

Thus for this mechanism, the rate of the reaction is proportional to the molar concentration; and is contrary to our experimental results.

(b) For a unimolecular decomposition of an ion:

$$R_3S^+X^- \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} R_3S^+ + X^-; \quad R_3S^+ \xrightarrow[\text{slow}]{k_b} R_2S + R^+ \xrightarrow[\text{fast}]{X^-} R_2S + RX \qquad (49)$$

The rate expression for this mechanism is[93],

$$-d[R_3S^+]/dt = k_b[R_3S^+] \qquad (50)$$

$$= k_b\alpha c \qquad [[R_3S^+] = \alpha c] \qquad (51)$$

In this expression the rate is proportional not to the molar concentration, but to the ionic concentration.

(c) If both the mechanism (a) and (b) are operative simultaneously, then, invariably, mixed kinetics would be obtained[96].

(d) An S_N2 reaction, such as the decomposition of trimethylsulfonium cation in ethanol, has been studied by Pocker and Parker[32]. The authors suggested the following rate expressions:

In the S_N2 process,

$$R_3S^+ + X^- \xrightarrow{k_c} R_2S + RX \qquad (52)$$

and

$$-d[R_3S^+]/dt = k_c[R_3S^+][X^-] \qquad (53)$$

$$= k_c\alpha^2c^2 \qquad (54)$$

$$= k_c(1-\alpha)c/K \qquad (55)$$

$$= k'c \qquad (56)$$

So, the bimolecular reaction: $R_3S^+ + X^- \longrightarrow R_2S + RX$ will follow first order kinetics in molar concentration (equation 56) if the sulfonium salt in chloroform solution is a weak electrolyte; whereas, a second order kinetics in molar concentration would be given, if the salt were a strong electrolyte in the solvent (54).

Equation (51) on integration gives the rate constant

$$k_b = \frac{2.303}{t} \log \frac{\alpha_o a}{\alpha_t (a-x)} \qquad (57)$$

where α_o and α_t are the degrees of ionization of the molar concentration a and (a - x) at the beginning time and at time t, respectively. For weak electrolytes,

$$\alpha = \Lambda/\Lambda^\circ \qquad (58)$$

and Λ° is a constant. By definition, the equivalent conductivity is given by

$$\Lambda = \frac{1000\ L}{C_{eq}} \qquad (59)$$

The specific conductance L is obtained from the cell constant ρ and the observed conductance C, from the relation,

$$L = \rho C \qquad (60)$$

Applying the relationship from (57) to (60), the rate constant is given by,

$$k_b = \frac{2.303}{t} \log \frac{C_o}{C} \qquad (61)$$

Since the rate of decomposition is not dependent on the concentration, and the observed rate is constant on the basis of the measured conductance, (equation (50)), case (b) is the most probable mechanism for the decomposition of the sulfonium salt in chloroform, and the reaction must go via either a single or a triple ion. Since at 0.05M the current is carried by triple ions almost exclusively, it is most likely that the reaction is going via the triple ion and not the single ion.

(a) Effect of salt concentration

Finding from the kinetic measurements that the decomposition of the sulfonium salt in chloroform is a first order reaction, which involves ionic concentration rather than molar concentration, it was thought to be useful to study the dependence of the first order rate constant with respect to the initial concentration of the sulfonium salt.

Hyne has studied the effect of salt concentration on the reaction rate for the solvolysis of dimethyl-t-butylsulfonium chloride in water and 0.55 mole fraction ethanol[33]. The point of major interest in these data is the effect of change of initial concentration of the salt on the observed rate. For solvolysis in water, variation of the concentration of the salt has no measurable effect on the rate; but in 0.55 mole fraction ethanol, the observed rates are significantly different at different concentrations of the sulfonium chloride used, and are higher for higher salt concentrations.

In the present studies, the rate constants for the decomposition of benzyldimethylsulfonium chloride, -bromide, and -iodide, have been measured at different concentrations, and the results are in Tables 15-17 respectively; the corresponding graphs are shown in Figs. 15-17.

In every case, it is found that the rate of decomposition decreases with increasing concentration of the salt, and at higher concentrations, this decrease in rate tends to reach a minimum. Considering the particular case of benzyldimethylsulfonium bromide, it is seen that, this salt suffers a decrease of about 15% in rate when the salt concentration is raised from 0.025 to 0.05M. Irrespective of whether the mechanism is unimolecular or bimolecular in the decomposition of sulfonium salts, the formal charge is dispersed (although to a different degree) in the transition state:

$$S_N1 \;:\; R_3S^{+} \longrightarrow \underset{\text{(transition state)}}{[\overset{+\delta}{R} \text{ ---- } \overset{+\delta}{SR_2}]} \xrightarrow[\text{fast}]{X^{-}} R_2S + RX$$

$$S_N2 \;:\; R\text{—}\overset{+}{S}R_2 + X^{-} \longrightarrow \underset{\text{(transition state)}}{[\, R_2\overset{+\delta}{S}\text{----}\overset{+\delta}{R}\text{----}\overset{-\delta}{X} \,]} \longrightarrow R_2S + RX$$

Since the charge is dispersed in the transition state, the rate of the reaction should decrease as the ionizing power of the medium is increased.

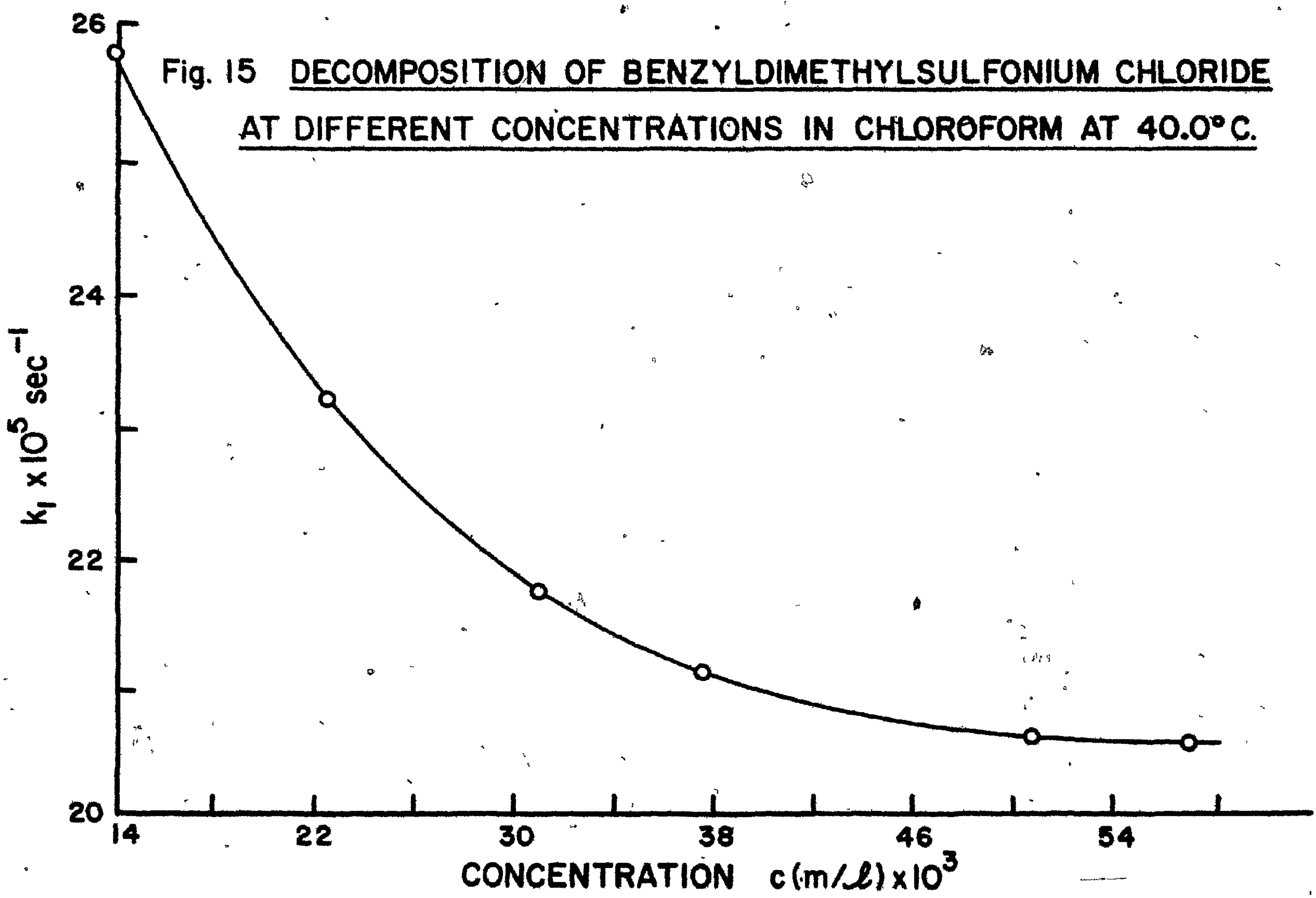


Fig. 15 DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM CHLORIDE AT DIFFERENT CONCENTRATIONS IN CHLOROFORM AT 40.0° C.

[redacted]

Table 15. Decomposition of benzyldimethylsulfonium chloride at different molar concentrations in chloroform at 40.0°C.

Concentration (M/l)x10^3	Rate constant (k_1x10^5 sec^{-1})
14.00	25.8
22.50	23.1
31.40	21.7
37.60	21.1
50.76	20.6
57.00	20.6

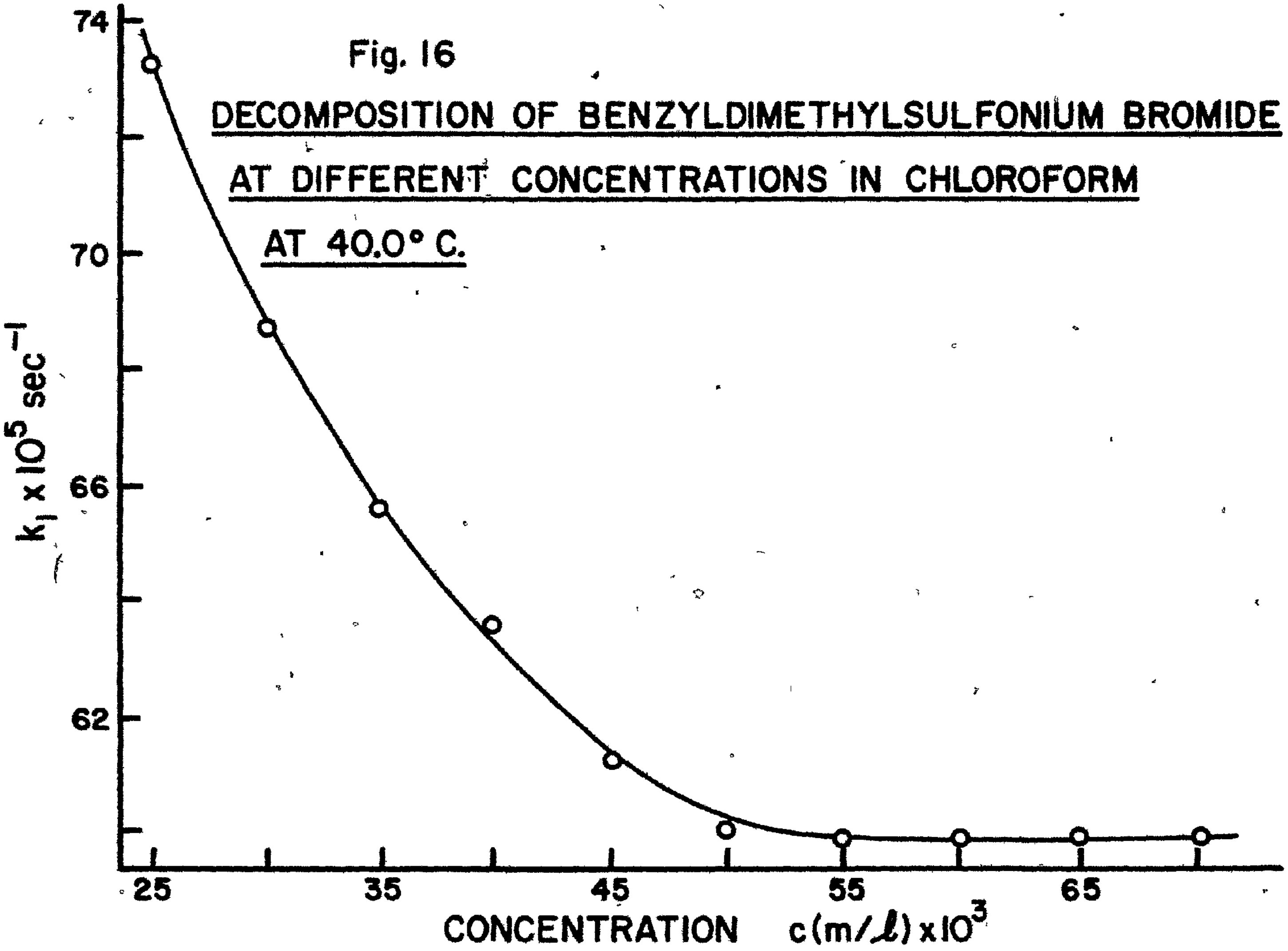


Fig. 16

DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM BROMIDE AT DIFFERENT CONCENTRATIONS IN CHLOROFORM AT 40.0° C.

Table 16. Decomposition of benzyldimethylsulfonium bromide at different molar concentrations in chloroform at 40.0°C.

Concentration (M/l)x10^3	Rate constant (k_1x10^5 sec^{-1})
25.0	73.2
30.0	68.6
35.0	65.8
40.0	63.7
45.0	61.3
50.0	60.0
55.0	60.0
60.0	60.1
65.0	60.0
70.0	60.0

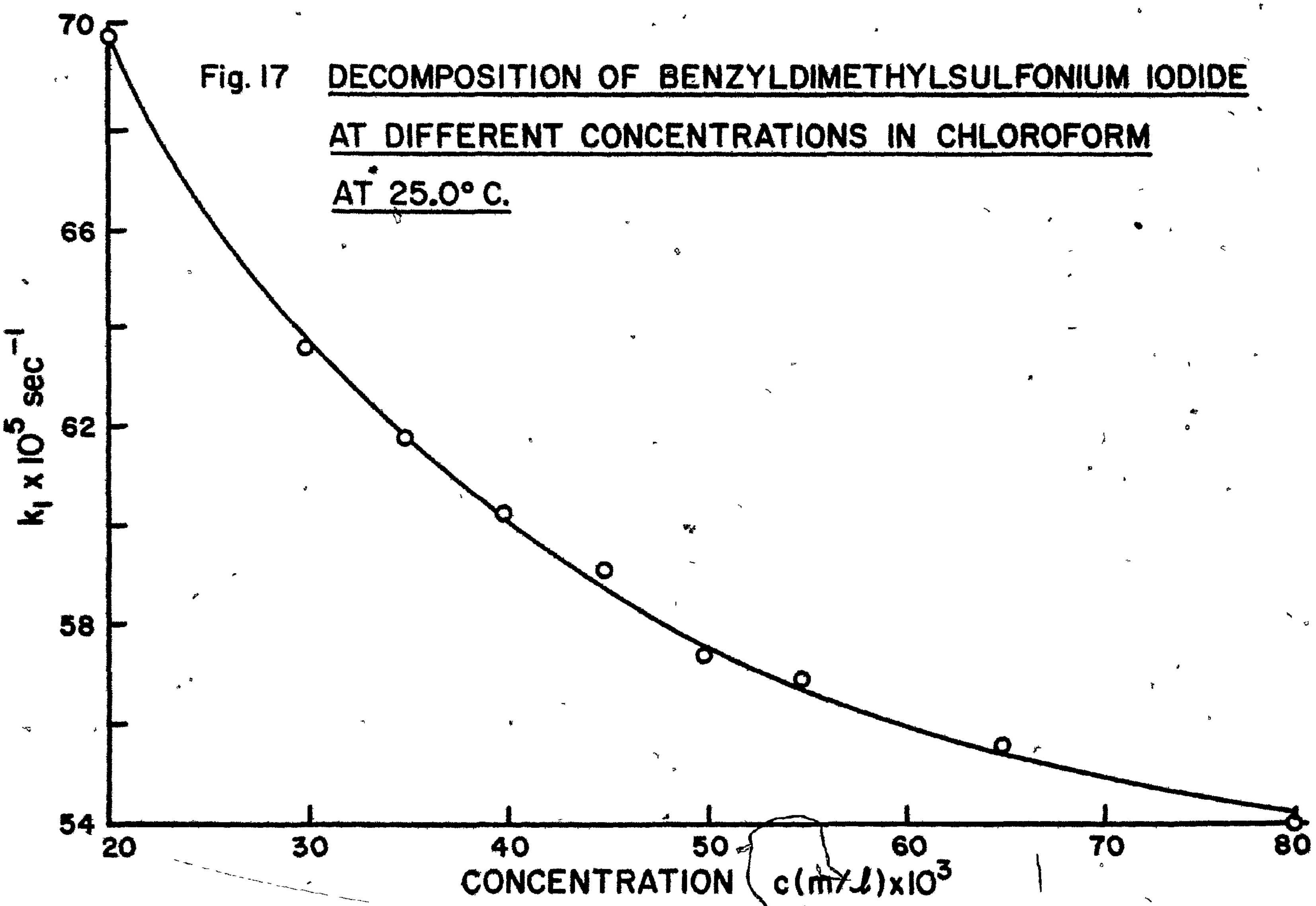


Fig. 17 DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM IODIDE AT DIFFERENT CONCENTRATIONS IN CHLOROFORM AT 25.0° C.

[redacted]

Table 17. Decomposition of benzyldimethylsulfonium iodide at different molar concentrations in chloroform at 25.0°C.

Concentration (M/l)x10^3	Rate constant (k x10^5sec^{-1})
20.0	69.8
30.0	63.5
35.0	61.8
40.0	60.3
45.0	59.2
50.0	57.3
55.0	56.8
65.0	55.6
80.0	53.9

Therefore, if this would have been only an effect due to increasing ionic strength of the medium, then the rate would continue to fall with increasing concentration of the salt, since irrespective of the mechanism, the charge is dispersed in the transition state.

From the electrochemical studies, it is evident that the sulfonium salt is mainly present as ion-pairs in chloroform solution, in the concentration range of the experiments. Since the decomposition of the ion-pair is inconsistent with the kinetic observation, and the rate is proportional to ionic concentration, it is possible that the decomposition proceeds via single sulfonium ion and/or a triple ion, which are present in this concentration range. At this stage it is difficult to explain the variation of the rate constant with the concentration of the substrate, but it is probable that, with increasing concentration, more sulfonium salt is tied up as stable species, such as ion-pair or other higher ionic aggregates. At sufficiently high concentration such as (.05M) the concentration of the decomposable species is also high and the reaction rate is not affected in noticeable degree.

In the case of the decomposition of ammonium salts, which was studied previously in these laboratories, the rate constant of the decomposition reaction, was found to be independent of the initial concentration of the ammonium salt. In this case, the ionic species that undergoes decomposition, is probably present in larger quantity, and is not affected by the change in concentration. If we compare the concentrations of the triple ions of the ammonium salt to that of the corresponding sulfonium salt, we see from Table 11, p.83 that the concentration of the ammonium triple ion is several times greater than that of the sulfonium triple ion.

(b) Effect of anion type

The influence of the anion type on the decomposition of the sulfonium salts has been studied quite extensively in different solvents and solvent mixtures other than chloroform. Pocker and Parker[32] studied the decomposition of the trimethylsulfonium cation with different anions at ionic strength 0.04 M in ethanol at 100°C, and observed that the reaction rates fit equation (62), where 'n' is the Swain and Scott nucleophilic constant of the anion in water:

$$\log k_2^{0.04} = -5.50 + 0.81(n) \qquad (62)$$

Hyne[33] found that for t-butyldimethylsulfonium salts, the rate dependence on the anion character is shown to develop as the dielectric constant of the medium is lowered; in pure aqueous medium, the rate of the sulfonium salts decomposition was independent of the nature of the anion.

Hughes, Ingold and Pocker[30] observed that for the reaction of trimethylsulfonium bromide, -chloride, and -iodide, although the first order rate coefficients appear to be more constant than the second order rate coefficients, the reactivity of the various halide ions is not the same. With 0.01M solutions at 100°C in ethanol, the iodide is ca. 9 times more reactive than the bromide, which in turn is about 4.4 times more reactive than the chloride.

All these results indicate that the anion is playing a significant role in the decomposition of the sulfonium salt.

