witnessing here the operation of a steric acceleration effect.[32] This factor also may be involved in interpreting many of the effects of substitution, but it does not appear to vitiate any of the conclusions we have reached above regarding polar influences in these acid-catalyzed solvolysis reactions.

[32] See for other examples, H. C. Brown and R. S. Fletcher, THIS JOURNAL, 71, 1845 (1949); H. C. Brown and A. Stern, *ibid.*, 72, 5068 (1950); H. C. Brown and H. L. Berneis, *ibid.*, 75, 10 (1953); F. Brown, T. D. Davis, I. Dostrovsky, O. J. Evans, and E. D. Hughes, *Nature*, 167, 987 (1951), as well as ref. 22, *inter alia*.

[CONTRIBUTION FROM THE STEELE CHEMISTRY LABORATORY OF DARTMOUTH COLLEGE, HANOVER, N. H.]

Specific Solvation in Binary Solvent Mixtures. Part I. Variations in Activation Energy of Reactions in Mixed Solvents

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Existing evidence for solvent sorting in the immediate vicinity of ionic solute species in binary solvent mixtures is reviewed briefly. A model is presented which considers the influence of such specific solvation on the activation energy of reactions in mixed solvents and is shown to account satisfactorily for data for solvolytic reactions. The effect of temperature dependence of bulk dielectric constant on activation energy is discussed and shown to be insufficient to account for the observed phenomena.

Introduction

In this paper, and subsequent papers of the series, the phenomenon of specific solvation, or solvent sorting in the immediate vicinity of solute species in binary solvent mixtures, will be considered in general. In particular, emphasis will be placed on the effect of this phenomenon as it is revealed in the activation parameters for kinetic processes in solution.

As early as 1927, Debye[2] attempted a quantitative treatment of the phenomenon, as it relates to systems of ions in binary solvent mixtures. Later Scatchard[2] considered the particular system of ions in ethanol–water mixtures and computed the magnitude of the differences between the solvent composition near the ion and in the bulk as a function of distance from the ion. Since these early attempts to treat the problem, several workers[3–5] have investigated the phenomenon both theoretically and experimentally and have established beyond doubt the reality of solvent sorting in a number of systems. Reference will be made at a later stage to many of these non-kinetic examples of the phenomenon, but paralleling these developments there has been an interest in specific solvation as a factor determining kinetic behavior.

Laidler and Eyring[6] and Scatchard[7] recognized the possible importance of specific solvation as a determining factor in the behavior of the rate constant. This apparently secondary effect on the rate constant, however, has been largely ignored in the many recent correlations of rate with structural and solvent properties.[8–10] The essentially linear nature of these rate correlations reflects the linear dependence of the free energy of activation, ΔF^*, on the correlation parameters. However, as has been amply demonstrated in the past, and most recently by Laidler,[11] the observed linear dependence of ΔF^* is due, in large part, to the compensatory behavior of the activation enthalpy and entropy.

$$\Delta F^* = \Delta H^* - T\Delta S^*$$

There are now many cases in the literature where the behavior of both the enthalpy and entropy of activation is far from linearly related to any property of a solvent medium which is being varied in composition. Many of these cases will be dealt with in detail in this and subsequent papers. The most striking of these deviations from linear behavior are to be found in the variations of the activation enthalpy or energy as a function of solvent composition and it is this parameter which will be emphasized in the treatment offered here.

Many workers[12–15] have attempted to account for the observed activation energy behavior in terms of the temperature dependence of the dielectric constant and have measured, or computed, "isodielectric" activation energies. It will be shown later, however, that this explanation can, at best, account for only part of the devious variations of the activation energy.

The suggestion that specific solvation or solvent sorting may play an important part in determining activation energy behavior has been made recently by several workers in the field.[16,17] The results of Tommila and co-workers are of particular sig-

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[1] Department of Chemistry, University of Alberta in Calgary, Calgary, Alberta, Canada.