In the present work, in order to investigate the dependence of the rate constant on the anion character, in chloroform medium, five sulfonium salts, namely, benzyldimethylsulfonium bromide, -chloride, -iodide, -cyanide, and -perchlorate were examined although the cyanide was found to be too insoluble in chloroform. It is apparent from Table 18 that in a 0.05M solution, the iodide decomposes 8 times faster than the bromide, and the latter is 3 times more reactive than the chloride; while the perchlorate did not decompose in chloroform even at elevated temperature.

When the nucleophilicity of these anions was plotted against the logarithm of respective rate constant, a linear relationship is observed, Fig.18. The nucleophilicity of the anions according to the Swain-Scott equation together with the rate constants is given below.

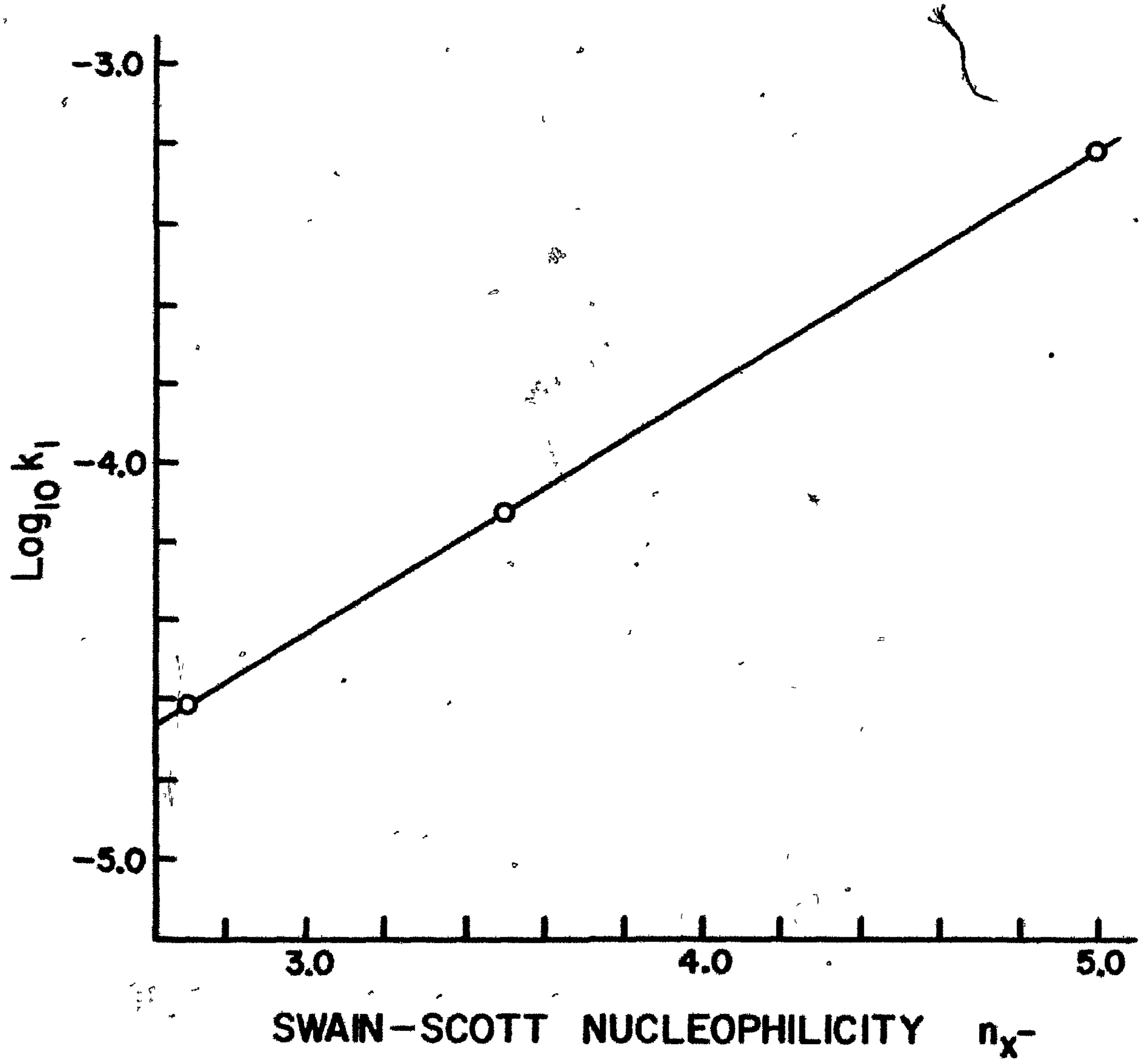
Table 18. The nucleophilicity of the halides and the rate constants for the decomposition of benzyldimethylsulfonium halides in chloroform at 25.0°C.

Anion	Nucleophilicity of anion(n_{X^-})[110]	$k_1 \times 10^5 sec^{-1}$	$\log_{10}k_1$
Cl^-	2.7	2.4	-4.62
Br^-	3.5	7.3	-4.14
I^-	5.0	57.3	-3.24

The slope of the straight line (Fig.18) equals 0.6. The slope measures the sensitivity of the sulfonium salt to changes in nucleophilicity, and is a constant of the substrate. This value of 0.6 is comparable to 0.8 obtained by Pocker and Parker for the decomposition of trimethylsulfonium salts in ethanol. This indicates that the benzylsulfonium cation in chloroform has similar sensitivity to that of trimethylsulfonium cation in alcohol towards nucleophiles.

This linear relationship between the nucleophilicity of the anion and the logarithm of rate constant clearly indicates that the anion is directly involved in the decomposition of the sulfonium salt. This is further confirmed by the fact that benzyldimethylsulfonium perchlorate did ~~not~~ decompose even at elevated temperature, as expected, because

Fig. 18 PLOT OF $LOG_{10}k_1$ vs NUCLEOPHILICITY (n_{X^-}) OF THE ANION



perchlorate is a very poor nucleophile. A similar result was also obtained by Swain and Kaiser, who observed that trimethylsulfonium perchlorate remained undecomposed in 90% acetone, even at 100°C.

Since the decomposition of the sulfonium salt onviously requires the nucleophilicity of the anion, the decomposition cannot proceed via a single sulfonium ion. The decomposition via an ion-pair has already been shown inconsistent with the kinetic results. That the rate of decomposition is proportional to ionic concentration, and it requires the nucleophile, is consistent only with the mechanism, which proceeds via a triple ion. Therefore, the decomposition of the sulfonium salt must proceed through $\mathrm{S^{+}Br^{-}S^{+}}$ and/or $\mathrm{Br^{-}S^{+}Br^{-}}$.

Although ammonium salts with different anions have not been studied in these laboratories, a comparison of the rate constant, obtained here, with that by Stewart and Weale[111] for the bromide shows that the iodide decomposes approximately ten times faster than the bromide. This result is similar to that obtained in the present investigation for the sulfonium salt; and indicates that in both the cases, the anion plays a significant role in the reaction.

Effects of added nucleophile

From the result of the previous experiment, that the nucleophilicity of the anion is essential in order to decompose the sulfonium salt, it was decided to study the decomposition of the sulfonium salt in the presence of n-tetrabutylammonium salts; the nucleophilicity of the anion of these salts varied from 'zero' (for perchlorate) to 'several hundreds' (for phenoxide, and thiophenoxide)[112]. It is hoped that the manner in which these added nucleophiles will affect the reaction rate and the products of the reaction, will furnish information valuable in establishing the reaction mechanism.

Benzyldimethylsulfonium bromide was allowed to decompose in the presence of each of n-tetrabutylammonium bromide, -iodide, -perchlorate, -phenoxide, and-thiophenoxide. In addition to these, both benzyldimethylsulfonium perchlorate and -iodide, were allowed to react in the presence of n-tetrabutylammonium bromide. The rate constants are presented in Tables 19A-22A together with the respective graphs in Figs. 19-22.

The results of this study are very interesting as seen from Figs. 19-22. Irrespective of the nature of the added anion, there is a sharp decrease in the rate constant of benzyldimethylsulfonium bromide decomposition for adding only 0.00125M of the ammonium salt in the reaction medium. Except for n-tetrabutylammonium iodide, this sharp fall in the rate constants then slackens and by the time the concentration of the added salt reaches 0.0025M the decrease in the rate constant is not only gradual but also linear.

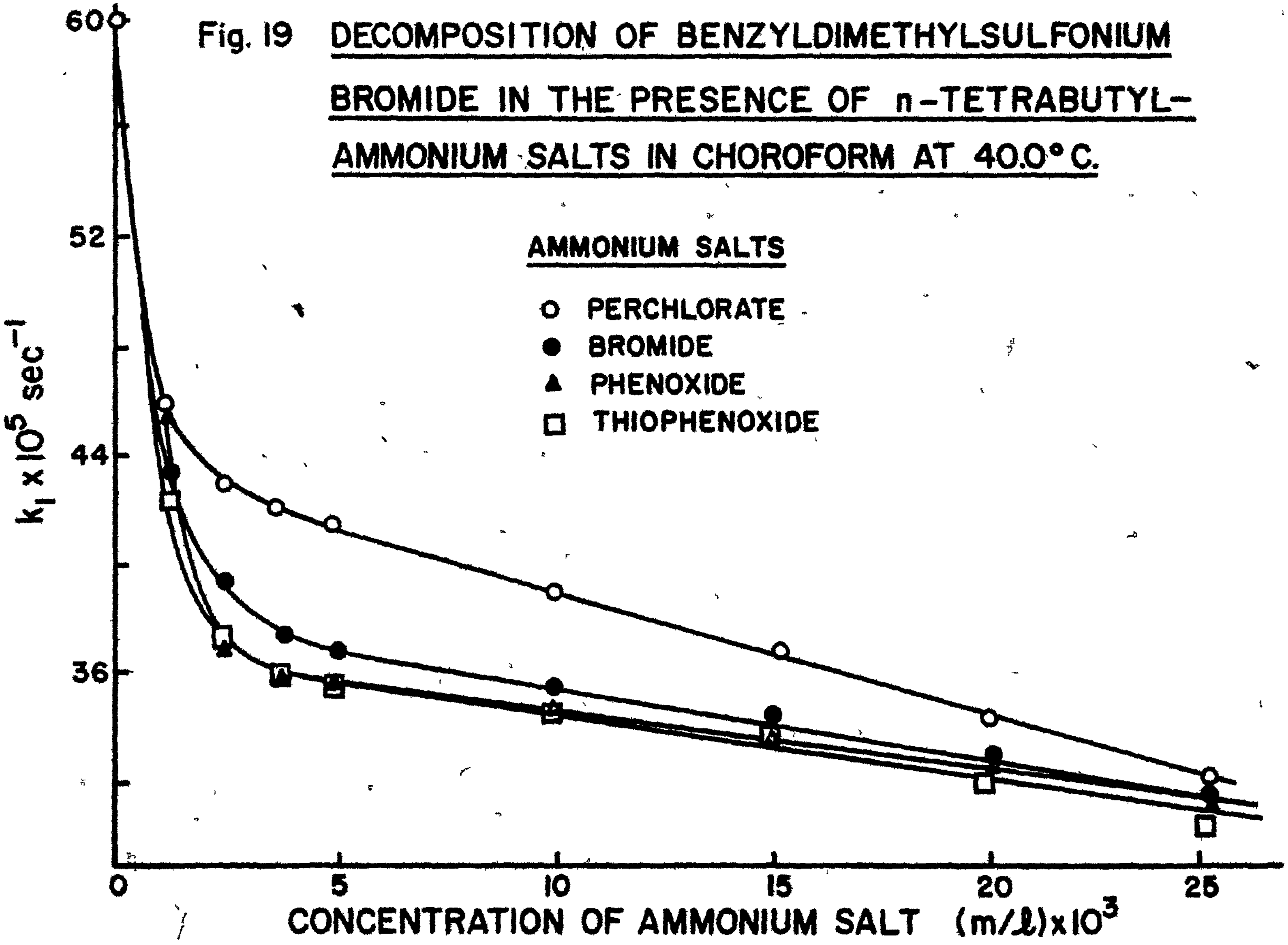


Fig. 19 DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM BROMIDE IN THE PRESENCE OF n-TETRABUTYLAMMONIUM SALTS IN CHOROFORM AT 40.0° C.

Table 19A. Decomposition of benzyldimethylsulfonium bromide in the presence of added tetra-n-butylammonium bromide in chloroform at 40.0°C.

Concentration of the Sulfonium Salt: 0.05 M/1

Concentration of added $n\text{-}Bu_4N^+Br^-$ (M/1)x10^3	Rate constant (k_1x10^5sec^{-1})
0.00	60.0
1.25	43.4
2.50	39.6
3.75	37.2
5.00	36.7
10.00	35.5
15.00	34.4
20.00	32.9
25.00	31.5

Table 19B. Decomposition of benzyldimethylsulfonium bromide in the presence of added tetra-n-butylammonium perchlorate at 40.0°C.

Concentration of the sulfonium salt: 0.05 M/l. Solvent: $CHCl_3$

Concentration of added n-$Bu_4N^+ClO_4^-$ (M/lx10^3)	Rate constant (k_1x10^5sec^{-1})
0.00	60.0
1.25	46.0
2.50	43.0
3.75	42.2
5.00	41.8
10.00	38.9
15.00	36.8
20.00	34.5
25.00	32.3
30.00	29.4

Table 19C. Decomposition of benzyldimethylsulfonium bromide in the presence of added Tetra-n-Butylammonium phenoxide in chloroform at 40.0°C.

Concentration of the sulfonium salt: 0.05 M/l

Concentration of added $n\text{-}Bu_4N^+PhO^-$ (M/l)x10^3	Rate constant (k_sx10^5sec^{-1})
0.00	60.0
1.25	45.8
2.50	37.0
3.75	36.0
5.00	35.9
10.00	34.8
15.00	34.0
20.00	32.9
25.00	31.3

Table 19D. Decomposition of benzyldimethylsulfonium bromide in the presence of added tetra-n-butylammonium thiophenoxide in chloroform at 40.0°C.

Concentration of the sulfonium salt: 0.05 M/1

Concentration of added $n\text{-}Bu_4N^+PhS^-(M/1)\times10^3$	Rate constant ($k \times 10^5 sec^{-1}$)
0.00	60.0
1.25	42.0
2.50	37.0
3.75	36.2
5.00	35.4
10.00	34.6
15.00	34.0
20.00	32.7
25.00	31.3

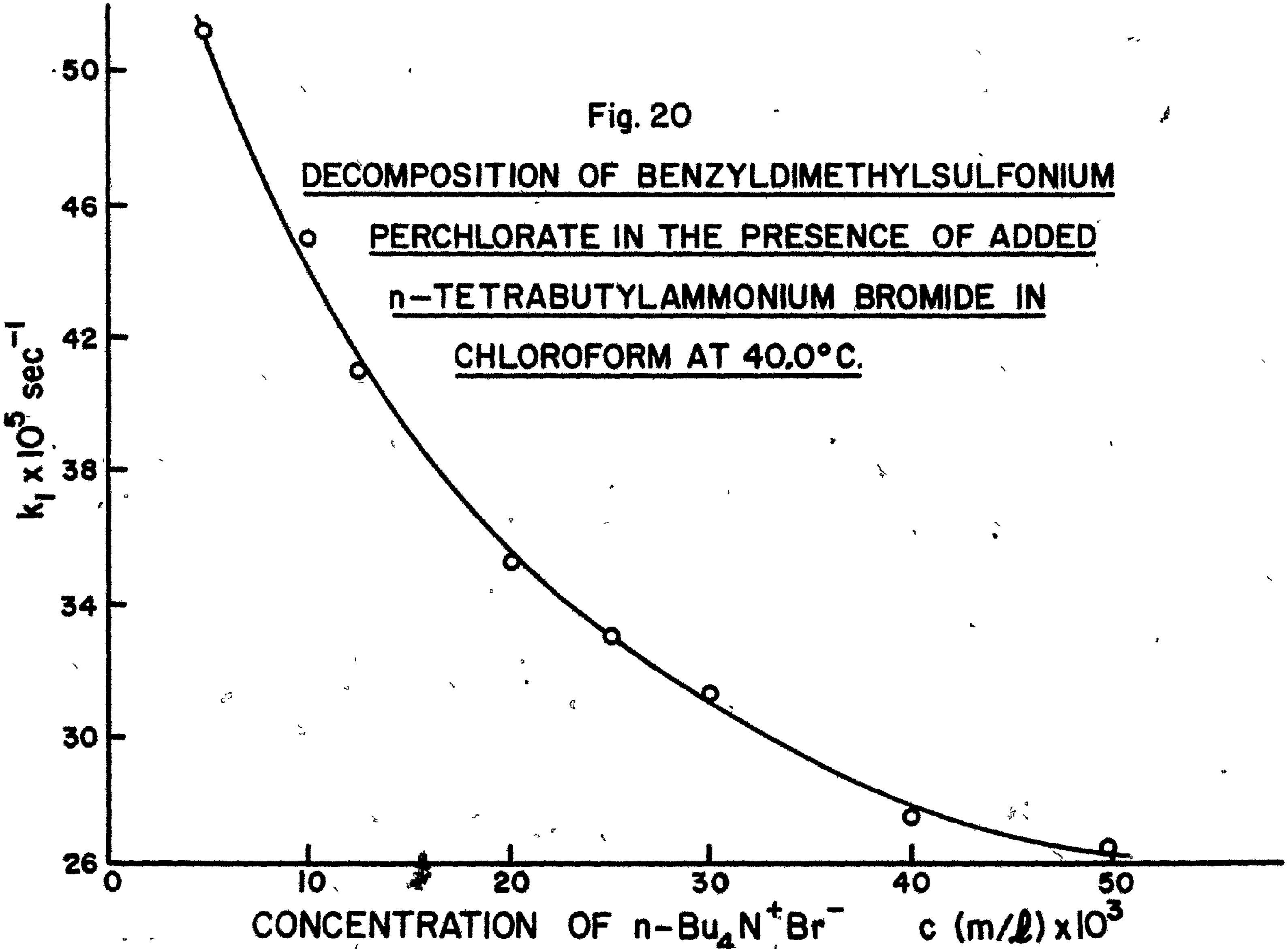


Fig. 20

DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM PERCHLORATE IN THE PRESENCE OF ADDED n-TETRABUTYLAMMONIUM BROMIDE IN CHLOROFORM AT 40.0°C.

[redacted]

Table 20A. Decomposition of benzyldimethylsulfonium perchlorate in the presence of added tetra-n-butylammonium bromide in chloroform at 40.0°C.

Concentration of the sulfonium salt: 0.025 M/1

Concentration of added $n\text{-}Bu_4N^+Br^-(M/1)\times10^3$	Rate constant $(k\times10^5 sec^{-1})$
0.00	–
5.00	51.3
10.00	45.0
12.50	41.1
20.00	35.3
25.00	33.0
30.00	31.3
40.00	27.6
50.00	26.6

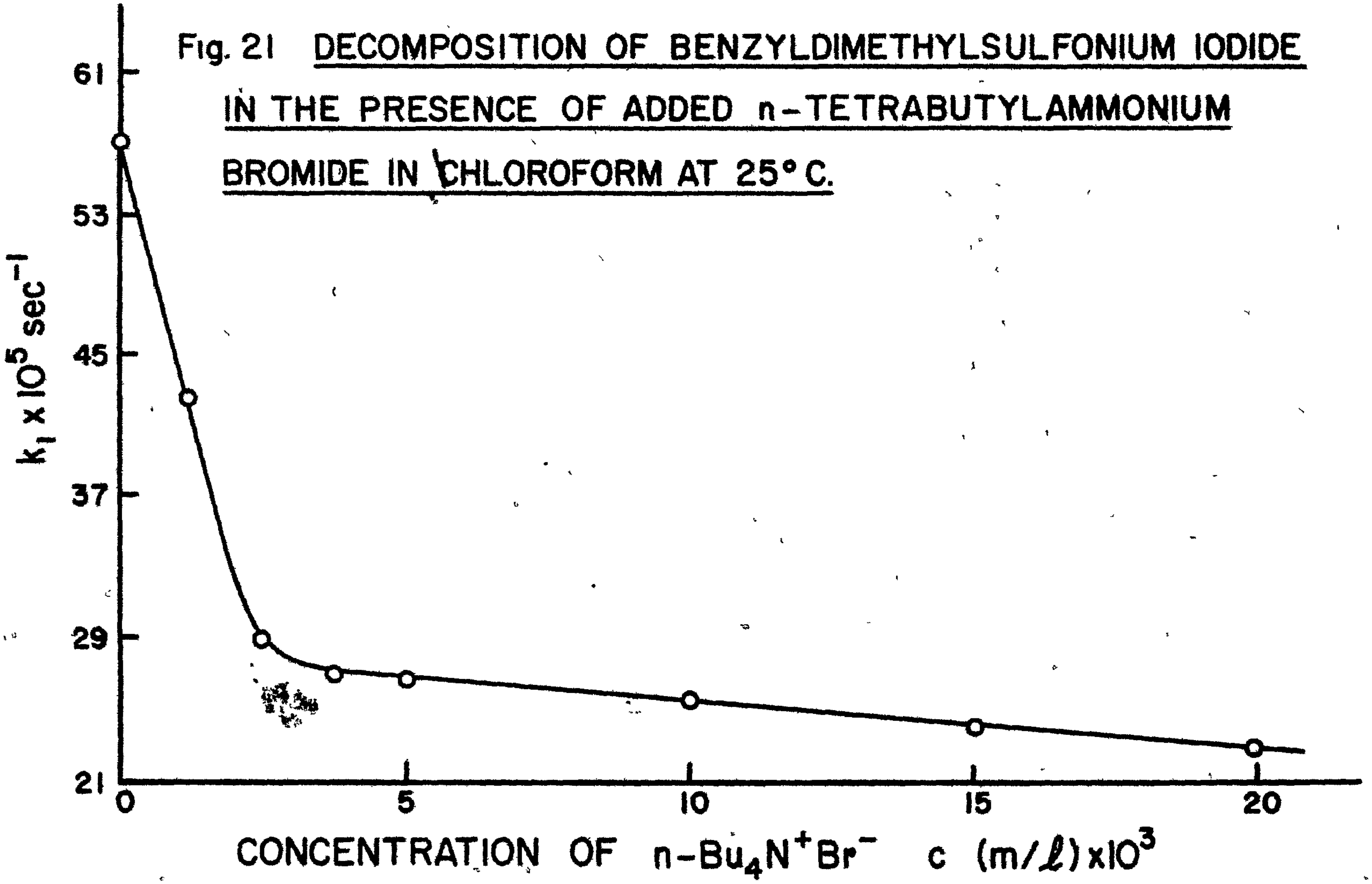


Fig. 21 DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM IODIDE IN THE PRESENCE OF ADDED n-TETRABUTYLAMMONIUM BROMIDE IN CHLOROFORM AT 25° C.

[redacted]

Table 21A. Decomposition of benzydimethylsulfonium iodide in the presence of added tetra-n-butylammonium bromide in chloroform at 25.0°C.

Concentration of the Sulfonium salt: 0.05 M/1

Concentration of added n-$Bu_4N^+Br^-$(M/1)x10^3	Rate constant (k x$10^5$$sec^{-1}$)
0.00	57.3
1.25	42.9
2.50	29.1
3.75	27.2
5.00	26.8
10.00	25.6
15.00	24.0
20.00	22.9

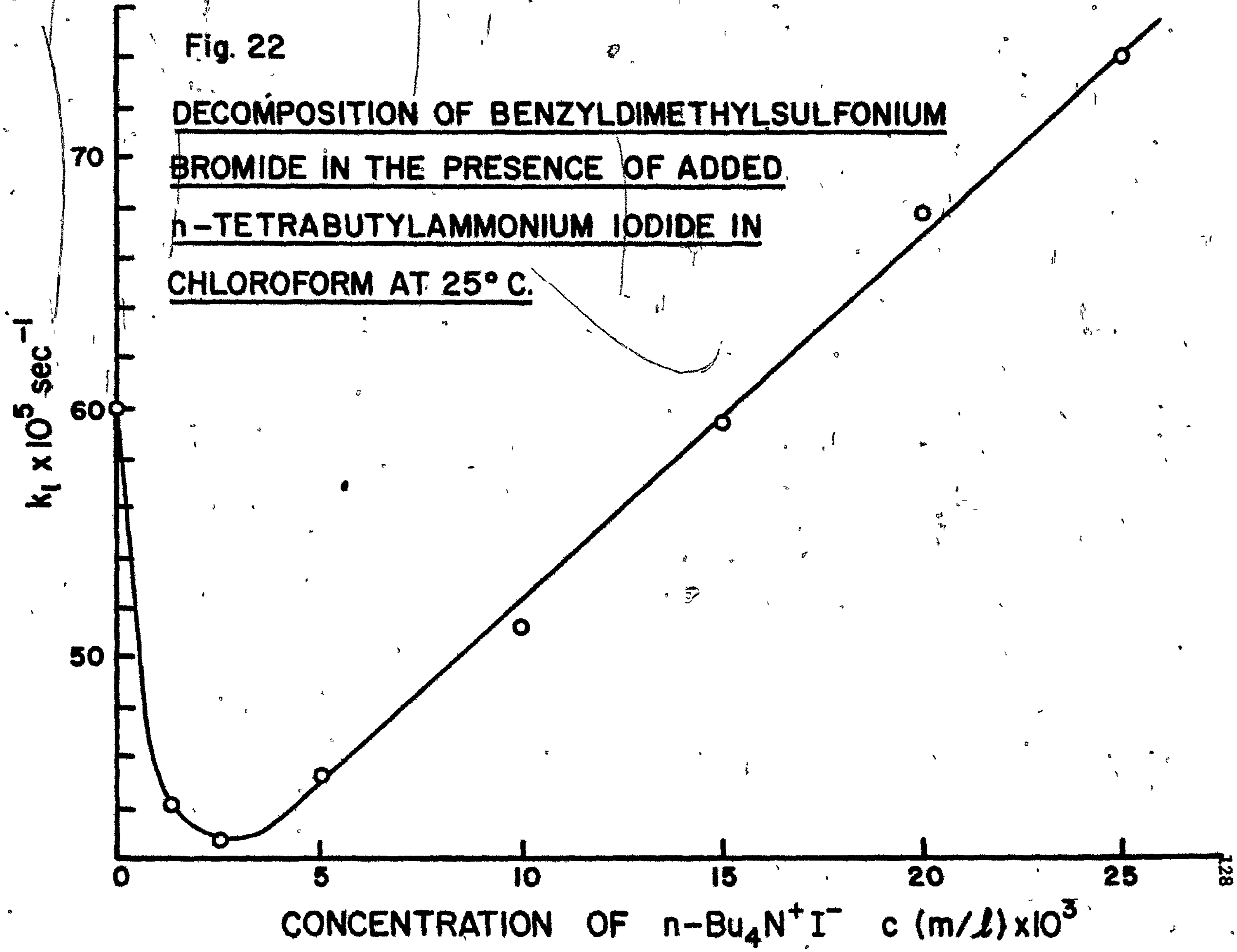


Fig. 22

DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM BROMIDE IN THE PRESENCE OF ADDED n-TETRABUTYLAMMONIUM IODIDE IN CHLOROFORM AT 25° C.

[redacted]

Table 22A. Decomposition of benzyldimethylsulfonium bromide in the presence of added tetra-n-butylammonium iodide in chloroform at 40.0°C.

Concentration of the sulfonium salt: 0.05 M/l

Concentration of added $n\text{-}Bu_4N^+I^-(M/l)\times10^3$	Rate constant $(k\ \times10^5 sec^{-1})$
0.00	60.0
1.25	44.2
2.50	42.7
5.00	45.4
10.00	51.3
15.00	59.6
20.00	67.9
25.00	74.1

In the case of n-tetrabutylammonium iodide and benzyldimethylsulfonium bromide, although the initial addition of the ammonium salt causes a sharp fall in the rate constant, the subsequent addition of the latter gradually increases the rate constant. When n-tetrabutylammonium bromide is added to benzyldimethylsulfonium iodide, a sharp decrease in rate constant is observed, followed by a gradual one.

Another very interesting result is the decomposition of benzyldimethylsulfonium perchlorate in the presence of added n-tetrabutylammonium bromide. From the results of the experiments with the pure sulfonium salts, we know that benzyldimethylsulfonium perchlorate does not decompose at all; but the addition of n-tetrabutylammonium bromide makes the sulfonium perchlorate decompose. In this case, instead of the usual sharp fall in the reaction rate, a rather gradual decrease in the rate constant is observed, as the concentration of the ammonium salt is increased.

In order to explain the characteristic sharp decrease, in the rate constant, due to the addition of ammonium salts, we must refer back to the electrochemical studies, which, together with the kinetic results, showed that the sulfonium salt decomposes via triple ions, which may be $S^+Br^-S^+$ and/or $Br^-S^+Br^-$.

The results of the electrochemical studies of the mixed salts in Table 12, p.84 clearly show that the addition of ammonium salt to sulfonium salt dramatically increases the concentration of $Br^-S^+Br^-$

and drastically reduces the concentration of $S^+Br^-S^+$. So, it is obvious that the decomposition of the sulfonium salt cannot be through $Br^-S^+Br^-$, otherwise the addition of the ammonium salt would result in a sharp increase in the reaction rate. Similarly it cannot be the simultaneous decomposition of both the triple ions, i.e., $Br^-S^+Br^-$ and $S^+Br^-S^+$; because, in this case, the reaction rate should go up as the addition of the ammonium salt increases the concentration of the former. Furthermore, it also cannot be the decomposition of the unsymmetrical triple ions, shown in Table 12; otherwise we would not expect the sulfonium salt to decompose at all, in the absence of the ammonium salt, as these unsymmetrical triple ions are not formed in the pure sulfonium salts.

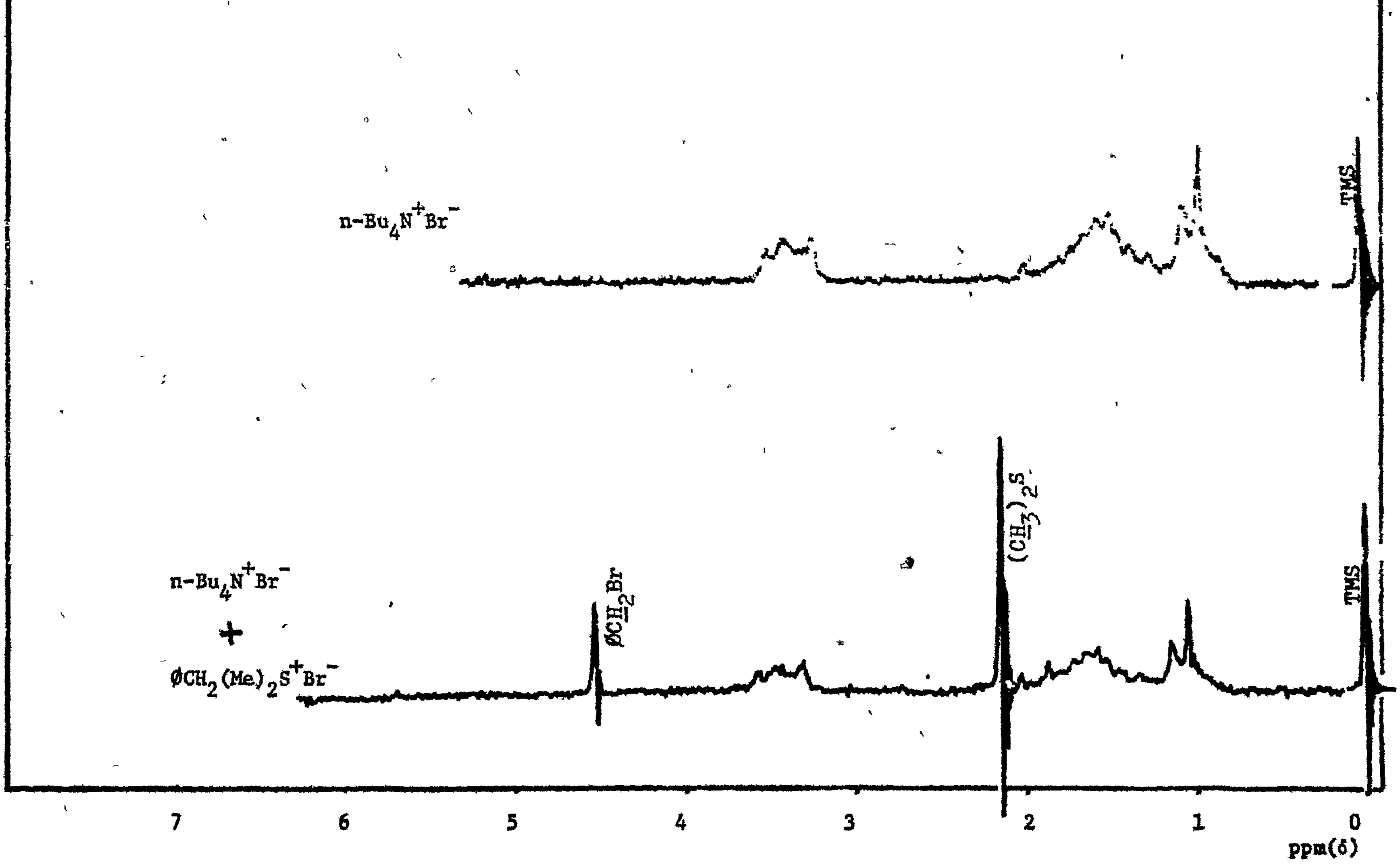
Therefore, it is now obvious from all these considerations that in chloroform medium, the sulfonium salt undergoes decomposition, through a symmetrical triple ion, consisting of two S^+ and an anion, i.e., $S^+X^-S^+$.

If this hypothesis is correct, then, we can explain, why benzyldimethylsulfonium perchlorate does not decompose alone, but does so in the presence of n-tetrabutylammonium bromide. In the pure sulfonium salt, the triple ion $S^+ClO_4^-S^+$, does not decompose, because of the poor nucleophilicity of the ClO_4^-. But in the presence of n-tetrabutylammonium bromide, obviously some $S^+Br^-S^+$ is formed, as shown in Table 12. That this is actually the decomposition of $S^+Br^-S^+$ is confirmed by the product analysis of the reaction mixture, which shows that benzyl bromide and dimethyl sulfide are formed during the reaction, Fig. 23.

Since there is no sharp depression in the concentration of $S^+Br^-S^+$, due to the addition of the ammonium salt, the characteristic sharp decrease in the rate constant is absent. But as the concentration of the ammonium salt is increased, the formation of the stable triple ions is favoured more than that of $S^+Br^-S^+$ ions, and consequently, the rate constant goes down, with increasing concentration of added ammonium salt (Table 12, p.84).

Similarly in the decomposition of benzyldimethylsulfonium bromide, in the presence of n-tetrabutylammonium iodide, the symmetrical triple ion, $S^+I^-S^+$, is formed in addition to $S^+Br^-S^+$. With increasing concentration of the ammonium salt, more and more $S^+I^-S^+$ must be formed, and consequently, the rate of the reaction goes up, because I^- is a better nucleophile than Br^-. On the other hand, the addition of n-tetrabutylammonium bromide, to benzyldimethylsulfonium iodide, after the first sharp decrease, shows a gradual decrease in the rate constant with increasing concentration of the ammonium salt. This should be expected, if the above explanation is valid. In the latter case, $S^+I^-S^+$ is already present in the system; and the addition of the n-tetrabutylammonium bromide is producing $S^+Br^-S^+$, which decomposes slower than $S^+I^-S^+$ does, and as a result, the rate goes down. That $S^+Br^-S^+$ as well as $S^+I^-S^+$ is

Fig. 23. Products analysis for the decomposition of benzyldimethylsulfonium perchlorate in the presence of n-tetrabutylammonium bromide.



formed in both cases, is in agreement with the product analyses which show that benzyl bromide and -iodide are obtained together with dimethylsulfide in each case (Figs. 24, 25).

That the addition of n-tetrabutylammonium phenoxide, and -thiophenoxide, decreases the reaction rate in the same way as does the addition of the corresponding bromide and perchlorate, is difficult to explain. In these cases, we should expect the triple ions like $S^+PhO^-S^+$ and $S^+PhS^-S^+$ to be formed and since PhO^- and PhS^- are several hundred times more nucleophilic than Br^-, the reaction rate should be greatly increased. However, experimentally, we do not observe such an increase in the reaction rate, nor do we find any benzyl phenoxide (δ for $\phi C\underline{H}_2OPh$ = 5.1) or benzyl thiophenoxide (δ for $\phi C\underline{H}_2SPh$ = 5.3, as suggested by Dr. D. L. Hooper) as reaction product. Instead in both these cases, the only products obtained are benzyl bromide and dimethyl sulfide, as seen from Fig . 26, 27.

A possible explanation of this can be that the highly nucleophilic anions must be tied up in the ion-pairs and in the unsymmetrical triple ions which do not decompose.

The gradual fall in the rate constant of the decomposition of the sulfonium salt can be explained by the fact that with the increasing concentration of the added ammonium salt, the concentration of the stable ionic species increases at the expense of the concentration of the decomposable ionic species, i.e., $S^+X^-S^+$, as seen in Table 12, p.84.

Fig. 24. Products analysis for the decomposition of benzyldimethylsulfonium iodide in the presence of n-tetrabutylammonium bromide.

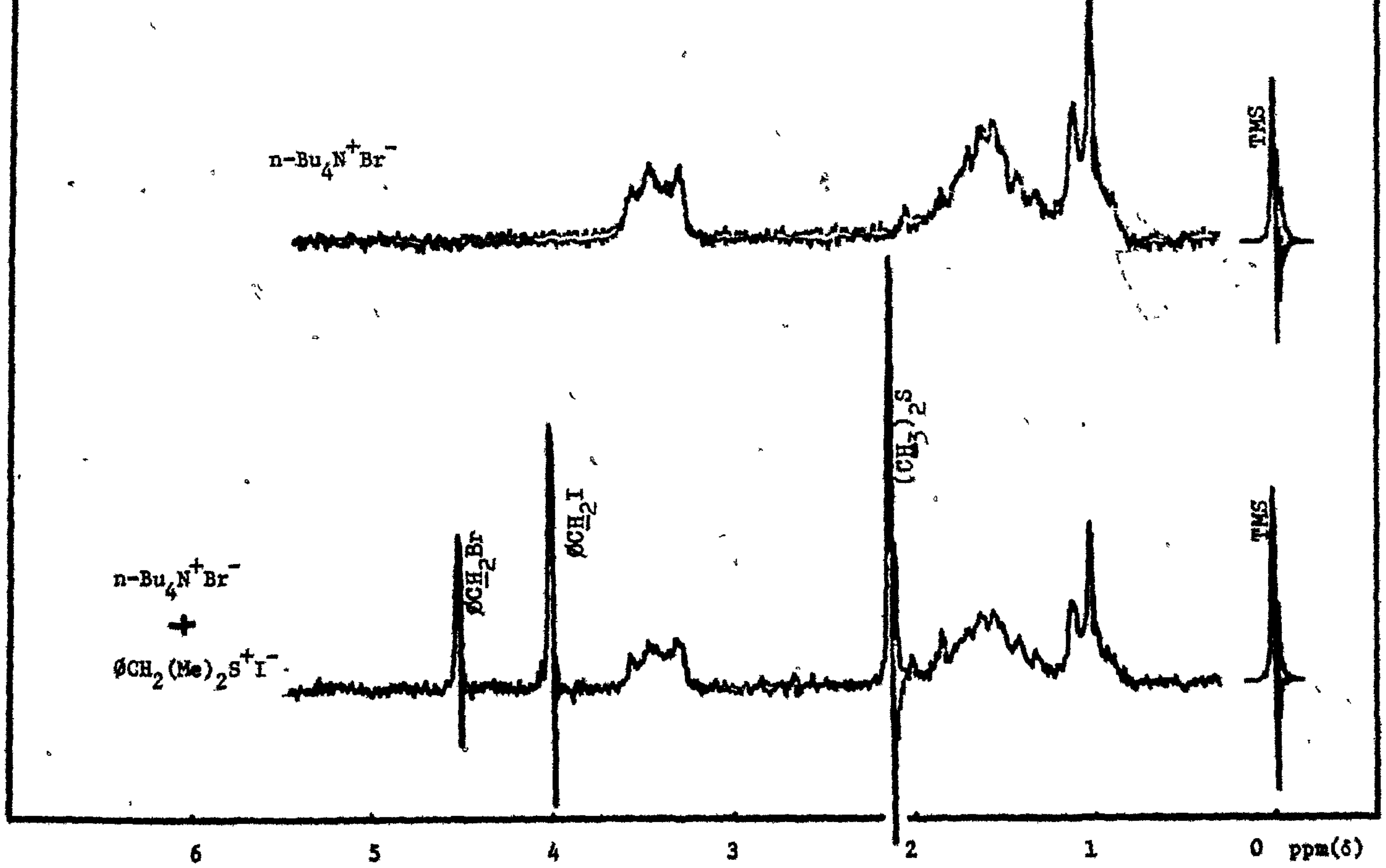


Fig.25. Products analysis for the decomposition of benzyldimethylsulfonium bromide in the presence of n-tetrabutylammonium iodide.