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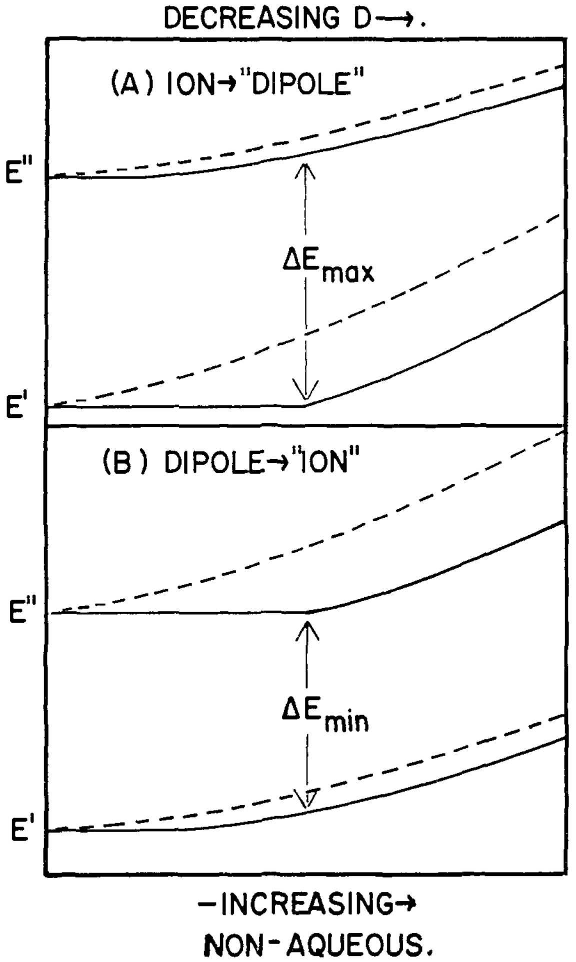

Fig. 1.—Origin of maxima and minima in ΔE^*.

nificance in this regard. None of these workers, however, did more than suggest the significance of specific solvation and it is the purpose of this work to extend and develop the principle by formulating a model from which the behavior of the activation energy can be predicted.

Hyne and Wonkka have observed recently[18] that the activation energy of the solvolysis of dimethyl-*t*-butylsulfonium iodide in water–ethanol mixtures passes through a maximum in water-rich solvents compared with the much more generally observed minima for the solvolysis of alkyl halides and benzenesulfonates. Since the change in charge density on going from initial to transition state in the two types is opposite, the parallel behavior of the activation energy commanded immediate attention.

In the subsequent sections of this paper a model is postulated and tested against the available data on activation energy behavior in mixed solvents.

Due to the variety of sources of activation energy data and the variable confidence which can be placed in the accuracy, the term activation energy (ΔE^*) is used throughout irrespective of whether the data are truly the Arrhenius ΔE^* or the activation enthalpy ΔH^*. Since the terms differ by the constant RT this approximation only affects the absolute magnitude of the term and not the magnitude of any changes in the term as a function of solvent composition.

The Specific Solvation Model.—The total energy E of a species in solution can be arbitrarily divided into two components

$$E = e_M + e_S$$

The subscript M denotes that part of the total energy within the species (chemical bonding) and subscript S denotes the energy of interaction between the species and the solvent environment. Using the double prime symbol to indicate the energies of the transition state and single prime for the initial state, we then have

$$E'' = e_M'' + e_S'' \text{ and } E' = e_M' + e_S'$$

$$\Delta E^* = E'' - E' = e_M'' - e_M' + e_S'' - e_S' \quad (1)$$

In this analysis we are concerned with the variation of the activation energy over a range of *water-rich solvents* in which it seems justifiable to assume, at least to a first approximation, that the mechanism of the reaction will not change markedly. Therefore the values e_M'' and e_M' should remain relatively constant as solvent composition is changed over the range under consideration. This is tantamount to saying that the initial and transition state configurations of the solute species do not change markedly over the water-rich range of solvent composition under consideration and hence the intramolecular energy components of the over-all energy, e_M' and e_M'', remain constant. The behavior of e_S' and e_S'' with solvent change, however, depends on the precise nature of the solvent environment around the solute species. If this environment differs between initial and transition states, then that part of the activation energy determined by $e_S'' - e_S'$ will vary as the environment varies.