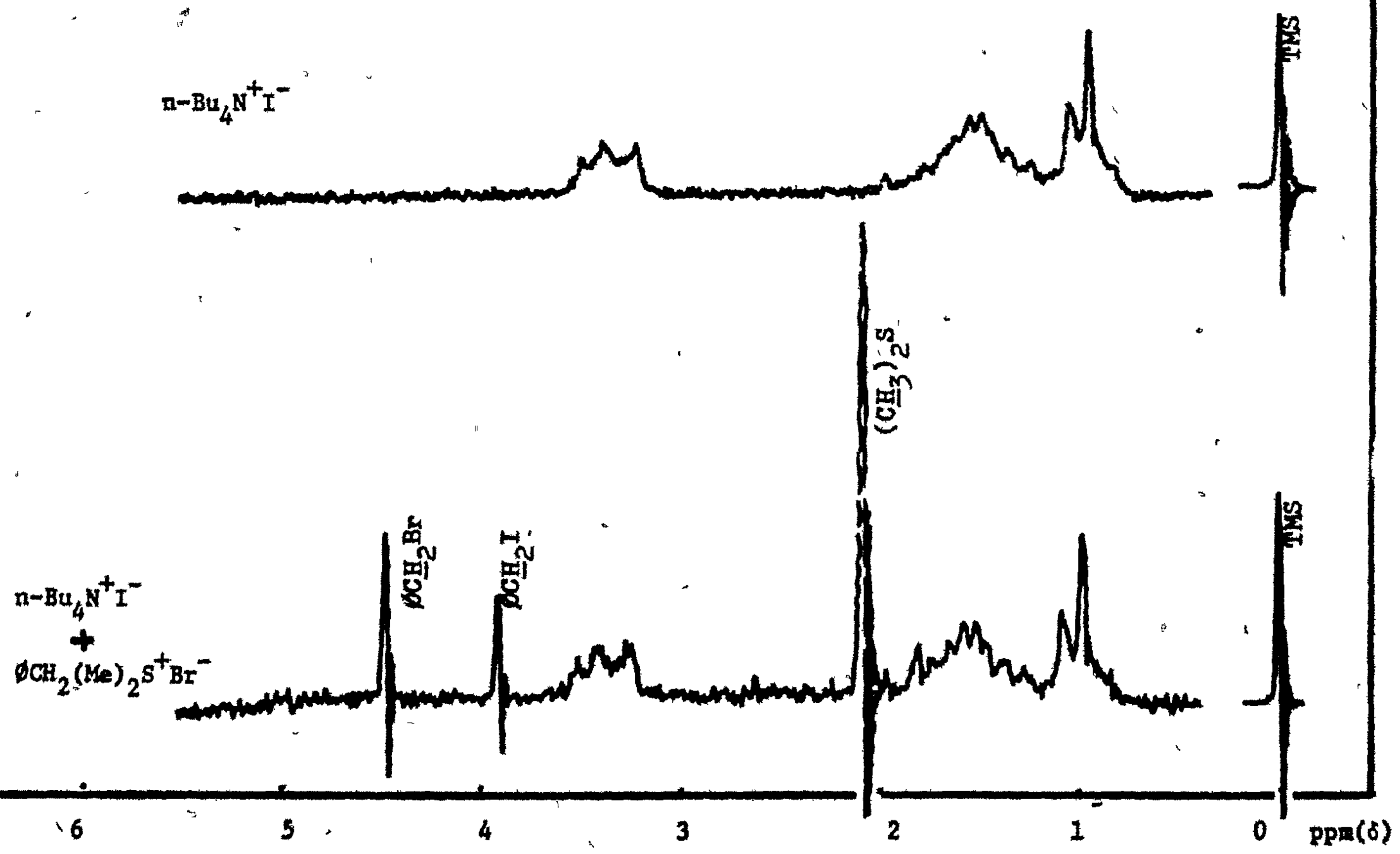


Fig. 26. Products analysis for the decomposition of benzyldimethylsulfonium bromide in the presence of n-tetrabutylammonium phenoxide.

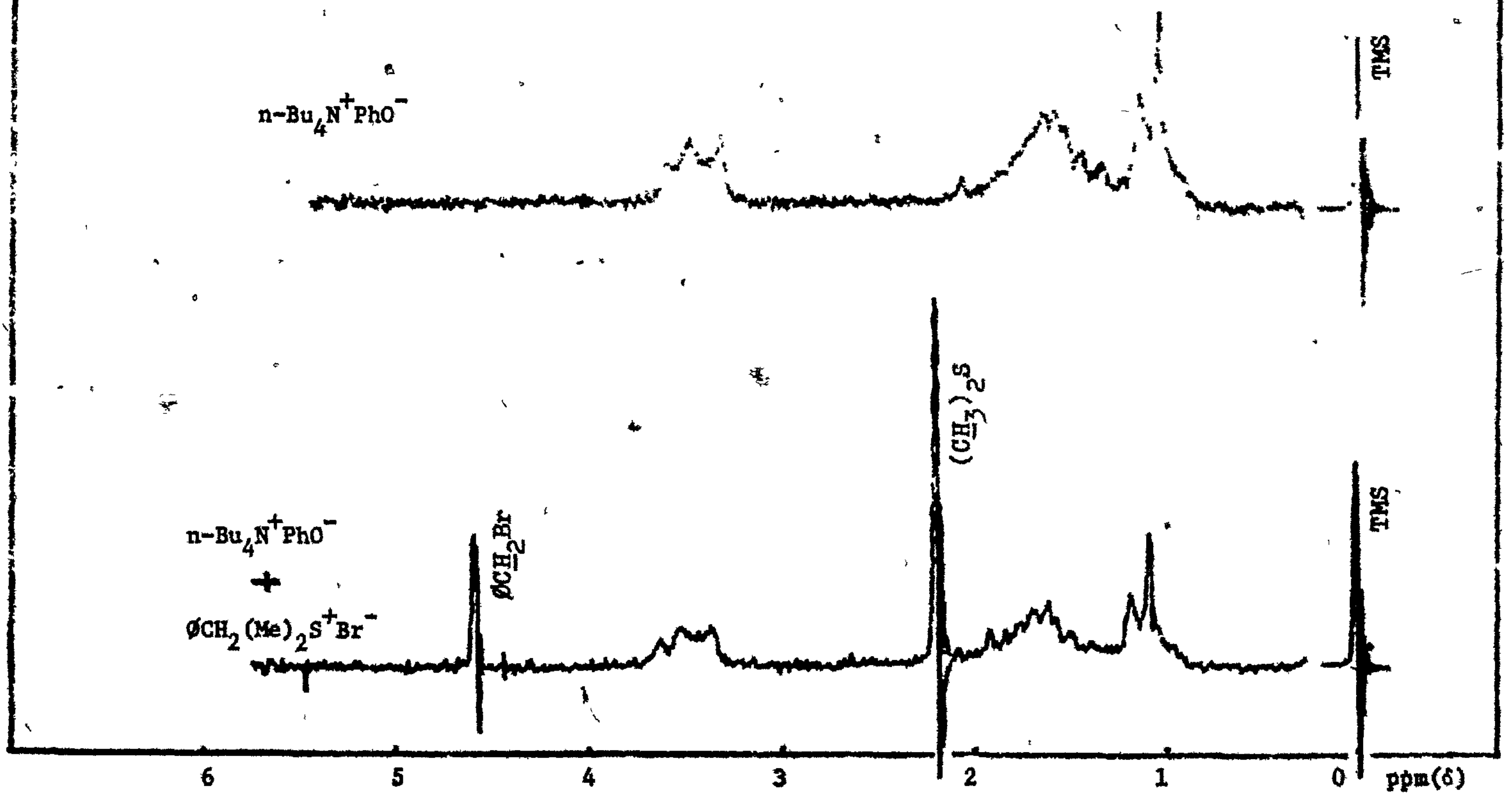
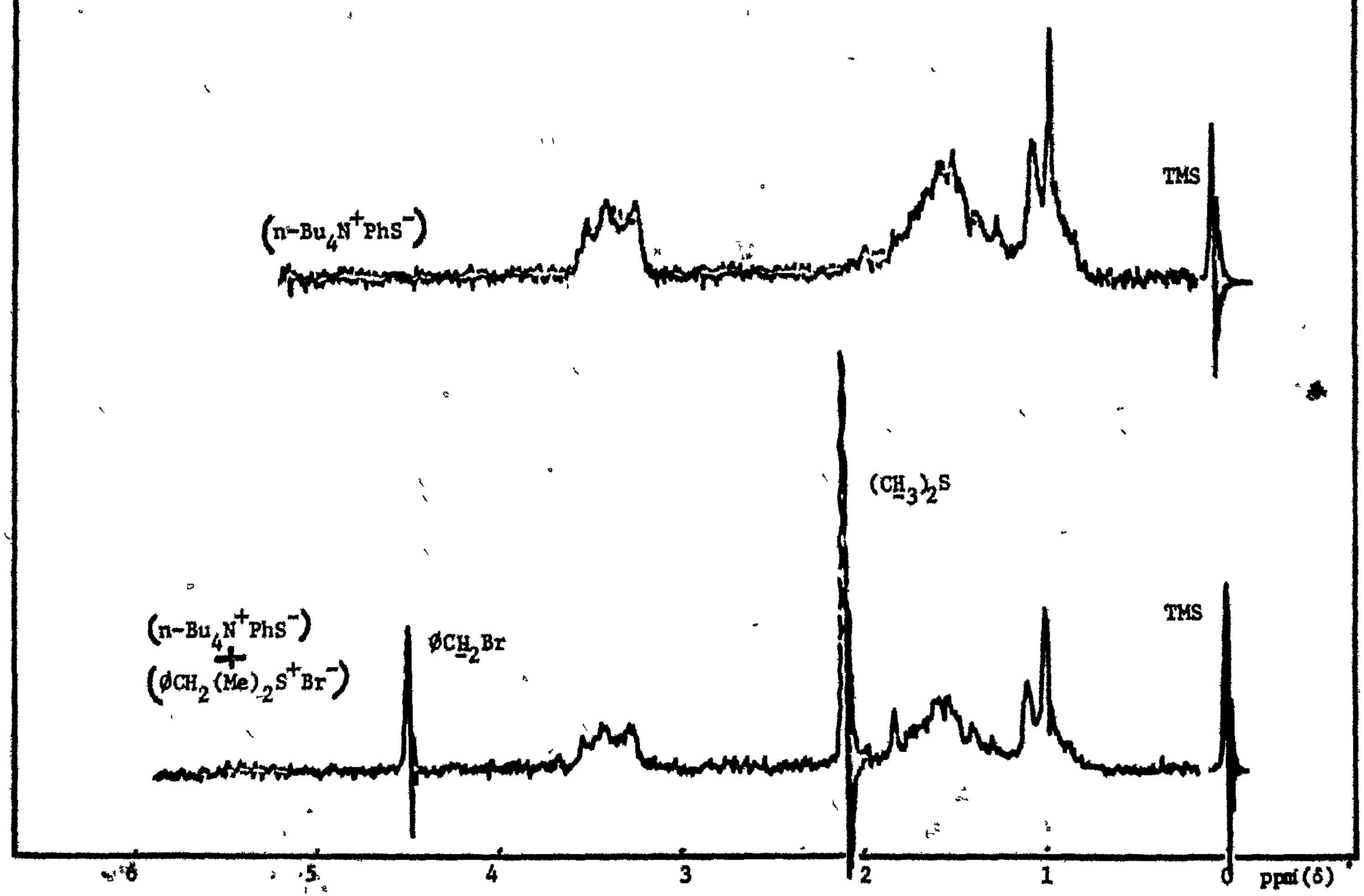


Fig. 27. Products analysis for the decomposition of benzyldimethylsulfonium bromide in the presence of n-tetrabutylammonium thiophenoxide.



C. Reaction parameters

From the rate equation of the transition state theory, the rate constant is given by[113],

$$k = (\kappa T/h)e^{-\Delta H^{\ddagger}/RT}\,e^{+\Delta S^{\ddagger}/R} \qquad (63)$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are enthalpy and entropy of activation, respectively. From equation (63)

$$\ln k = \ln(\kappa T/h) - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R \qquad (64)$$

or, $$\log k = \log(\kappa T/h) - \frac{\Delta H^{\ddagger}}{2.303RT} + \frac{\Delta S^{\ddagger}}{2.303R} \qquad (65)$$

The enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation for the decomposition of the protium compound (benzyldimethylsulfonium bromide) in chloroform were calculated by means of a least square fit to equation (65). The values obtained are:

$$\Delta H^{\ddagger} = 25.48 \pm 0.18 \text{ kcal mole}^{-1} \qquad (66)$$

$$\Delta S^{\ddagger} = 8.03 \pm 0.58 \text{ cal mole}^{-1}\text{deg}^{-1} \qquad (67)$$

The ease with which the reaction proceeds even at room temperature may be seen to be due to the positive entropy of activation. From equation (65) the plot of log(k/T) vs. 1/T should give a straight line. The rate constants for the decomposition reaction were measured at 5°

intervals between 25 and 50°C; and Fig. 28 shows a graph of $\log_{10}(k/T) + 8$ versus 1000/T.

The positive value of $\Delta S^{\ddagger}$ indicates that there is more randomness in the transition state than in the initial state and thus suggests a unimolecular type mechanism.

The fact that the activation energy plot shows no curvature over a reasonably wide temperature range, lends support in terms of a single mechanism. If more than one ionic species were undergoing simultaneous decomposition, with different activation energies, deviations from linearity would be expected in Fig. 28.

D. Secondary deuterium isotope effect

The secondary deuterium isotope effects for the decomposition of sulfonium salts are not available in the literature. A study of the temperature dependence of the secondary deuterium isotope effects of benzyldimethylsulfonium bromide in chloroform solution over a temperature range of 25°C was carried out and the experimental results are presented in Table 28C.

The k_H/k_D ratio is found to be approximately constant, at 1.08±0.01. The k_H/k_D ratios were fitted to equation (68) by the method of least squares:

$$\log_{10}(k_H/k_D) = \frac{(\Delta H_D^{\ddagger} - \Delta H_H^{\ddagger})}{2.303\ RT} - \frac{(\Delta S_D^{\ddagger} - \Delta S_H^{\ddagger})}{2.303\ R} \qquad (68)$$

Fig. 28

PLOT OF $\mathrm{LOG}_{10} \frac{k_{H(D)}}{T} + 8$ AGAINST $\frac{1000}{T}$

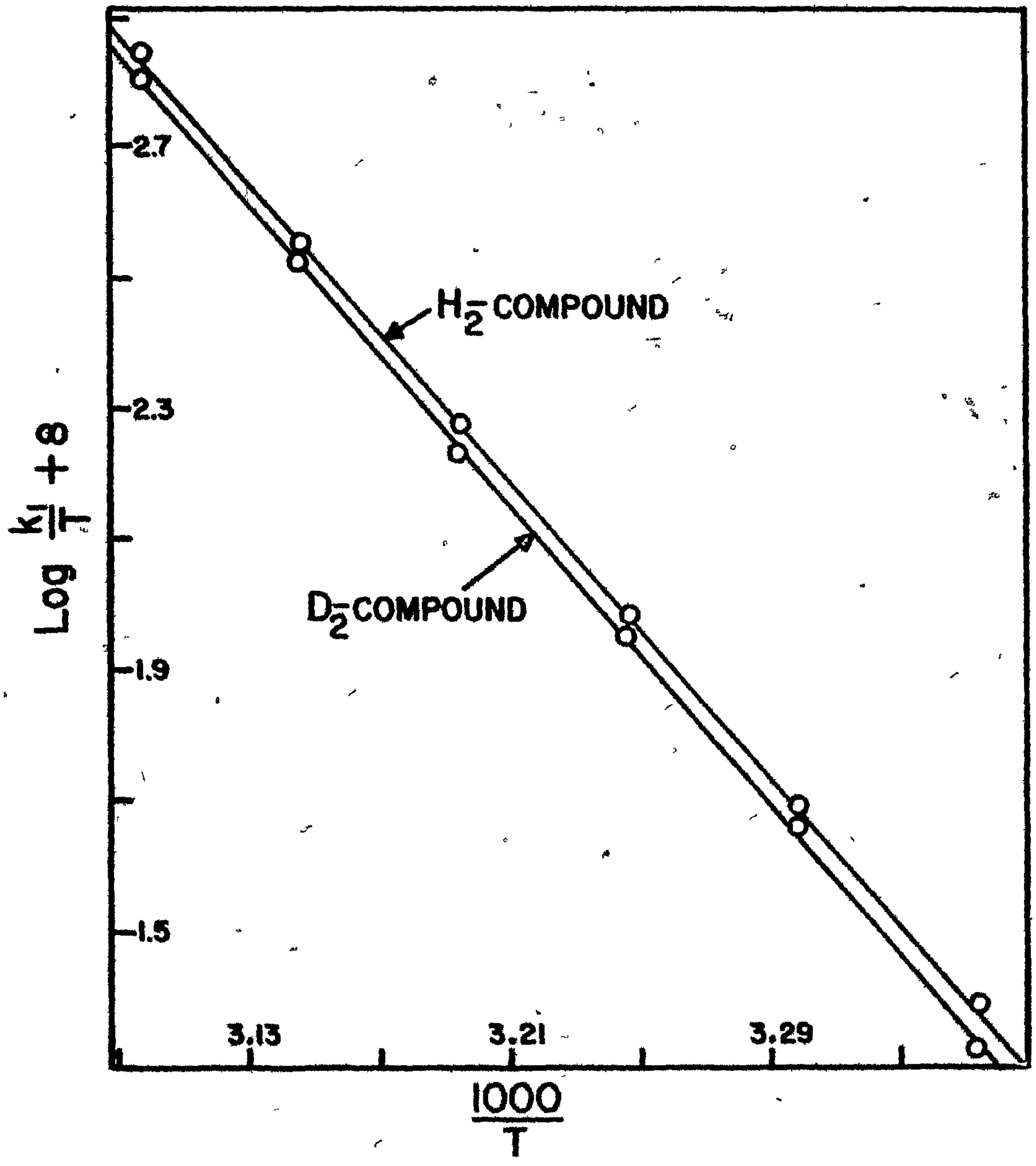


Table 28A. Temperature dependence of the decomposition of benzyldimethylsulfonium bromide in chloroform.

Cell #1.

Temperature °C	°K	1/T°K x 10^3	k_H x $10^5 sec^{-1}$ (average)	$\log_{10}(k_H/T) + 8$
25	298	3.36	7.492	1.400
30	303	3.36	15.241	1.700
35	308	3.25	30.196	1.990
40	313	3.26	59.996	2.282
45	318	3.15	115.985	2.560
50	323	3.10	228.185	2.850

Table 28B. Temperature dependence of the decomposition of α-d_2-benzyldimethylsulfonium bromide in chloroform.

Cell #2

Temperature °C	°K	1/T°K x 10^3	$k_D x 10^5 sec^{-1}$ (average)	$log_{10}(k_D/T) + 8$
25	298	3.36	7.024	1.330
30	303	3.30	14.148	1.670
35	308	3.25	28.258	1.962
40	313	3.20	54.966	2.244
45	318	3.15	108.420	2.532
50	323	3.10	210.260	2.831

Table 28C. Temperature dependence of secondary deuterium isotope effects for the decomposition of benzyldimethylsulfonium bromide in chloroform solution.

Cell #1 & 2

Temp. °C	$k_H x10^5 sec^{-1}$	$k_D x10^5 sec^{-1}$	[illegible]/k_D
25.0	7.492±0.012	7.024±0.006	1.07±0.003
30.0	15.241±0.014	14.148±0.027	1.08±0.003
35.0	30.196±0.072	28.258±0.057	1.07±0.005
40.0	59.996±0.152	54.966±0.120	1.[illegible]0.005
45.0	115.985±0.197	108.420±0.360	1.07±0.015
50.0	228.185±0.865	210.260±0.757	1.08±0.008

The enthalpy and entropy differences so obtained are given below, together with their standard deviations:

$$(\Delta H_D^{\ddagger} - \Delta H_H^{\ddagger}) = -0.07 \pm 0.08 \text{ kcal mole}^{-1} \qquad (69)$$

$$(\Delta S_D^{\ddagger} - \Delta S_H^{\ddagger}) = -0.36 \pm 0.25 \text{ cal mole}^{-1}\text{deg}^{-1} \qquad (70)$$

Because of the larger standard deviation in $(\Delta H_D^{\ddagger} - \Delta H_H^{\ddagger})$ than its actual value, this result is probably zero. The isotope effect in this case may be due to the difference, mainly in $\Delta S^{\ddagger}$ term, rather than the enthalpy, generally expected in a zero-point energy difference explanation.

The isotope effect observed in this case, is found to be approximately independent of temperature (k_H/k_D = 1.08±0.01). This indicates some type of compensating changes in force constants, and hence zero-point energy difference. Therefore, it is probable that a nucleophile is participating in the transition state, such that a strong interaction between the nucleophile, and the reacting carbon atom increases bending frequencies of the C-H bond, but at the same time electronic charges associated with the formation of the new bond and breaking of the old bond, tend to decrease stretching frequencies. Had there been no participation of the anion, the temperature-dependency of the isotope effect would have been expected.

The normal isotope effect observed previously for the ammonium salt decomposition was of somewhat greater magnitude, and origin of which was found to be in both the enthalpy and entropy terms.

E. Summary

The important experimental observations and mechanistic deductions for the reaction are summarized below.

Electrochemical studies

1. In a 0.05M/1 solution in chloroform, both the sulfonium and ammonium salt are present mainly as the ion-pair and the conductivity of the solution is largely due to triple ions.
2. The concentrations at which triple ion formation is appreciable, are around 0.004 and 0.002M/1 for the sulfonium and ammonium salt respectively.
3. Addition of ammonium salt to sulfonium bromide, drastically reduces the concentration of $S^+Br^-S^+$ and dramatically increases that of $Br^-S^+Br^-$.
4. In the case of mixed salts, the ionic species that is in highest concentration, is the one consisting of the ion-pair of the ammonium salt and the anion of the sulfonium salt.
5. A comparison of the concentrations of the ionic species of pure sulfonium and ammonium salts indicates that the triple ion concentration of the latter is several-fold higher than that of the corresponding sulfonium salt.

Kinetic studies

1. The decomposition of benzyldimethylsulfonium bromide produces only benzyl bromide and dimethyl sulfide and the reaction goes to completion.

2. The reaction rate of the decomposition of sulfonium salt is proportional to the conductivity rather than molar concentration.

3. The reaction rate decreases slowly as the concentration of the salt increases from 0.025 to 0.05M/l; beyond the latter concentration, the decrease in the reaction rate is minimal.

4. There is a linear relationship between the nucleophilicity of the anion and the logarithm of the reaction rate constant.

5. Benzyldimethylsulfonium perchlorate does not decompose alone, but does so in the presence of n-tetrabutylammonium bromide.

6. Addition of small amount of ammonium salt causes a sharp decrease in the rate constant of the sulfonium salt. This sharp fall in the rate constant then becomes gradual and linear. However, the addition of small amounts of n-tetrabutylammonium iodide to benzyldimethylsulfonium bromide decreases the rate constant, but greater amounts of the iodide gradually and linearly increase the rate constant.

7. Addition of n-tetrabutylammonium bromide, -perchlorate, -phenoxide, and -thiophenoxide, to benzyldimethylsulfonium bromide

produces only benzyl bromide and dimethyl sulfide. These two are also the only products, when n-tetrabutylammonium bromide is added to benzyldimethylsulfonium perchlorate; the latter does not decompose alone.

8. When n-tetrabutylammonium iodide is added to benzyldimethylsulfonium bromide, benzyl iodide, in addition to benzyl bromide and dimethyl sulfide is formed.

From the results summarized in the previous pages, the mechanism may be deduced of the decomposition of sulfonium salts in chloroform.

The kinetic studies show that the reaction rate is proportional to ionic species rather than molar concentration, which at once suggests that for the pure sulfonium salt, the reaction must proceed either through single sulfonium ion S^+, or through triple ions $S^+X^-S^+$ and $X^-S^+X^-$ or their different combinations, since these are the ionic species present in the sulfonium salt in that concentration range.

Since the kinetic experiments have proved that the nucleophilicity of the anion controls the rate of decomposition of the sulfonium salt, the decomposition via a single sulfonium ion is impossible, and so the decomposition must proceed through the symmetrical triple ions, i.e., $S^+X^-S^+$ and/or $X^-S^+X^-$.

The kinetic studies indicate that the addition of a small amount of the ammonium salt, drastically decreases the rate of decomposition of the sulfonium salt. Now if we compare the concentration of triple ions which are common to sulfonium salt alone, and in mixture with the ammonium salt, we find that on addition of the ammonium salt, there is a tremendous increase in the concentration of $Br^{-}S^{+}Br^{-}$. So it is concluded that the reaction does not proceed via $Br^{-}S^{+}Br^{-}$, otherwise, a very sharp increase in rate constant would have been obtained, when the ammonium salt is added.

On the other hand, the addition of the ammonium salt extensively cuts down the concentration of $S^{+}Br^{-}S^{+}$. Therefore, the sharp fall in the reaction rate of the decomposition of the sulfonium salt, as observed, due to addition of ammonium salt, is consistent only if the reaction is the decomposition of $S^{+}Br^{-}S^{+}$.

That only one type of ionic species is undergoing decomposition is further supported by the fact that the activation energy plot shows no curvature over a reasonably wide range of temperature. Simultaneous decomposition of more than one ionic species, with different activation energies, would lead to non-linearity for such a plot.

The magnitude and origin of the secondary deuterium isotope effect suggests that the substitution is not a usual type of S_N1 or S_N2 substitution.

Therefore, considering all these points, the most likely mechanism for the decomposition of the sulfonium salts in chloroform may be formulated as the following:

$$3\ \phi CH_2S^+(CH_3)_2X^- \underset{\longleftarrow}{\xrightarrow{fast}} (\phi CH_2S^+(CH_3)_2)_2X^- + \phi CH_2S^+(CH_3)_2X_2^- \qquad (71)$$

The benzyl group will have some character of a carbonium ion, due to delocalization of the positive charge:

$$\begin{array}{l} \phi CH_2{-}{-}S(CH_3)_2X^- \phi \overset{+\delta}{C}H_2S^{+\delta}(CH_3)_2 \ + \ \phi CH_2^-S(CH_3)_2X_2 \qquad (72) \\ \qquad\quad \Big\downarrow \text{slow} \\ \phi CH_2X \ + \ (CH_3)_2S \ + \ 2\phi CH_2(CH_3)_2X \end{array}$$

This mechanism is then a special type of substitution, which has been described as an "ionic internal nucleophilic substitution"[93].

In the present investigation, we have, therefore shown actually what happens to a reaction which is particularly dependent on ions in a polar medium when the reaction is carried out in a non-aqueous solvent of low polarity. It is seen that although the electrolyte in such systems remain mainly as ion-pairs, a certain small fraction must be present as simple ions, triple ions, as well as, other more complex ionic aggregates. This study further reveals that only one particular type of ionic species is responsible for the reaction, and the reaction rate constant is dependent on the concentration of this ionic species and the nucleophile of the latter controls the rate of the reaction.

It is, therefore, very likely that other compounds of similar type, e.g., substituted ammonium and possibly phosphonium salts, will follow a similar type of mechanism, in their reactions when performed in a non-aqueous solvent of low polarity.

IV EXPERIMENTAL

A General

(a) Procedures

All salts were dried for at least half an hour over phosphorus-pentaoxide in vacuum just before weighing. The conductivity cells were thoroughly cleaned with hot ethanol, then several times with chloroform, and thereafter, kept filled with the solvent chloroform. The cells were rinsed three times with the solution before being filled up to a certain volume for conductance measurements.

The melting points (corrected) were recorded on a Fisher-Johns Melting point Apparatus, and the boiling points are more properly the distillation temperatures.

(b) Apparatus

The constant temperature bath

For the bulk of the kinetic runs measured by the conductance method, a Townson and Mercer model TM Series II thermostat with a temperature constancy of ±0.02°C was used. The bath was filled with Esso Nuto H44 with a viscosity of about 35 centistokes at 40°C.

Conductivity bridge

A Wayne-Kerr Universal bridge, model B221, having a quoted accuracy of ±0.2% was used in measuring all the conductance data.

Gas-liquid chromatography (GLC)

This was performed on a Wilkens Aerograph Autoprep model A-700.

Nuclear magnetic resonance spectrometer (NMR)

The nuclear magnetic resonance spectra were recorded on a Varian T-60 NMR spectrometer, at a frequency of 60 MHz.

Balance

A Mettler, type B6 serial #61975 was used in all the weighings throughout this work.

Calculations

The rate constants and other thermodynamic properties were calculated by the computer, model CDC 6400, while equivalent conductances and other conductance parameters were computed in the Wang electronic calculator, model 320.

B. Syntheses

(a) Preparation of thiophenol

In a 1-l. round bottom flask equipped with a reflux condenser were placed 360 g of cracked ice, and 65 ml (1.17 mole) of concentrated sulfuric acid; the temperature being kept at -5 to 0.0°C by an ice-salt bath. To this, 30 g (0.17 mole) of crude benzenesulfonyl chloride was gradually introduced (½ hr), with stirring, followed by 60 g (0.92 atoms) of zinc dust. The latter was added in portions and as rapidly as possible without allowing the temperature to rise over 0°C. After 1½ hr, the ice bath was removed and the reaction mixture was allowed to warm up spontaneously. After the first ebullition had subsided, the mixture was heated to boiling with continuous stirring until the solution was clear (4 hr).

The thiophenol so formed was steam distilled, separated from water, and finally dried over anhydrous calcium chloride. The crude material weighed 18 g (96%) and the pure compound distilling at 167-8°C (Lit.[114] b.p. 166-9°C) was collected.

(b) Preparation of α-bromo-α-d_2-toluene

To a solution of 2.40 g (0.025 mole) α-d_3-toluene in carbon tetrachloride (15 ml), in a 50 ml round-bottom flask, fitted with a reflux condenser and a calcium chloride guard tube, 3.56 g (0.02 mole) of N-bromosuccinimide together with a little benzoyl peroxide was added. The mixture was refluxed for 20 minutes, and then filtered. The filtrate was distilled first at atmospheric pressure to remove the solvent and then at reduced pressure to obtain α-d_2-benzyl bromide, 4.12 g (95%), b.p. 137-9°C at 22 mm of Hg (Lit.[115] b.p. 135-8°C at 22 mm of Hg,)

(c) Preparation of quaternary ammonium salts

Since analogous preparative methods were used to obtain these salts, only one experimental procedure is given below as an example.

n-Tetrabutylammonium thiophenoxide

To a solution of n-tetrabutylammonium iodide (5.0 g, 0.0135 mole) in 25 ml of methanol, excess of freshly prepared silver oxide (0.01 mole) washed with methanol was added with stirring. The stirring was continued until the supernatant liquor gave no test for iodide with acidified silver nitrate solution. The solution was then filtered, and neutralized with thiophenol in methanol. The methanolic solution was then evaporated under reduced pressure, and the salt was crystallized from ethyl acetate.

(d) Preparation of sulfonium salts

Sulfonium salts with anions other than halides were synthesized from the corresponding sulfonium bromide in the similar method to that used for the preparation of quaternary ammonium salts with anions other than halides. Since sulfonium halides were prepared in a similar way, a representative method is given below. All salts were purified by recrystallization to their constant melting point, when the purity was found to be better than 99% by potentiometric titration of the anion with silver nitrate solution.

Benzyldimethylsulfonium bromide

28.5 g (0.165 mole) of benzyl bromide was allowed to react with an excess of dimethyl sulfide, (15.5 g, 0.257 mole) in a 250 ml round bottom flask, equipped with a reflux condenser and a calcium chloride guard tube. The reaction was allowed to proceed overnight with continuous magnetic stirring; the white crystals of benzyldimethylsulfonium bromide were removed and washed with dry ether by suction filtration in nitrogen atmosphere, 38.0 g (98%), m.p. 100-.5°C. Potentiometric analysis for bromide showed: trial 1, and 2, found 34.31%, calculated, 34.30%.

Benzyldimethylsulfonium perchlorate

Benzyldimethylsulfonium bromide (5.0 g, 0.0215 mole) was dissolved in 25 ml of methanol, and an excess of freshly prepared silver oxide (0.02 mole) washed with methanol, was added with stirring. The stirring was continued until the supernatant liquor gave a negative test for bromide with acidified silver nitrate solution. The solution was then filtered, and the filtrate was concentrated under reduced pressure, to obtain benzyldimethylsulfoxide (3.6 g, 94%). The latter was dissolved in 15 ml of water and the aqueous solution was neutralized with perchloric acid. The filtered solution, which gave no test for bromide or silver ions, was concentrated under reduced pressure at room temperature. The white crystals (4.0 g, 91%), recrystallized from acetone-methanol mixture was found to melt at 105-7°C (Lit. m.p. 106-7°C (116).).

All the sulfonium and ammonium salts, used in the present work, together with their melting points and titration data, are given below:

Anion	Solvent	Melting point °C		% of anion	
		Observed	Lit.	Found	Calculated
(a) n-Tetrabutylammonium salt:					
bromide	ether-ethanol	118-9	119[a]	24.80	24.81
chloride	ether-ethyl-acetate	108-10	110[a]	12.78	12.80
iodide	dilute acetone	145-6	145-6[a]	34.38	34.40
perchlorate	ether-ethanol	213-5	213[a]		
phenoxide	ether	132-5	-	27.72	27.72
thiophenoxide	ethyl acetate	69-70	-	31.00	31.02
(b) Benzyldimethylsulfonium salt:					
bromide	ethanol-ether	100-.5	99-100[b]	34.31	34.30
chloride	2-propanol-ether	109-10	105-10[b]	17.94	17.95
iodide	2-propanol-ether	103-5	102-4[b]	45.33	45.33
perchlorate	ethanol-acetone	105-7	106-7[c]		

Anion	Solvent	Melting point °C Observed	Lit.	% of anion Found	Calculated
(c) Diethylmethylsulfonium salt:					
bromide	ethanol-ether	234-5	235[d]	43.19	43.20
iodide	ethanol-ether	40-1	39.5[d]	54.70	54.71

a: ref.117; b: ref.118; c: ref.116; d: ref.119.

C. Solvent and other chemicals

The chloroform solvent used throughout this study was chromatoquality reagent grade 99+ mol per cent, and was purchased from Matheson Coleman, and Bell. This solvent was used without any further purification, in all kinetic runs and conductance measurements. An approximate 20 ml sample of this chloroform in the conductance cell left in the thermostat at 40°C for overnight showed almost no change in conductance, indicating that no conductance change could be expected from the cell and the solvent during any particular run. The gas chromatogram supplied by Matheson, Coleman and Bell, with the chloroform sample, showed the presence of traces of hydrocarbon stabilizer, and traces of two other unidentified impurities.

α-d_3-Toluene was purchased from Merck, Sharp and Dohme, of Canada Ltd., Montreal, Canada; Benzyl bromide, and -iodide, were obtained from Matheson, Coleman and Bell; while benzyl chloride was procured from

British Drug Houses (Canada) Ltd., Toronto, Canada. Both diethyl- and dimethyl sulfide, methyl bromide, benzenesulfonyl chloride and n-tetrabutylammonium bromide were products of the Eastman Organic Chemicals, Rochester 3, N.Y., U.S.A. Ethyl bromide and N-bromosuccinimide were supplied by Fisher Scientific Co., Chemical Manufacturing Division, Fair Lawn, New Jersey, U.S.A. n-Tetrabutylammonium iodide and -perchlorate were provided by Dr. K.T.Leffek.

D Analyses

(a) Reaction products analysis

The products of the decomposition reaction of the sulfonium salts, with and without added electrolytes were analyzed by (i) vapour phase chromatography, and (ii) nuclear magnetic resonance spectroscopy.

(i) The chromatographic analysis was carried out on an Autoprep chromatograph, model A-700, the column (20'x¼" O.D.) being packed with silicone gum rubber SE 30 on HMDS chromosorb, mesh size 80-100. The reaction mixture was allowed to stand in the thermostat, at the temperature of the reaction, for about 25 "half-lives" before it was concentrated under reduced pressure to remove most of the solvent. The experiment was performed with a 10 μl of the concentrated sample, at a column temperature of 198±0.5°C, a flow rate of 125 cc/min, and a filament current of 150 ma, nitrogen being used as the carrier gas. The reaction products were identified by matching the retention times of the individual components with those of the authentic samples.

(ii) The spectroscopic identification of the reaction products on the actual reaction mixture was made on a Varian T-60 N.M.R. Spectrometer, tetramethyl silane being the internal reference. The spectra were taken at a frequency of 60 Mcps, under the following conditions:

Spectrum amplitude: 2.5
Spinning rate (RPS): 28
Sweep time (sec): 250
Filter: 2
RF power level: 0.005
Sweep width 500

The products were identified from the δ-values of the different peaks, of the authentic samples.

(b) Deuterated compounds analysis

Both α-d_2-benzyl bromide, and α-d_2-benzyldimethylsulfonium bromide were analyzed by N.M.R. spectroscopy. The absence of the peak at about

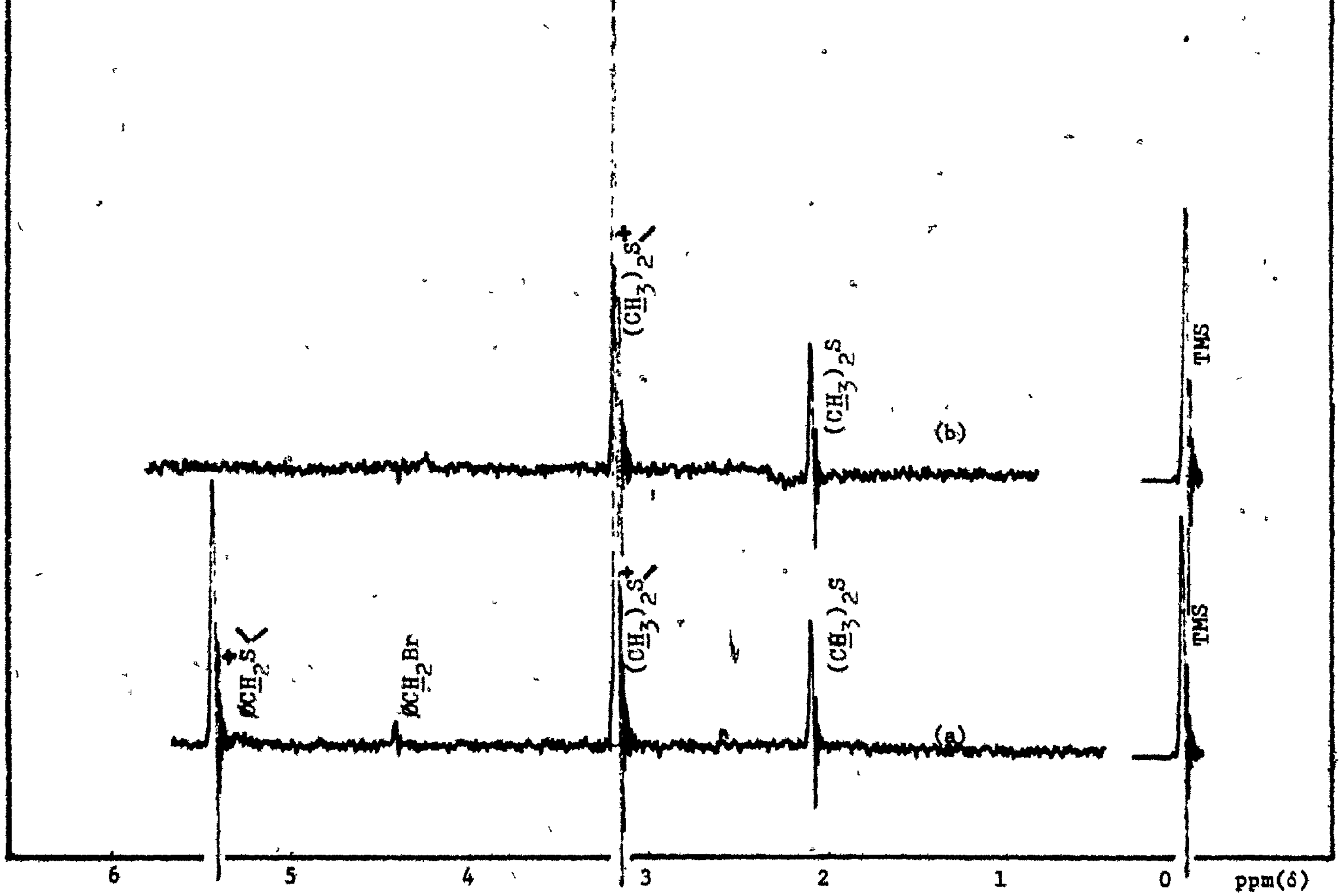
4.5 ppm(δ), indicates that the α-positions of α-d_2-benzyl bromide was completely deuterated. α-d_2-Benzyldimethylsulfonium bromide showed no peaks due to methylene protons of ϕ-$C\underline{H}_2$-S^+ group, indicating that a very high degree of deuteration was achieved in the sulfonium compound. The N.M.R. spectra of these two substrates are shown in Fig. 29.