In an attempt to predict qualitatively the dependence of e_S on solvent environment, we consider two types of solute species, ions and dipoles. In the former case e_S is the energy of interaction, or solvation energy, of an ion in a dipolar solvent, while in the latter e_S is the solvation energy of a dipole in a medium of dipolar solvent molecules. Qualitatively e_S for an ion must be considerably more sensitive to changes in solvent composition than e_S for a dipole.[19,20]

Considering all the factors above, E' and E'' are represented in Fig. 1 as functions of solvent composition for two model cases: the first where an ionic initial state goes to a "dipolar" transition state and the second where a dipolar initial state goes to an "ionic" transition state. These curves are shown in Fig. 1 by broken lines, the distance between the lines representing the activation energy at any given solvent composition. In a solvent continuum where any solvent sorting phenomenon is ignored these curves would approximate the real behavior of the system. However, in the binary solvent mixtures under consideration the polarity of the two components is considerably different. It is at this point that the

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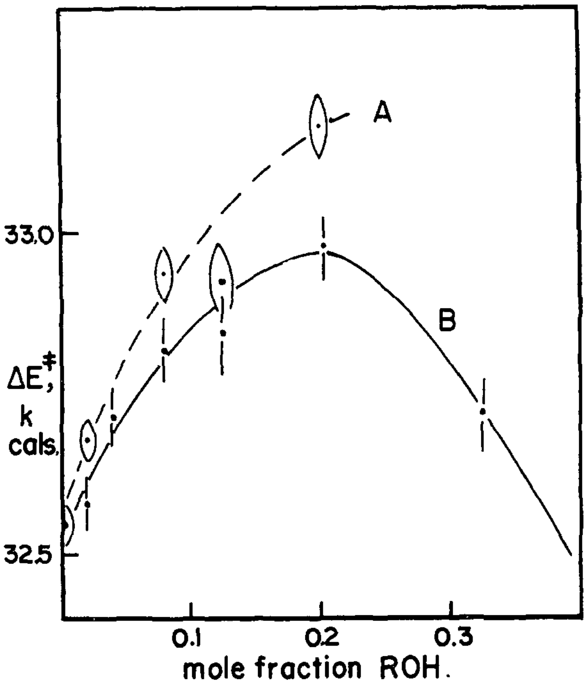


Fig. 2.—Activation energies for solvolysis of dimethyl-*t*-butylsulfonium iodide[18] in: A, *t*-butyl alcohol–water mixtures; B, ethanol–water mixtures; points not shown on figure, 0.55 EtOH, $\Delta E^* = 32.25$; 0.73 EtOH, $\Delta E^* = 32.09$ kcal.

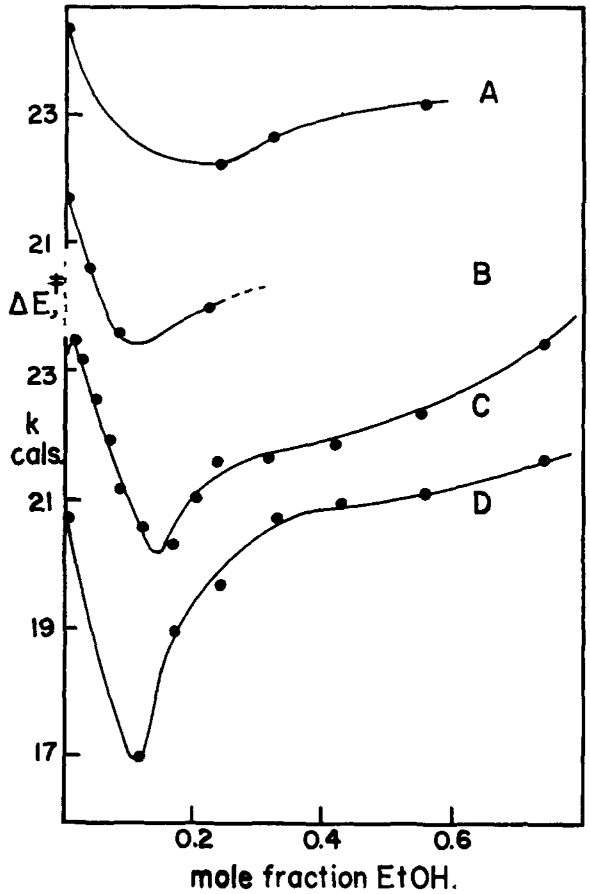


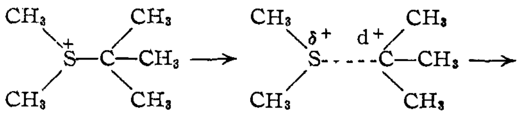
Fig. 3.—Activation energies for solvolysis of alkyl halides in ethanol–water: A, isopropyl bromide[9,21–23]; B, benzyl chloride[18,24]; C, *t*-butyl chloride[25a]; D, α-phenylethyl chloride,[25b] ΔE^* in water from $k^0 = 1.52 \times 10^{-3}$ sec.$^{-1}$; $k^{13.1} = 9.56 \times 10^{-3}$ sec.$^{-1}$.[18] Note this value differs from extrapolated value of ref. 25b where k^0 of ref. 26 was used.

concept of specific solvation or solvent sorting about the dissolved species is introduced.

Both the ionic and dipolar types of solute will tend to be solvated by the more polar component of the binary mixture. Therefore, neither the bulk dielectric constant nor the mole fraction will be a true measure of the system in the kinetically important immediate environment of the solute species. As the less polar component of the mixture is added, the composition of the immediate environment of the solute species will not follow that of the bulk. In colloquial terms, the solute will be unaware of the change in bulk composition until a sufficient amount of the less polar component has been added to overcome the selectivity of the solute for the more polar component. Since the variation of E with solvent has been attributed to changes in e_S, and since e_S cannot change unless the microdielectric changes, the broken lines in Fig. 1 must be displaced as shown by the full lines. Further, the selectivity of an ion must be greater than that of a dipole and so the displacement is greater for the ion than for the dipole. It is now clear from Fig. 1 that depending upon whether the initial or transition state is the more ionic species the difference in energy, or the activation energy $\Delta E^* = E'' - E'$, will pass through a maximum or a minimum with change in solvent composition.

The solvolysis in ethanol–water mixtures of sulfonium salts and alkyl halides represents the two kinetic cases of ion to "dipole" and dipole to "ion" in moving from initial to transition state. The former shows a maximum in the activation energy and the latter a minimum as illustrated in Figs. 2 and 3. Although the magnitudes of the maxima in the sulfonium salt solvolysis are small, their reality is beyond question. Rate determinations were reproducible to ±0.4% and activation energies to ±75 cal. As will be discussed later, there is good reason for the small size of these maxima.