E. Calibration curves

(a) Calibration of conductance-concentration relation

The calibration curve was obtained by measuring the conductance of chloroform solutions, containing different concentrations of benzyldimethylsulfonium bromide and its decomposition products. The total concentration was made up to 0.05M. The concentration of the salt was decreased while that of the products increased at 0.005M intervals, such that the sum of the concentrations of the salt and products was always 0.05M. For each system about ten readings were taken at definite time intervals from which the conductance of the particular system at "zero" time was extrapolated. In order to minimize the error in the conductance readings due to decomposition of the salt, the calibration curve was obtained at 25°C.

Fig.29. NMR spectra of (a) Ø$CH_2(CH_3)_2S^+Br^-$ and (b) Ø$CD_2(CH_3)_2D^+Br^-$



Linear conductance-concentration relationship for quaternary ammonium salts have been reported in the literature[120,121]. In the present study on the sulfonium salt in chloroform, the relation resulted in a curve, concave upward and was very similar to that obtained previously in these laboratories, for quaternary ammonium salts in chloroform[122]. The calibration curve obtained in the present study, is shown in Fig.30 and the data are presented in Table 30A.

(b) Calibration of peak-height-concentration relation

This calibration curve was obtained by measuring the height of the peak (arbitrary unit), due to the methyl protons of the $(CH_3)_2S^+$ group. The calibration solutions were made in the same way as described in the previous section. The peak-height thus gave a direct measure of the concentration of benzyldimethylsulfonium bromide. The operating conditions were similar to those described in section D(a)ii. The calibration curve so constructed is shown in Fig.31; the corresponding experimental data are collated in Table 31A.

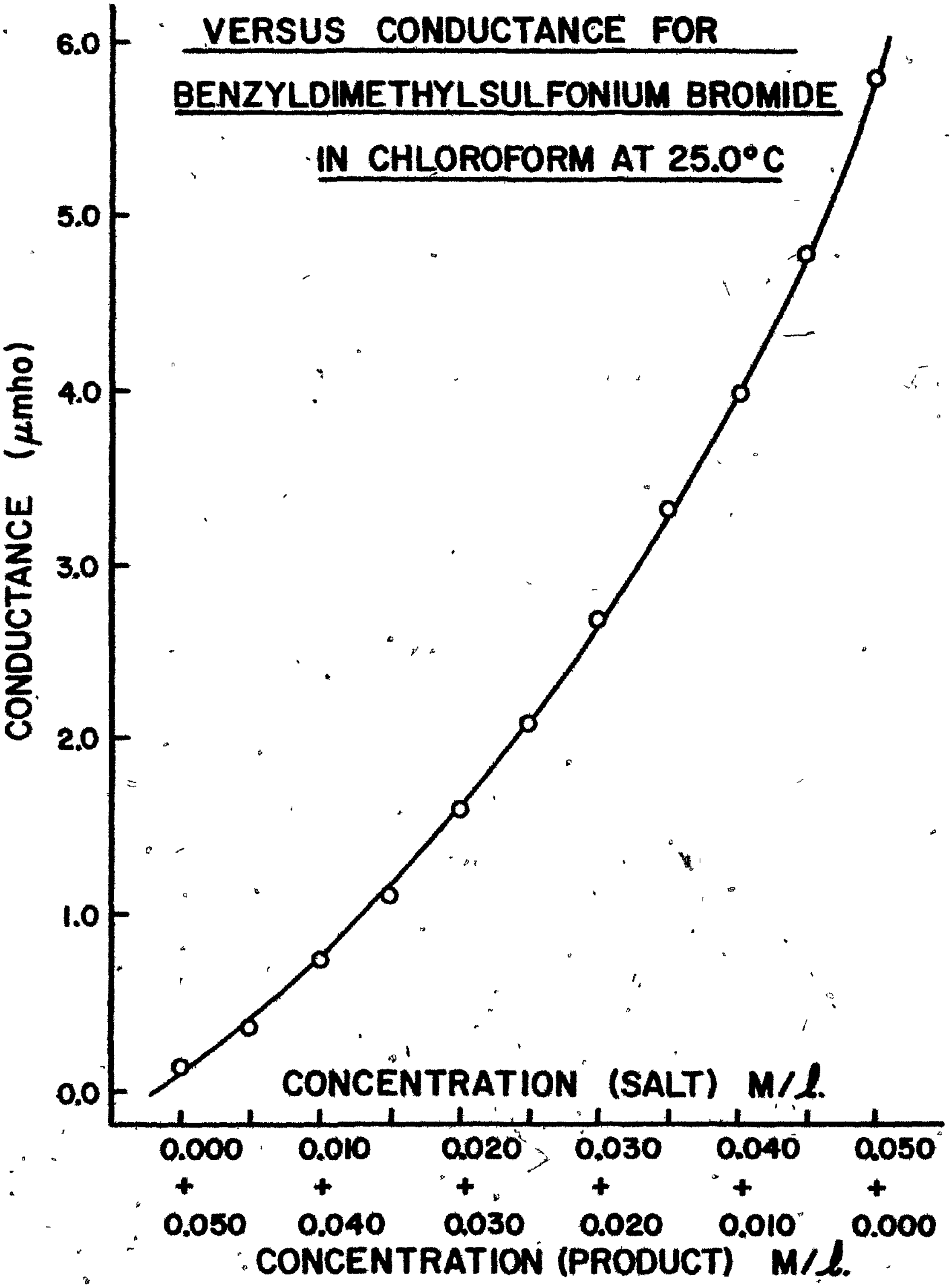


Fig. 30 CALIBRATION GRAPH OF CONCENTRATION VERSUS CONDUCTANCE FOR BENZYLDIMETHYLSULFONIUM BROMIDE IN CHLOROFORM AT 25.0°C

Table 30A. Calibration of conductance-concentration relation of benzyldimethylsulfonium bromide in chloroform solution at 25.0°C.

Cell No.3.

Concentration (M/1) Salt		Product	Conductance (μ mho)
0.050	+	0.000	5.80
0.045	+	0.005	4.80
0.040	+	0.010	4.00
0.035	+	0.015	3.33
0.030	+	0.020	2.70
0.025	+	0.025	2.10
0.020	+	0.030	1.60
0.015	+	0.035	1.10
0.010	+	0.040	0.75
0.005	+	0.045	0.35
0.000	+	0.050	0.13_5

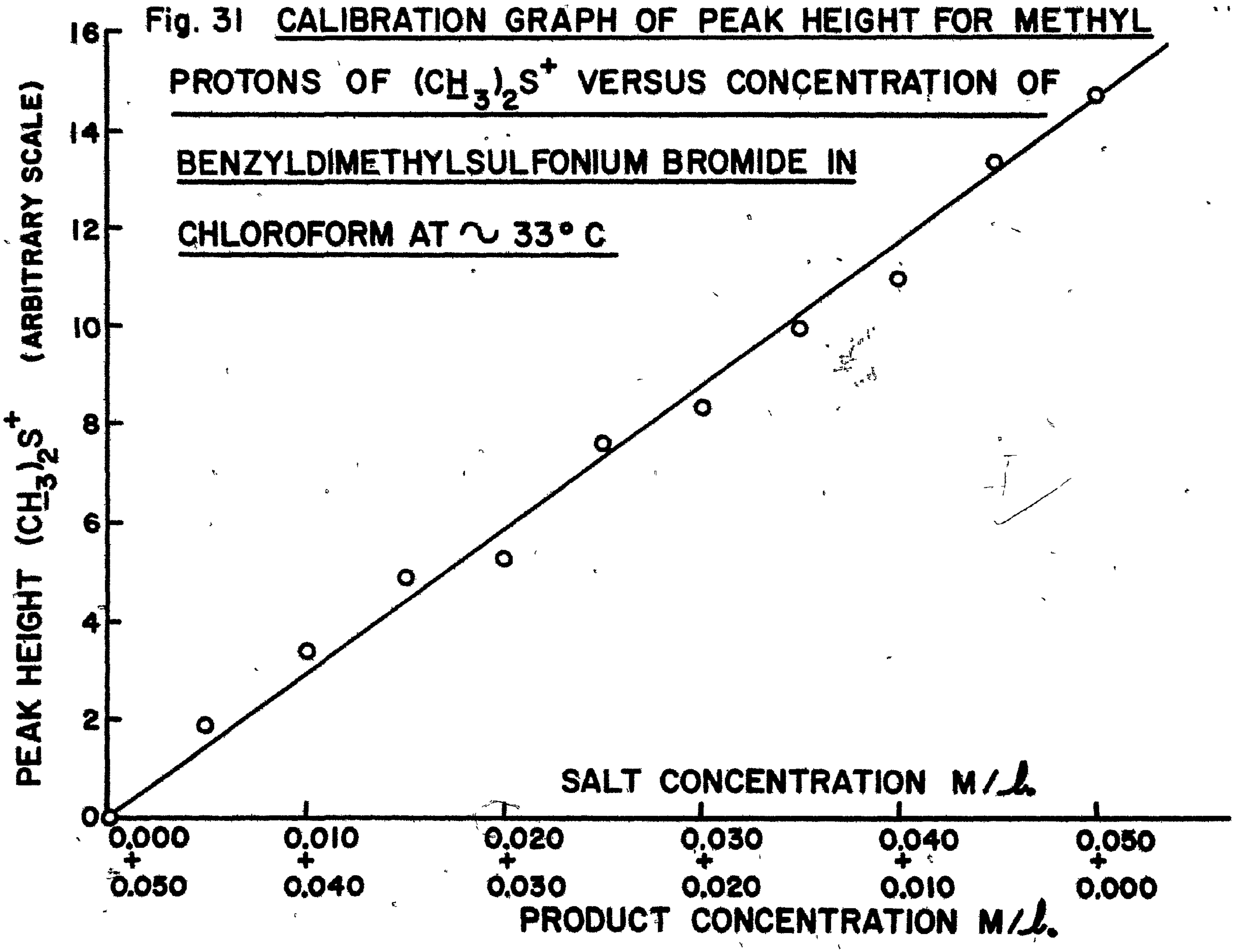


Fig. 31 CALIBRATION GRAPH OF PEAK HEIGHT FOR METHYL PROTONS OF $(CH_3)_2S^+$ VERSUS CONCENTRATION OF BENZYLDIMETHYLSULFONIUM BROMIDE IN CHLOROFORM AT ∿ 33° C

[redacted]

Table 31A. Calibration of concentration-peak height of N.M.R. signal for methyl protons of benzyldimethylsulfonium ion in chloroform.

Reaction: $\phi CH_2S^+(CH_3)_2Br^- \longrightarrow \underset{\text{(products)}}{CH_3SCH_3 + \phi CH_2Br}$

Concentration (M/1)			Peak-height (arbitrary unit)
Salt		Products	
0.050	+	0.000	14.8
0.045	+	0.005	13.4
0.040	+	0.010	11.0
0.035	+	0.015	10.0
0.030	+	0.020	8.4
0.025	+	0.025	7.7
0.020	+	0.030	5.3
0.015	+	0.035	4.9
0.010	+	0.040	3.4
0.005	+	0.045	1.9
0.000	+	0.050	0.0

F Kinetic Technique

1. In the kinetic runs, two conductivity cells, each having roughly a volume of 25 ml., and two other mini conductivity cells, each of an approximate capacity of 5 ml were used. The kinetic runs for the deuterated compounds were always measured in the mini cells. For measuring the rate ratios of the protium and deuterium compounds, kinetic runs in the mini cells were obtained simultaneously in the same thermostat. Duplicate runs were always obtained simultaneously, except for the ones at 45 and 50°C when the half-life of the reaction was inconveniently short.

2. The Guggenheim method[123] was applied to all kinetic measurements in order to avoid any errors caused by the initial and/or infinity reading(s). This method enables one to ignore the infinity reading in a run. The essence of the method may be described as follows: Let $C_1 \ldots\ldots C_i \ldots\ldots C_n$ be n readings taken at times $t_1, \ldots\ldots t_i \ldots\ldots t_n$, in the first half-life of the reaction; and that n more readings, $C'_1 \ldots\ldots, C'_i \ldots\ldots C'_n$, be recorded in the third half-life, after a constant time interval t at times $(t_1+t) \ldots\ldots (t_i+t) \ldots\ldots (t_n+t)$. Then from the rate equation of unimolecular reaction,

$$C\alpha - C_i = (C\alpha - C_o)e^{-kt_i} \quad (73)$$

$$C\alpha - C_i' = (C\alpha - C_o)e^{-kt_i - kt} \quad (74)$$

$$\text{or, } (C_i' - C_i) + (C\alpha - C_o)(1 - e^{-kt})e^{-kt_i} \quad (75)$$

$$\text{or, } kt_i + \ln(C_i' - C_i) = \ln(C\alpha - C_o)(1 - e^{-kt}) \quad (76)$$

$$= \text{Constant} \quad (77)$$

Thus a graph of the $\log_{10}(C_i - C_i')$ against time will have a slope of $-k/2.303$, where k is the rate constant, the negative sign implying that the conductance-value decreases as time increases.

These results were then treated by a least squares analysis. A computer program for a least squares study of the first order rate constants for the Guggenheim data for model CDC6400 was used. The output gave both the least squares rate constants and the standard deviation for each run. The computer programs for rate constants and for the Arrhenius equation are given in the appendices D and E respectively.

A few representative runs on the decomposition of the sulfonium salts, both with and without added electrolytes are found in Figs. 32-36 together with the experimental data in Tables 32A-36A.

Fig. 32 PLOT OF LOG$_{10}$(c−c') VERSUS t FOR THE DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM CHLORIDE

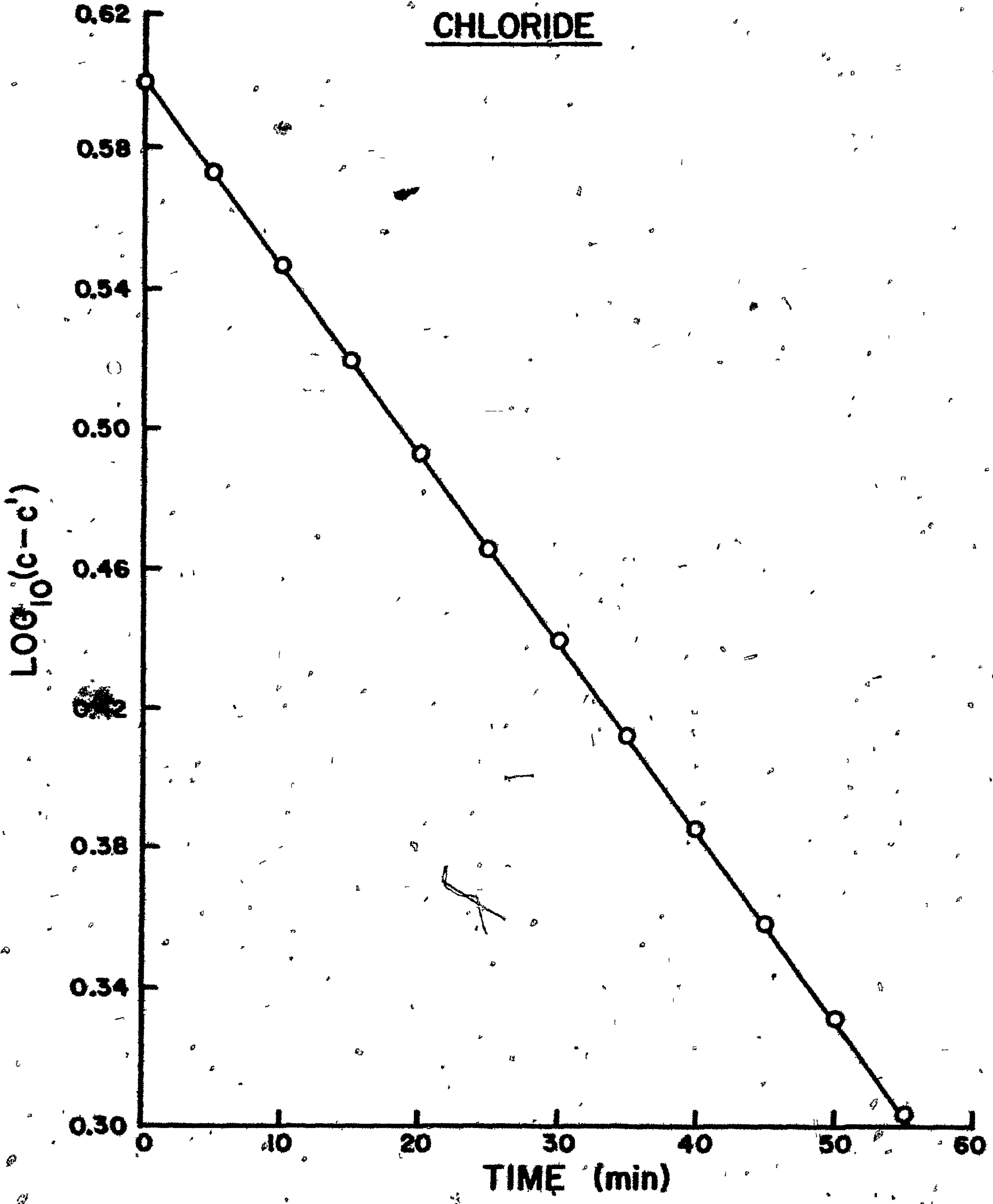


Table 32A. Decomposition of benzyldimethylsulfonium chloride in chloroform at 40.0°C.

Concentration of salt: 0.057 M/1

Cell #3, constant: 0.2375 cm^{-1}

Time (t,min)	Conductance (μ mho) (C, at t)	Conductance (μ mho) (C', at 110+t)	(C-C')	$\log_{10}$(C-C')
0	5.157	1.177	3.980	0.5999
5	4.844	1.094	3.750	0.5740
10	4.532	1.016	3.516	0.5460
15	4.249	0.939	3.310	0.5198
20	3.983	0.872	3.111	0.4930
25	3.729	0.805	2.924	0.4660
30	3.496	0.748	2.748	0.4391
35	3.276	0.691	2.585	0.4125
40	3.068	0.639	2.429	0.3854
45	2.870	0.589	2.281	0.3581
50	2.686	0.543	2.143	0.3310
55	2.513	0.499	2.014	0.3040

From the slope of the straight line, $k_1=20.6\times10^{-5}\,sec^{-1}$

Fig. 33 PLOT OF $LOG_{10}(c-c')$ VERSUS t FOR THE DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM BROMIDE

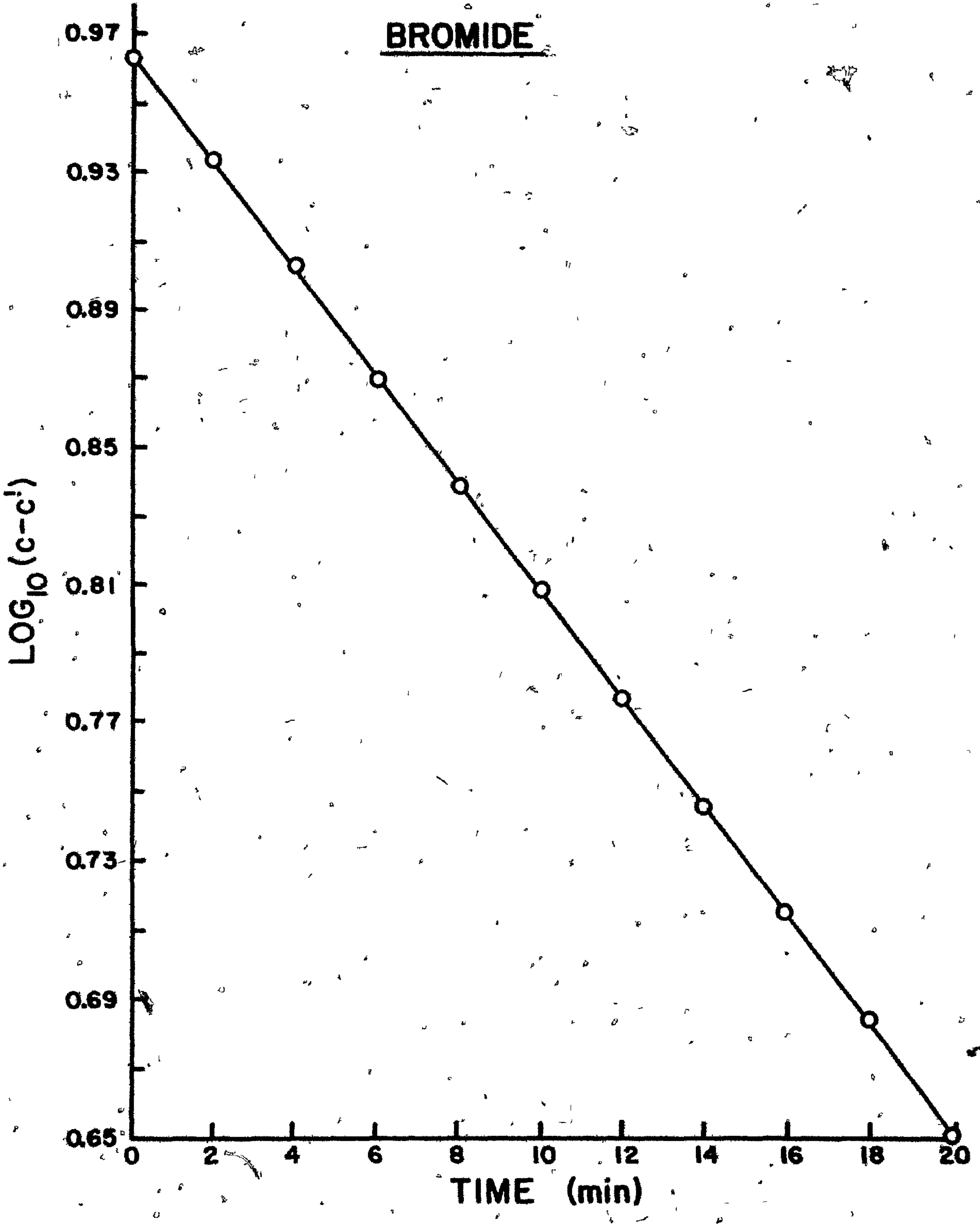


Table 33A. Decomposition of benzyldimethylsulfonium bromide in chloroform at 40.0°C.