In discussing the theoretical background for the maxima and minima we approximated the real situation in the experimental systems being offered as examples. The sulfonium salts are ionic in the initial state but "charge delocalized" in the transition state. The rate-determining step in the water-rich solvolysis of dimethyl-*t*-butylsulfonium salts has been established as the SN1 formation of a carbonium ion. In the transition state, therefore, the positive charge must undergo delocalization preliminary to carbonium ion formation. Consideration of the transition state



$$\mathrm{(CH_3)_2\overset{+}{S}{-}C(CH_3)_3 \longrightarrow (CH_3)_2\overset{\delta+}{S}{\cdots}\overset{d+}{C}(CH_3)_3 \longrightarrow}$$

as a "dipole" therefore seems a valid approximation. In the case of alkyl halides, the initial state is dipolar whereas the transition state must involve

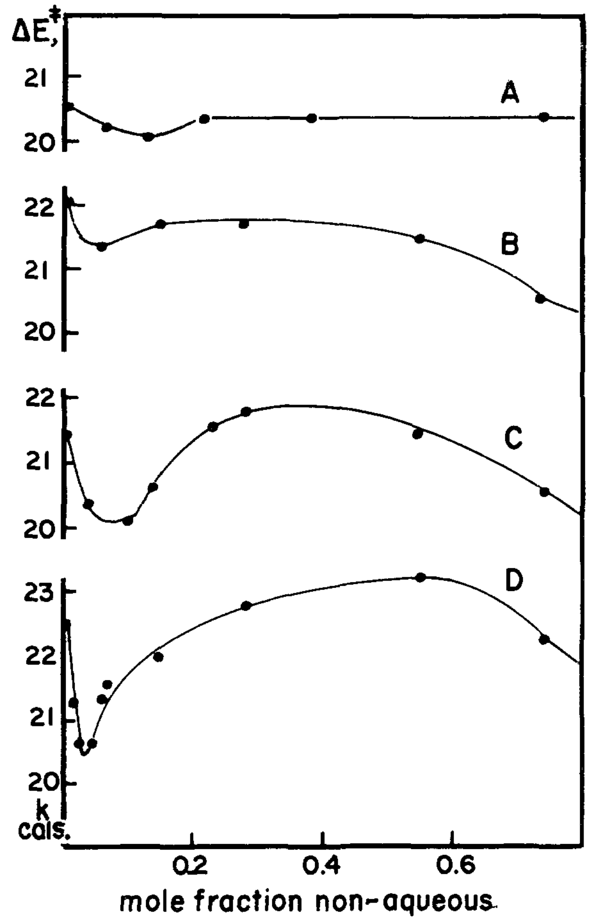


Fig. 4.—Activation energies for solvolysis of alkyl benzenesulfonates in mixed solvents: A, methyl benzenesulfonate in ethanol–water[27]; B, ethyl benzenesulfonate; C, *n*-propyl benzenesulfonate; D, isopropyl benzenesulfonate, all in acetone–water.[28]

either dipole intensification in the case of S_N2 type reactions or partial ionic character in S_N1 type reactions preliminary to the formation of carbonium ions.

$$\overset{\rightarrow}{\text{R—X}} \longrightarrow \overset{\delta^+}{\text{R}}\text{- - - -}\overset{\delta^-}{\text{X}} \longrightarrow$$

Approximation of the transition state in this case to an "ion" therefore seems reasonable. These arguments are essentially similar to those employed by various workers in attempts to explain the dependence of rate on dielectric constant, *e.g.*, Ingold, Winstein, Swain and their co-workers.

Satisfactory though this argument may be by itself, the further interpretation of the magnitude of the minima discussed in the next section provides substantial support for the treatment.

The Magnitude of ΔE* Minima and Maxima in Neutral Solvolysis Reactions.—Two factors appear to influence the magnitude of the minima and maxima as far as can be judged from the data presently available. These are the nature of the alkyl group in the solute and the nature of the solvent.

Variation of Solute.—The data plotted in Figs. 3 and 4 represent the sum total of examples where activation energies have been determined with sufficient precision to warrant a quantitative analysis of the phenomena. This does not imply that all activation energies used are equally accurate but the internal consistency which is apparent in Table I leaves little doubt that the orders of magnitude of the minima are correct. Unfortunately the data are limited to cases where minima are observed since the sulfonium salt example available involves solvent variation only.

The model discussed in the previous section for systems having polar initial states and "ionic" or "dipole intensified" transition states would predict that the greater the difference in charge density between initial and transition states the greater will be the minimum. This results from the relative specificity of solvation in the two states and accordingly the relative distances the energy curves are displaced along the solvent axis (Fig. 1). The series of alkyl halides and benzenesulfonates in Table I contain alkyl groups varying from methyl to α-phenylethyl which represent a spectrum of alkyl substituents covering the range from very poor to excellent positive charge acceptors. The extent to which "ion" like character is developed in the transition state should depend upon the degree to which the process of charge separation has progressed and this should be greatest for the alkyl group best able to accommodate the developing positive charge. In other words, the greater minima should be observed in those cases where the alkyl group exists as a relatively long lived carbonium ion. The depths of the minima for a series of alkyl halides and benzenesulfonates are shown in Table I. The order of increasing depth of minimum is precisely that of increasing carbonium ion stability as measured both by the heat of ionization in the gas phase[29] of the alkyl halide and by the Winstein, Grunwald and Jones correlation *m*-values.[9] These latter are essentially a measure of the S_N1-like character of the reaction and are constant for a given solute in various solvents.

It should be noted that the data for three of the alkyl benzenesulfonates in Table I are for reactions in acetone–water rather than ethanol–water mixtures. As will be seen from Table II, however, these two solvent mixtures have very similar solvent effects on the activation energy behavior so that the change of organic component in the solvent mixtures does not seriously affect the values of the minima reported in Table I.

Tommila, *et al.*,[16] have shown in one case that the depth of the minimum is temperature dependent, the magnitude decreasing as the median temperature of the range over which ΔE* was determined

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TABLE I

DEPTH OF MINIMA ($\Delta\Delta E^*$ RELATIVE TO $\Delta E^*_{H_2O}$) AS A FUNCTION OF ALKYL GROUP: SOLVOLYSIS IN ETHANOL–WATER MIXTURES

Alkyl series	CH_3	C_2H_5	*n*-C_3H_7	*i*-C_3H_7	$C_6H_5CH_2$	*t*-C_4H_9	$CH_3(C_6H_5)CH$
$C_6H_5SO_3^-$	0.4	0.7[c]	1.5[c]	2.0[c]			
Halide				2.1	2.3	3.1	3.9
ΔH kcal.[a]	220	192	177	168	152	149	
m[b]	0.23[d]	0.28[d]		0.41[d] 0.55	0.43	1.00	1.2

[a] ΔH for gas phase $RCl \rightarrow R^+ + Cl^-$.[29] [b] m-Values of Winstein, Grunwald and Jones correlation $\log k/k_0 = mY$. [c] Solvent mixture acetone–water. [d] Values for benzenesulfonates others for halides.

TABLE II

NUMERICAL VALUES (KCAL.) OF $\Delta\Delta E^*$ MAXIMA AND MINIMA FOR VARIOUS SOLVOLYSES AS A FUNCTION OF ORGANIC COMPONENT OF BINARY SOLVENT MIXTURE

Organic solute component	Glycol	MeOH	AcOH	Dioxane	Acetone	EtOH	*n*-PrOH	*i*-PrOH	*t*-BuOH
Methyl benzenesulfonate[27]		0.2				0.4			
t-Butyl chloride[25c]		1.9	2.0	2.2	2.9	3.1			
t-Butyl bromide[25a]		2.0		2.6		3.2			
α-Phenylethyl chloride[25b,18]		0.8		1.0		3.9			
Dimethyl-*t*-butyl sulfonium iodide[18]						0.4			0.6
Ethyl acetate + OH^-[16]	Nil	Very small		0.6	1.0	1.0	2.0	2.4	3.1
Dielectric constant	38	33	7	2	21	25	20	19	10

increases. This is in keeping with the concept of solvent sorting since an increase in the total thermal energy content of the system would be expected to reduce the specific nature of the solvation process. Effects of this kind indicate that if all ΔE^* values were measured at the same median temperature the absolute magnitudes of the minima would be different from those shown in Table I. Since the ΔE^* values for certain groups of the solvolysis reactions which do show *different* depths of minima were determined at the *same* median temperature, however, such effects would not appear to alter the order of magnitudes observed. Furthermore it would be extremely fortuitous if such temperature effects were responsible for the excellent agreement between order of carbonium ion stability and order of magnitude of ΔE^* minima. Such effects, however, may well be partly responsible for the rather small maxima observed in the sulfonium salt cases where the median temperature of the ΔE^* determinations is 62°.