Concentration of the salt: 0.055M/1

Cell #4, constant: 0.2625 cm^{-1}

Time	Conductance (μ mho)		(C-C')	($\log_{10}$(C-C')
(t,min)	(C, at t)	(C',at 40+t)		
0	11.731	2.500	9.231	0.9652
2	10.910	2.300	8.610	0.9350
4	10.733	2.113	8.020	0.9042
6	9.372	1.941	7.431	0.8710
8	8.709	1.790	6.919	0.8401
10	8.101	1.642	6.459	0.8102
12	7.497	1.495	6.002	0.7782
14	6.960	1.370	5.590	0.7474
16	6.458	1.250	5.208	0.7168
18	5.982	1.141	4.841	0.6848
20	5.540	1.051	4.489	0.6522

From the slope of the st line, $k_1 = 60.0 \times 10^{-5} sec^{-1}$

Fig. 34 PLOT OF $LOG_{10}(c-c')$ VERSUS t FOR THE DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM IODIDE

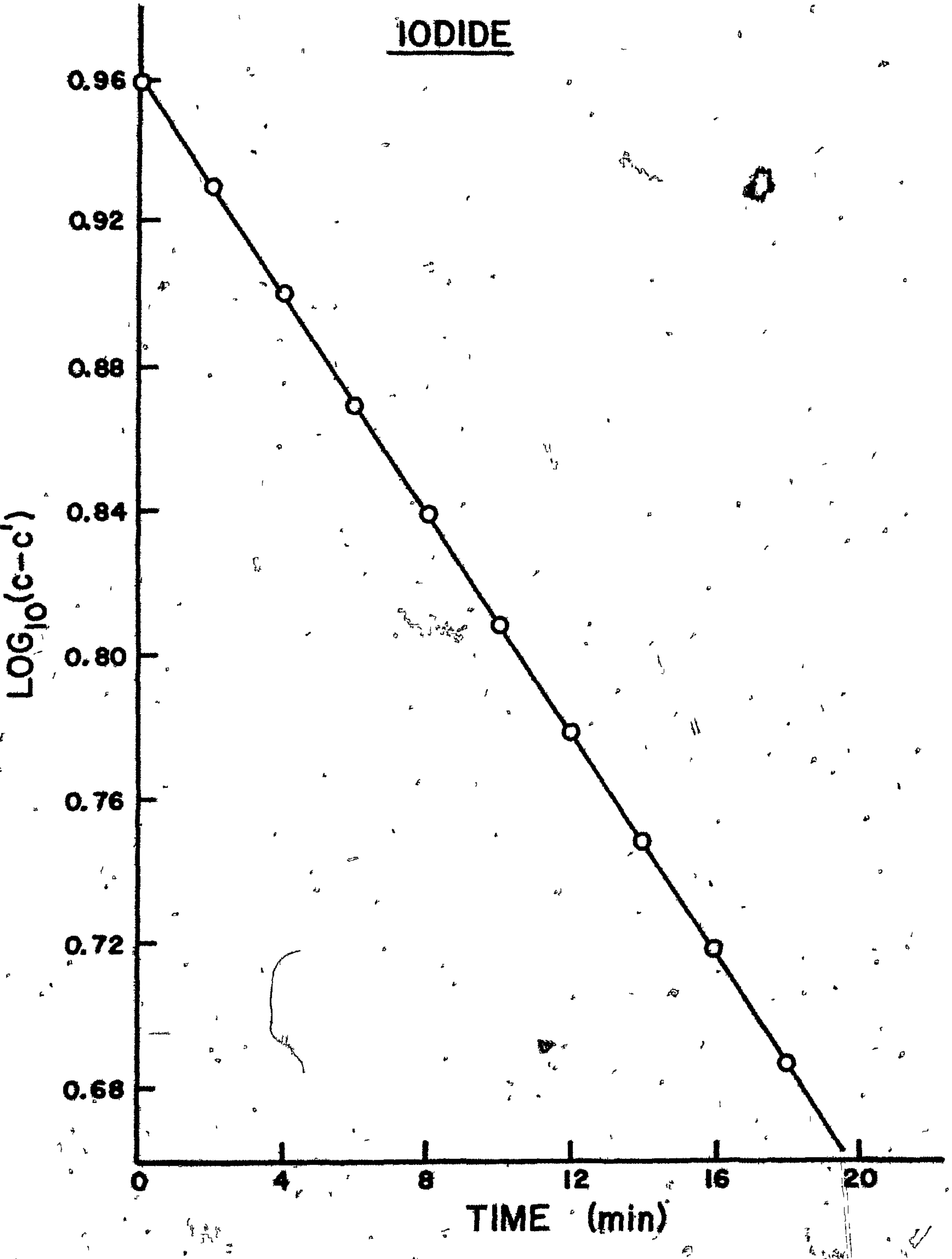


Table 34A. Decomposition of benzyldimethylsulfonium iodide in chloroform at 25.0°C.

Concentration of salt: 0.05 M/1

Cell #3, constant: 0.2375 cm^{-1}

Time	Conductance (μ mho)		(C-C')	$\log_{10}$(C-C')
(t,min)	(C, at t)	(C',at 36+t)		
0	11.82	2.72	9.10	0.9590
2	10.98	2.47	8.51	0.9299
4	10.18	2.23	7.95	0.9004
6	9.41	2.02	7.39	0.8686
8	8.72	1.82	6.90	0.8388
10	8.07	1.64	6.43	0.8082
12	7.48	1.47	6.01	0.7783
14	6.91	1.31	5.60	0.7482
16	6.39	1.16	5.23	0.7185
18	5.90	1.04	4.86	0.6866

From the slope of the straight line, $k_1 = 57.3 \times 10^{-5}$ sec^{-1}

Fig. 35 PLOT OF $LOG_{10}(c-c')$ VERSUS t FOR THE DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM BROMIDE IN THE PRESENCE OF n-TETRABUTYLAMMONIUM PERCHLORATE

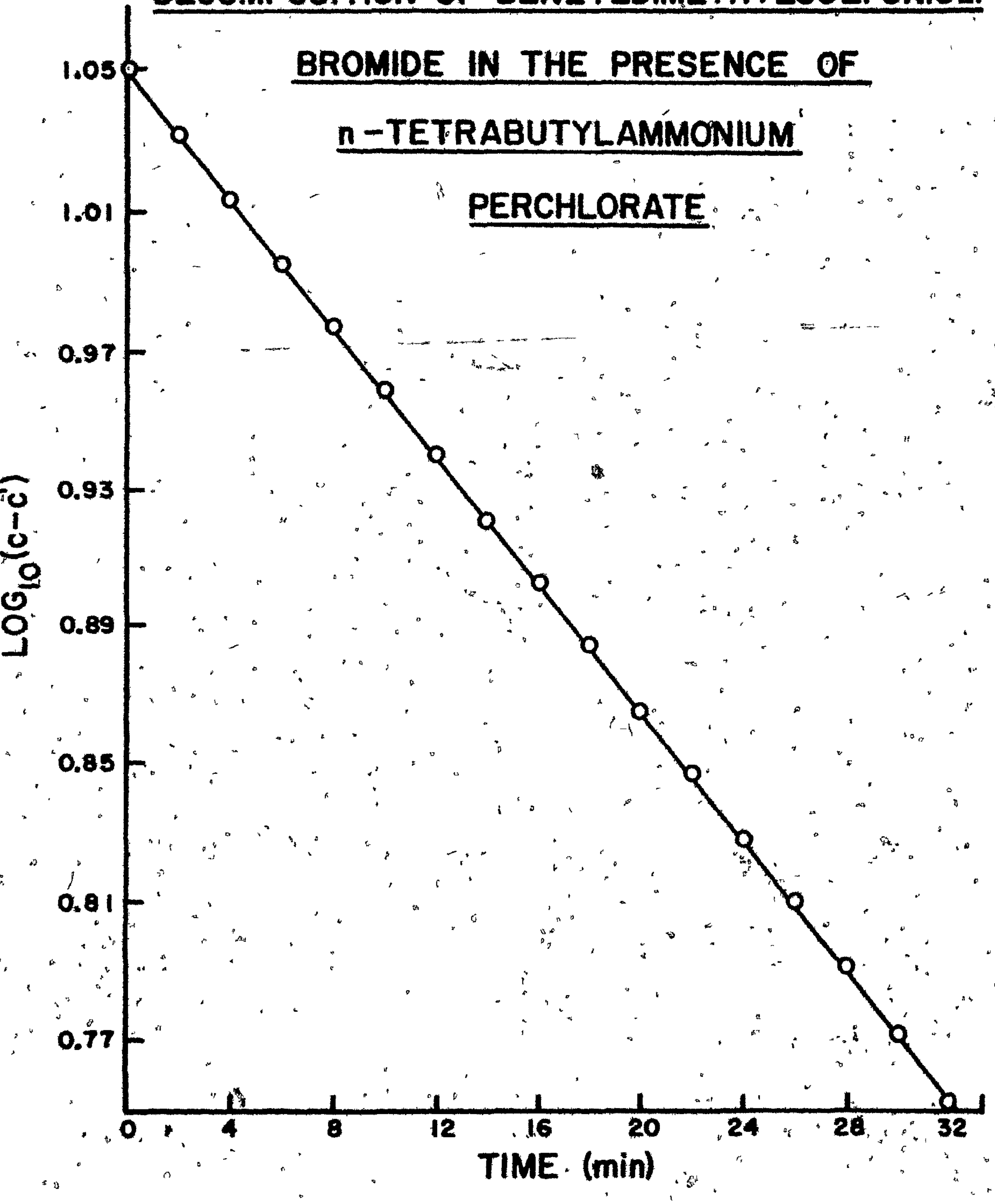


Table 35A. Decomposition of Benzyldimethylsulfonium bromide in the presence of added n-tetrabutylammonium phenoxide in chloroform at 40.0°C.

Concentration of the sulfonium salt: 0.05M/1

Concentration of the ammonium salt: 0.005M/1

Time	Conductance (μ mho)*		(C-C')	$\log_{10}$(C-C')
(t,min)	(C,at t)	(C'at 68+t)		
0	18.07	6.79	11.28	1.0523
2	17.42	6.63	10.79	1.0330
4	16.81	6.49	10.32	1.0136
6	16.23	6.35	9.88	0.9948
8	15.70	6.22	9.48	0.9768
10	15.17	6.10	9.07	0.9576
12	14.69	5.99	8.70	0.9395
14	14.21	5.87	8.34	0.9212
16	13.77	5.77	8.00	0.9031
18	13.35	5.67	7.68	0.8854
20	12.93	5.58	7.35	0.8663
22.	12.54	5.49	7.05	0.8482
24	12.17	5.42	6.75	0.8293
26	11.82	5.35	6.47	0.8109
28	11.47	5.28	6.19	0.7917
30	11.14	5.22	5.92	0.7723
32	10.83	5.17	5.66	0.7528
34	10.53	5.13	5.40	0.7324

*Conductance due to the ammonium salt: 4.76 μ mho

From the slope of Fig. 35, $k_1 = 35.9 \times 10^{-5} \sec^{-1}$

Fig. 36 PLOT OF $\mathrm{LOG}_{10}(c-c')$ VERSUS t FOR THE DECOMPOSITION OF BENZYLDIMETHYLSULFONIUM PERCHLORATE IN THE PRESENCE OF n-TETRABUTYLAMMONIUM BROMIDE

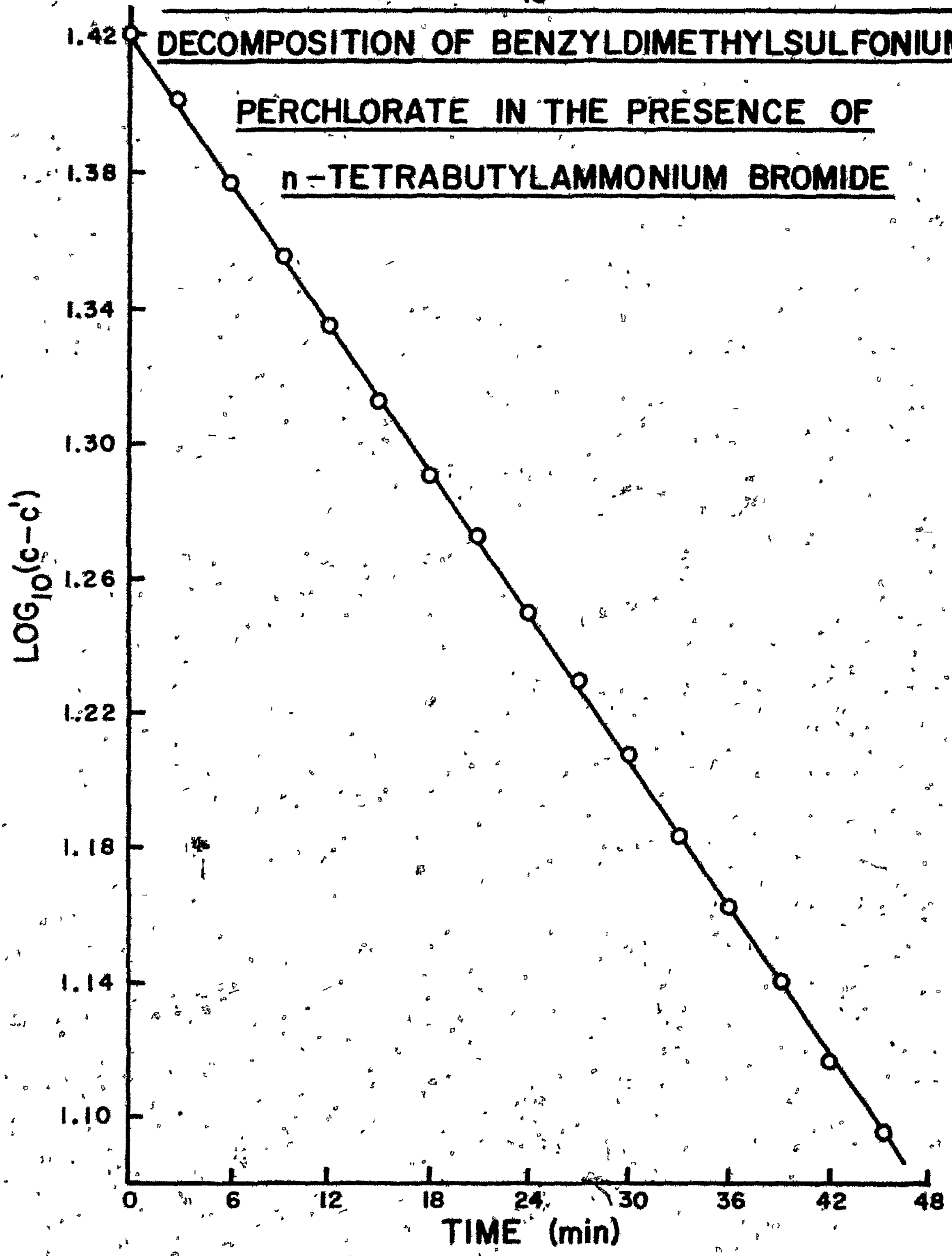


Table 36A. Decomposition of benzyldimethylsulfonium perchlorate in the presence of added n-tetrabutylammonium bromide in chloroform at 40.0°C.

Concentration of the sulfonium salt: 0.025 M/1

Concentration of the ammonium salt: 0.04 M/1

Time	Conductance (μ mho)*			
(t, min)	(C, at t)	(C', at 92+t)	(C-C')	$\log_{10}$(C-C')
0	200.4	174.0	26.4	1.4216
3	119.0	173.7	25.3	1.4031
6	197.2	173.4	23.8	1.3766
9	195.7	173.0	22.7	1.3560
12	194.4	172.7_5	21.6_5	1.3355
15	193.0	172.5	20.5	1.3118
18	191.7	172.2	19.5	1.2900
21	190.7	171.9_5	18.7_5	1.2730
24	189.5	171.7	17.8	1.2504
27	188.5	171.5	17.0	1.2304
30	187.4	171.2_5	16.1_5	1.2081
33	186.3	171.0_5	15.2_5	1.1832
36	185.4	170.8_5	14.5_5	1.1629
39	184.5	170.7	13.8	1.1399
42	183.6	170.5_5	13.0_5	1.1156
45	182.8	170.3_5	12.4_5	1.0952

*Conductance due to the ammonium salt: 168.0 μ mho.

From the slope of Fig.36, k_1 $27.6\text{x}10^{-5}$ sec^{-1}

G Conductance measurements

(a) Single salts

Conductance was measured for the following ammonium salts: n-Tetrabutylammonium bromide, -iodide, and -perchlorate, at different concentrations ranging from 0.05 to 0.0001M, in chloroform solvent at 25.0°C.

The sulfonium salts employed for the same purpose were diethylmethylsulfonium chloride, -bromide, -iodide, -perchlorate, and benzyldimethylsulfonium bromide; the concentrations ranging from 0.05 to 0.0001M, in chloroform at 25.0°C.

(b) Mixed salts

The conductance of the mixed salts was always obtained for equimolar mixtures of sulfonium and ammonium salts. The concentration range and the temperature were similar to those of the single salts. Equimolar mixtures of diethylmethylsulfonium bromide with each of n-tetrabutylammonium bromide, n-tetrabutylammonium iodide, and n-tetrabutylammonium perchlorate were used in this investigation.

H Cell constant and its determination

The resistance, R, of any conductor varies directly as its length ('ℓ' cm) and inversely as its area ('a' sq. cm); mathematically,

$$R = L\,\ell/a \text{ ohms,} \tag{78}$$

where the constant, L, is the specific resistance, or, resistivity, of the conducting material. The specific conductance designated by, K_{sp}, of a given material is defined as 1/L $\text{ohm}^{-1}\text{cm}^{-1}$. So equation (78) becomes

$$R = \ell/K_{sp}a \tag{79}$$

If the conductance of the solution is C, then,

$$C = 1/R = K_{sp}a/\ell \text{ ohms}^{-1} \tag{80}$$

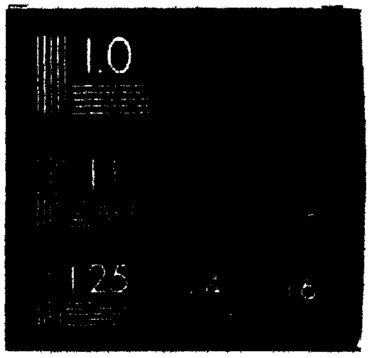
For a given cell, 'ℓ' and 'a' are constant, and the quantity ℓ/a is called the 'cell constant'.