Variation of Solvent.—Table II contains all available data pertinent to the influence of solvent variation on the magnitude of ΔE^* maxima and minima in neutral solvolysis reactions. The table also includes the extensive data of Tommila, *et al.*,[16] for alkaline solvolysis of ethyl acetate. Although the Tommila data are not strictly comparable with those of the neutral solvolysis reactions, the striking similarity of order of solvent effect on the activation energy behavior is worth noting.

The order of the solvents from methanol to *t*-butyl alcohol is that for increasing magnitude of maxima or minima and is obeyed by all of the solute systems included. The only apparent deviation is that in methanol–water and dioxane–water mixtures; α-phenylethyl chloride has a smaller minimum than it should have on the basis of the effect of alkyl groups. However, it should be noted that the α-phenylethyl chloride ΔE^* minimum has not been accurately defined experimentally as yet and the values are *no smaller* than those shown in the table.

The order of solvents clearly indicates that the specific solvation phenomena in aqueous mixtures of these solvents are not determined solely by the relative difference of bulk dielectric constants of water and the organic solvent. Considering the alcohols alone, the order is as expected and follows the order of increasing difference in dielectric constant. Acetic acid–water and dioxane–water mixtures, however, should show very marked specificity of solvation on the basis of dielectric constant difference between the solvent components and consequently should show very large ΔE^* minima. The fact that they do not is indicative of another important factor operative in determining the effect of solvent variation.

The additional influential factor is, in all probability, the same one claimed by Scatchard[2a] as partially responsible for the deviations between calculated and observed behavior in ionic systems in ethanol–water, namely, the discrete molecular structure of the solvent components. Although by considering solvent sorting the model is improved over that assuming a dielectric continuum, no allowance has been made for the discrete nature of the solvent molecular species. Such an argument is supported by the fact that the dielectric constant is a fair measure of solvating power when the systems being compared are limited to a single chemical type, namely, the alcohols. Similarly, solvolysis of *t*-butyl chloride in mixtures of acetic and formic acids[25c] shows no maximum or minimum in ΔE^* despite a difference of 40 in dielectric constant. Here the similarity of the molecular type presumably reduces the effect of dielectric constant difference and emphasized the considerable importance of the discrete molecular structure of the solvent components. A further example of the importance of molecular type is to be found in the comparison of quaternization reactions in benzene–nitrobenzene mixtures,[30] $\Delta D = 34$, and solvolysis in benzene–ethanol mixtures,[31] $\Delta D = 23$.

(30) H. C. Raine and C. N. Hinshelwood, *J. Chem. Soc.*, 1378 (1939).