Instead of direct measurement, the cell constant is usually obtained by means of a solution of known specific conductance. Potassium chloride solutions are invariably used for this purpose, because, they have been measured with great accuracy in cells of known dimensions.

A given solution of KCl of specific conductance, K_{sp}, is placed in the experimental cell, and its conductance, C_o, is measured; then the cell constant, ρ, is equal to,

$$\rho = K_{sp}/C_o \tag{81}$$

3 OF/DE 3



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The cell constant was calculated from the true conductance obtained from the observed conductance of a 0.02M/1 solution of potassium chloride. True conductance was obtained from observed conductance, by making allowance for the 'lead correction', as shown below.

Experimental data:

Observed conductance for 0.02 M/1 KCl in cell #3 ...... 0.011635 mho

Observed conductance for doubly distilled water (cell #3) 0.0000036 mho

Conductance for KCl solution in cell #3 ...... 11.6264 mho.

Lead correction[124]:

$$R_p = 1/C = 86.01 \text{ ohm}$$

$$X_p = 1/2\pi fc = 1/10^4 x 0.256 x 10^{-6} = 390.6 \text{ ohm}$$

$$Q = R_p/X_p = 0.2202; \quad Q^2 = 0.0485$$

$$R_s = R_p/(1 + Q^2) = 82.03$$

The following values were obtained from the literature supplied by Wayne Kerr[125].

$$R_{S(transformer)} = 0.042 \text{ ohm}$$

$$R_{(leads)} = 0.14 \text{ ohm}$$

Therefore, $R_{st} = R_s - R_{s(transformer)} - R_{(leads)} = 81.85$ ohm

$R_{p(true)} = R_{st} x(1 + Q^2) = 85.82$ ohm

Therefore, the true conductance of KCl solution is,

$1/R_{p(true)} = 11.6523$ mho

Therefore, the cell constant for cell #3,

$0.002768^*/0.0116523$

0.2375 cm^{-1}.

Similar calculations for cell #2 gives

$0.002768^*/0.010542$

0.2625 cm^{-1}

---

* Ref. 126

V APPENDICES

APPENDIX A

Calculation of Λ°

Assuming the equilibrium between the ions and the undissociated molecules of a binary electrolyte AB, i.e.,

$$A^+ + B^- \rightleftarrows AB, \qquad (1)$$

if the stoichiometric concentration is c, and the average fraction of solute free to carry the current is γ, then the various concentrations are:

$$[A^+] = [B^-] = c\gamma$$

$$[AB] = c(1 - \gamma)$$

where $\frac{1}{2}([A^+] + [B^-]) + [AB] = c$

The equilibrium function for reaction (1) is given by

$$\frac{[A^+]_{fA^+}[B^-]_{fB^-}}{[AB]_{fAB}} = K$$

where the activity coefficients are represented by f, and $f_{AB} = 1$,

Assuming $f_{A^+} = f_{B^-}$

$$K = \frac{c\gamma^2 f^2}{(1 - \gamma)} \qquad (2)$$

For convenience in later manipulation, a variable x is defined by:

$$x = (1 - \gamma)/\gamma^2 = cf^2/K$$

For a solution containing $c\gamma/1000$ equivalents per cc of anions and cations with mobilities ν_B- and ν_A+, respectively, the specific conductance, κ is given by:

$$1000\ \kappa = Fc\gamma(\nu_A+ + \nu_B-) \qquad (3)$$

where $F = 96{,}494$ international coulombs per equivalent. the equivalent conductance is defined as:

$$\Lambda = 1000\ \kappa/c \qquad (4)$$

According to interionic attraction theory the mobilities vary linearly with the square root of the ion concentration. Using Debye's equation to represent this change, we have in view of equation (3) and (4),

$$\Lambda = \gamma(\Lambda^\circ - \alpha\sqrt{c\gamma}) \qquad (5)$$

where Λ° is the limiting value of the equivalent conductance, and α has the value computed by Onsager

$$\alpha = \frac{8.18 \times 10^5}{(DT)3/2}\,\Lambda^\circ + \frac{82}{\eta(DT)^{\frac{1}{2}}} \qquad (6)$$

where η is the viscosity of the solvent.

The value of the limiting conductance Λ° is obtained from the conductance data as follows:

An approximate value of γ' of γ is obtained by replacing γ in the interionic attraction term of (5) by Λ/Λ°, i.e.

$$\gamma = \frac{\Lambda}{\Lambda^\circ - \alpha\sqrt{c\gamma}} = \frac{\Lambda/\Lambda^\circ}{1 - \alpha\Lambda^{\circ -1}\sqrt{c\gamma}} ,$$

and $$\gamma' = \frac{\Lambda/\Lambda^\circ}{1 - \alpha\Lambda^{-2}\sqrt{c\Lambda}}$$

and so on until it is constant.

APPENDIX B

To show $\Lambda = Ac^{-\frac{1}{2}} + Bc^{\frac{1}{2}}$

Let us consider the simplified case of an extremely dilute solution where the activity coefficients can be equated to unity and the limiting conductivity at infinite dilution is a sufficient approximation to the conductivity of a fully dissociated salt solution at this low concentration: let the solvent be one of low dielectric constant so that the degree of dissociation of ion-pairs is very small and $(1 - \alpha) = 1$.

Then for the reaction

$$MX \underset{}{\overset{K_2}{\rightleftarrows}} M^+ + X^-$$

$$K_2 = \alpha^2 c$$

and

$$(MXM)^+ \overset{K_3}{\rightleftarrows} (MX) + M^+$$

$$(XMX)^- \overset{K_3}{\rightleftarrows} MX + X^-$$

let

$$K_3' = \frac{[M^+][MX]}{[MXM^+]} = \frac{[X^-][MX]}{[XMX^-]}$$

an equality which implies that there is equal probability of forming (MXM^+) or (XMX^-). The total concentration is,

$$c = [MX] + \tfrac{1}{2}[M^+] + \tfrac{1}{2}[X^-] + 3/2[MXM^+] + 3/2[XMX^-]$$

but $\alpha_T = [MXM^+]/c = [XMX^-]/c$

so that if α and α_T are small

$$K_3 = \frac{\alpha}{\alpha_T}c \quad \text{and} \quad \alpha_T = \frac{\sqrt{K_2 c}}{K_3}$$

Let $\Lambda°$ be the limiting conductivity at infinite dilution of the simple ions, i.e.

$$\Lambda° = \lambda°_{M^+} + \lambda°_{X^-}$$

and $\Lambda°_T$ that of the triple ions, i.e.

$$\Lambda°_T = \lambda°_{MXM^+} + \lambda°_{XMX^-}$$

Then the observed conductivity will be

$$\Lambda = \alpha\Lambda° + \alpha_T\Lambda°_T$$

$$= \sqrt{\frac{K_2}{c}}\,\Lambda° + \sqrt{\frac{K_2 c}{K_3}}\quad\Lambda°_T$$

which is of the form

$$\Lambda = Ac^{-\frac{1}{2}} + Bc^{\frac{1}{2}}$$

APPENDIX C

To show $[Br^-] = R$

$$R = (cK_{2m})^{\frac{1}{2}} \times F$$

$$= (cK_{2m})^{\frac{1}{2}} \equiv L$$

$$\times \left\{1 + \frac{cs}{4K_{2m}}\right\}^{\frac{1}{2}} \equiv M$$

$$\times \left\{1 + \frac{c}{K_{3M}}\right\}^{-\frac{1}{2}} \equiv N$$

$$L = (cK_{2m})^{\frac{1}{2}} = [c \times \tfrac{1}{2}(K_{2x} + K_{2y})]^{\frac{1}{2}}$$

$$= [c \times \tfrac{1}{2}\left(\frac{[S^+][Br^-]}{[S + Br^-]} + \frac{[N^+][Br^-]}{[N^+Br^-]}\right)^{\frac{1}{2}}$$

$$= \left([S^+][Br^-] + [N^+][Br^-]\right)^{\frac{1}{2}} \quad \left(\because [S^+Br^-] = [N^+Br^-] = c/2\right)$$

$$M = \left\{1 + \frac{cs}{4K_{2m}}\right\}^{\frac{1}{2}}$$

$$= \left\{1 + \frac{c\left(\frac{K_{2x}}{K_{3x}} + \frac{K_{2y}}{K_{3y}} + \frac{K_{2x}}{K_{3yx}}\right)}{4 \times \frac{1}{2}(K_{2x} + K_{2y})}\right\}^{\frac{1}{2}}$$

$$= \left\{ 1 + \frac{c\left(\frac{[S^+][Br^-]}{[S^+Br^-]} \times \frac{[Br^-S^+Br^-]}{[S^+Br^-][Br^-]} + \frac{[Br^-][N^+]}{[N^+Br^-]} \times \frac{[Br^-N^+Br^-]}{[N^+Br^-][Br^-]} + \frac{[S^+][Br^-]}{[S^+Br^-]} \times \frac{[S^+Br^-N^+]}{[N^+Br^-][S^+]} \right)}{2\left(\frac{[S^+][Br^-]}{[S^+Br^-]} + \frac{[N^+][Br^-]}{[N^+Br^-]} \right)} \right\}^{\frac{1}{2}}$$

$$= \left\{ 1 + \frac{\frac{4c}{c^2}\left([S^+][Br^-S^+Br^-] + [N^+][Br^-N^+Br^-] + [Br^-][S^+Br^-N^+] \right)}{\frac{4}{c}\left([S^+][Br^-] + [N^+][Br^-] \right)} \right\}^{\frac{1}{2}}$$

$$= \left\{ \frac{[S^+][Br^-] + [N^+][Br^-] + [S^+][Br^-S^+Br^-] + [N^+][Br^-N^+Br^-] + [Br^-][N^+Br^-S^+]}{\left([S^+][Br^-] + [N^+][Br^-] \right)} \right\}^{\frac{1}{2}}$$

$$\left(\because [S^+Br^-] = [N^+Br^-] = c/2 \right)$$

$$N = \left\{1 + \frac{c}{K_{3m}}\right\}^{-\frac{1}{2}}$$

$$= \left\{1 + \frac{c}{2}\left(\frac{1}{K_{3x}} + \frac{1}{K_{3y}}\right)\right\}^{-\frac{1}{2}}$$

$$= \left\{1 + \frac{c}{2} \times \left(\frac{[Br^- S^+ Br^-]}{[S^+Br^-][Br^-]} + \frac{[Br^- N^+ Br^-]}{[N^+Br^-][Br^-]}\right)\right\}^{-\frac{1}{2}}$$

$$= \left\{1 + \frac{c}{2[Br^-]}\left(\frac{[N^+Br^-][Br^- S^+ Br^-] + [S^+Br^-][Br^- N^+ Br^-]}{[S^+Br^-][N^+Br^-]}\right)\right\}^{-\frac{1}{2}}$$

$$= \left\{1 + \frac{c \times \frac{c}{2}}{[Br^-] \times 2 \times \frac{c^2}{4}}\left([Br^- S^+ Br^-] + [Br^- N^+ Br^-]\right)\right\}^{-\frac{1}{2}}$$

$$= \left\{1 + \frac{[Br^- S^+ Br^-] + [Br^- N^+ Br^-]}{[Br^-]}\right\}^{-\frac{1}{2}} \qquad \left(\because [S^+Br^-] = [N^+Br^-] = \frac{c}{2}\right)$$

$$R = L \times M \times N$$

$$= \frac{\left([S^+][Br^-] \times [N^+][Br^-]\right)^{\frac{1}{2}} \times \left([S^+][Br^-] + [N^+][Br^-] + [S^+][Br^-S^+Br^-] + [N^+][Br^-N^+Br^-] + [Br^-][S^+Br^-N^+]\right)^{\frac{1}{2}} \times \left([Br^-]\right)^{\frac{1}{2}}}{\left([S^+][Br^-] + [N^+][Br^-]\right)^{\frac{1}{2}} \times \left([Br^-] + [Br^-S^+Br^-] + [Br^-N^+Br^-]\right)^{\frac{1}{2}}}$$

$$= \left\{\frac{[S^+][Br^-] + [S^+][Br^-] + [Br^-][S^+Br^-S^+] + [Br^-][N^+Br^-N^+] + [S^+][S^+Br^-N^+]}{\left([Br^-] + [Br^-S^+Br^-] + [Br^-N^+Br^-]\right)}\right\}^{\frac{1}{2}} \times \left\{[Br^-]\right\}^{\frac{1}{2}}$$

$$\left(\because [S^+][Br^-S^+Br^-] = [Br^-][S^+Br^-S^+]\right)$$

and $\left([N^+][Br^-N^+Br^-] = [Br^-][N^+Br^-N^+]\right)$

From charge balance,

$$[N^+] + [S^+] + [S^+Br^-S^+] + [N^+Br^-N^+] + [S^+Br^-N^+] = [Br^-] + [Br^-S^+Br^-] + [Br^-N^+Br^-]$$

$$R = \frac{[Br^-]^{\frac{1}{2}} \left([S^+] + [N^+] + [S^+Br^-S^+] + [N^+Br^-N^+] + [N^+Br^-S^+]\right)^{\frac{1}{2}} x \left([Br^-]\right)^{\frac{1}{2}}}{\left([Br^-] + [Br^-S^+Br^-] + [Br^-N^+Br^-]\right)^{\frac{1}{2}}}$$

$$\therefore R \neq [Br^-]$$

APPENDIX D

```
                                  CDC 6600 FTN V3.0-P213 OPT = 1  19/04/72

C     FOR RATE FROM FIRST ORDER KINETIC DATA
C     TIMES THEN CHANGES IN O.D.
      PROGRAM DELTAA (INPUT,OUTPUT)
      DIMENSION X (30), Y(30)
   99 FORMAT (15)
  100 FORMAT (* TOTAL NUMBER OF RUNS*,15)
  101 FORMAT (15,2A4)
  102 FORMAT(*ORUN   *,2A4)
  103 FORMAT(10F8.4)
  104 FORMAT(6F13.3)
  105 FORMAT(*OSLOPE*,E14.5,10X,*P.F.OF SLOPE*,E14.3)
  106 FORMAT(* C.C.*,F10.5)
  107 FORMAT(* Y-INTERCEPT*,F10.5,10X,*P,E. OF &-INT. *, F10.5)
  108 FORMAT(* COMMON LOG OF SLOPE*, F10,7,10X,*HALF-LTFE*,E14.5)
      READ 99,LRUNS
      PRINT 100,LRUNS
      DO 500 J=1,LRUNS
      READ 101,N,ID1,ID2
      PRINT 102,ID1,ID2
```

```
    READ 103,(X(I),I=1,N)
    READ 103,(Y(I),I=1,N)
    PRINT 104,(X(I),I=1,N)
    PRINT 104,(Y(I),I=1,N)
    DO 200 I=1,N
    X(I)=60.0*X(I)
200 Y(I)=ALOG(Y(I))
    SUMX=0.0
    SUMY=0.0
    SUMXY=0.0
    SUMXX=0.0
    SUMYY=0.0
    DO 300 I=1,N
    SUMX=SUMX+X(I)
    SUMY=SUMY+Y(I)
    SUMXY=SUMXY+X(I)*Y(I)
    SUMXX=SUMXX+X(I)**2
    SUMYY=SUMYY+Y(I)**2
300 CONTINUE
    YINT=(SUMY*SUMXX-SUMX*SUMXY)/(N*SUMXX-SUMX**2)
    B=(N*SUMXY-SUMX*SUMY)/(N*SUMXX-SUMX**2)
    DIF=0.0
    DO 400 K=1,N
```

```
  400 DIF=DIF+(Y(K)-B*X(K)-YINT)**2
      VARI=DIF/(N-2)
      DEX=SQRT(N*SUMXX-SUMX**2)
      DEY=SQRT(N*SUMYY-SUMY**2)
      PEI=0.6745*SQRT(SUMXX*VARI/DEX**2)
      PEB=0.6745*SQRT(N*VARI/DEX**2)
      CC=(N*SUMXY-SUMX*SUMY)/(DEX*DEY)
      HL=0.693147/B
      YINT=EXP(YINT)
      PEI=EXP(PEI)
      PEI=0.5*YINT*(PEI-1.0/PEI)
DELTAA                       CDC 6600 FTN V3.0-P213 OPT=1 19/04/72
      PEB=0.6745*SQRT(N*VARI/DEX**2)
      PRINT 106,CC
      PRINT 105,B,PEB
      PRINT 107,YINT,PEI
      PRINT 108,BL,HL
  500 CONTINUE
      STOP
      END
```

APPENDIX E

```
                                 CDC 6600 FTN V3.0-P213 OPT=1  18/05/72
C     TO CALCULATE ENTHALPY, ENTROPY, ENERGY OF ACTIVATION
C     TEMPS IN CENTIGRADE, THEN RATES X A SPECIFIED CONSTANT
      PROGRAM ACTPAR (INPUT,OUTPUT)
      DIMENSION X(30),Y(30)
   99 FORMAT(15)
  100 FORMAT(*TOTAL NUMBER OF RUNS*,15)
  101 FORMAT(15,2A4)
  102 FORMAT(*0RUN   *,2A4)
  103 FORMAT(8F10.4)
  104 FORMAT(* TEMP.   *,6F12.2)
  105 FORMAT(* K  *,6F12.7)
  106 FORMAT(* C.C.*,F10.5)
  110 FORMAT(*DELTA-H*,F10.2,10X,*P.E.OF DELTA H*,F10.2,10X,*E OF ACT.
     1  *,F10.2)
  111 FORMAT(* A-FACTOR*,E14.3,*  AT*,F10.2,*DEG. C.  P.E. OF A-FACTOR
     1R*,E14.3)
  112 FORMAT(*  DELTA S*,F10.2,10X,*P.E. OF DELTA S*, F10.2)
  113 FORMAT(8F12.8)
      READ 99,LRUNS
      PRINT 100,LRUNS
      DO 500 J=1,LRUNS
```

```
      READ 101,N,ID1,ID2
      PRINT 102,ID1,ID2
      READ 103,(X(I),I=1,N)
      READ 103,(Y(I),I=1,N)
      PRINT 104,(X(I),I=1,N)
      PRINT 105,(Y(I),I=1,N)
      DO 200 I=1,N
      X(I)=1.0/(273.16+X(I))
  200 Y(I)=ALOG(Y(I)+ALOG(X(I))
      PRINT 113,(X(I),I=1,N)
      PRINT 113,(Y(I),I=1,N)
      SUMX=0.0
      SUMY=0.0
      SUMXY=0.0
      SUMXX=0.0
      SUMYY=0.0
      DO 300 I=1,N
      SUMX=SUMX+X(I)
      SUMY=SUMY+Y(I)
      SUMXY=SUMXY+X(I)*Y(I)
      SUMXX=SUMXX+X(I)**2
      SUMYY=SUMYY+Y(I)**2
  300 CONTINUE
```

```
         YINT=(SUMY*SUMXX-SUMX*SUMXY)/(N*SUMXX-SUMX**2)
         B=(N*SUMXY-SUMX*SUMY)/(N*SUMXX-SUMX**2)
         DIF=0.0
         DO 400 K=1,N
     400 DIF=DIF+(Y(K)-B*X(K)-YINT)**2
         VARI+DIF/(N-2)
         DEX=SQRT(N*SUMXX-SUMX**2)
         DEY=SQRT(N*SUMYY-SUMY**2)
         PEI=0.6745*SQRT(SUMXX*VARI/DEX**2)
         PEDS=1.987*PEI
ACTPAR                       CDC 6600 FTN V3.0-P213 OPT=1  18/05/72
         PEB=0.6745*SQRT(N*VARI/DEX**2)
         PEB=0.001987*PEB
         CC=(N*SUMXY-SUMX*SUMY)/(DEX*DEY)
         T=1.0/(SUMX/N)
         B=0.001987*B
         DS=1.987*(YINT-23.75997)
         E=B+(0.001987*T)
         AF=EXP(YINT+ALOG(T)+1.0)
         AFL=AF-AF*(1.0-1.0/EXP(PEI))
         AFU=AF+AF*(EXP(PEI)-1.0)
         AF=(AFU+AFL)/2.0
```

```
      PEAF=AF-AFL
      T=T-273.16
      PRINT 106,CC
      PRINT 110,B,PEB,E
      PRINT 112,DS,PEDS
      PRINT 111,AF,T,PEAF
  500 CONTINUE
      STOP
      END
```

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