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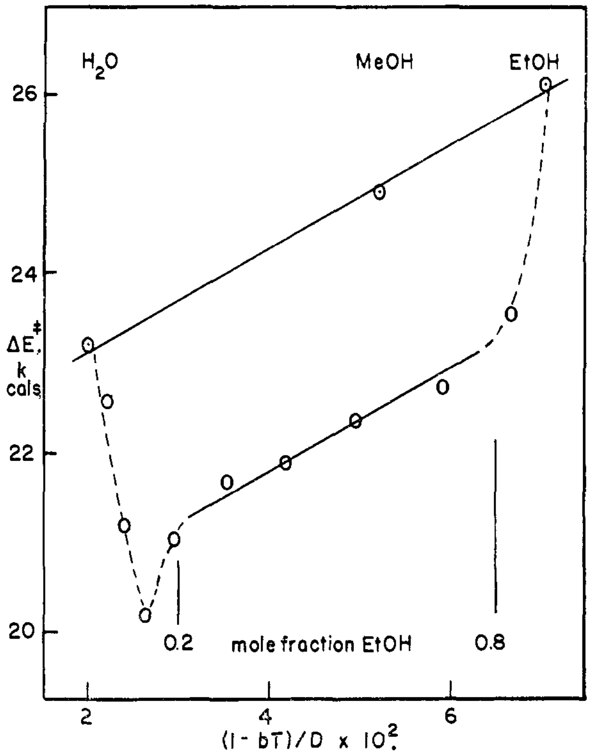

Fig. 5.—Dielectric constant dependence of ΔE^* for solvolysis of *t*-butyl chloride in series of pure and mixed solvents.

The former show marked ΔE^* deviations indicating considerable solvent sorting while ΔE^* values for the latter actually follow a simple relation with dielectric constant indicative of little or no solvent sorting.

Comparison of the order of solvents with the Winstein–Grunwald–Jones *Y*-values is limited by the fact that such values are available only for pure solvents which can act as solvolysing species. The order of *Y*-values for methanol, acetic acid and ethanol, however, are in the same order as that shown in Table II.

The precise nature of the dependence of specificity of solvation on the discrete molecular structure of the solvent components remains to be defined, but the present evidence is ample proof of the importance of this factor.

In view of the present uncertainty attached to the values of the position of the minima on the solvent composition scale, no attempt has been made here to give quantitative significance to these changes in position. While the depth of the minima depends primarily on the difference in slope of the E'' and E' lines in Fig. 1, the position depends only on the degree to which specificity of solvation persists as bulk solvent composition changes. Even with solute species which show a considerable difference in charge type between initial and transition state, and hence difference in slope of the E'' and E' lines, the specificity of solvation may not persist as solvent composition changes. As examples of this type of behavior we might consider the difference in behavior of, say, isopropyl chloride and α-phenylethyl chloride. The degree of charge creation in the transition state compared with the initial state is considerably greater for the latter halide and so the α-phenylethyl chloride will show a deeper minimum. However, the charge character of this halide is associated with a more bulky system than isopropyl chloride and as a consequence the solvation specificity, although considerable in water, may fall off more rapidly with solvent composition change than in the isopropyl case. Although it would be unwise to draw any firm conclusions from the presently available data, the position of the minima on the solvent composition scale does seem to show a trend toward the more aqueous end of the scale as the solute species increases in size.

The Effect of Temperature Dependence of Bulk Dielectric Constant.—Since determination of the activation energy involves rate measurements at at least two temperatures, the bulk dielectric constant of a fixed composition solvent will not be the same at both ends of the temperature range. It is therefore worth investigating the possibility that the difference in dielectric constant at the two temperatures as a function of solvent composition might pass through maxima or minima and so account for the observed ΔE^* behavior. Several workers have considered such effects in the past[12–15] and have attempted to measure the "isodielectric" activation energy (ΔE_D^*) by varying the composition of a mixed solvent with temperature in order to maintain a fixed dielectric constant.

Braude's[15] expression for the relationship between observed activation energy (ΔE^*) and isodielectric activation energy involves a correction

$$\Delta E_D^* = \Delta E^* + 2.3RT_1T_2m.b \qquad (2)$$

term where m is a constant for the given reaction and is independent of solvent composition and b is a coefficient for the dielectric constant variation with temperature and varies with solvent composition

$$D = a - b(t - 20) \qquad (3)$$

If ΔE^* shows maximum–minimum behavior and ΔE_D^* does not, then for a fixed T_1T_2 range b must vary in a like maximum–minimum manner. Scrutiny of the available data on b variation with composition for all the solvent mixtures considered in this study failed to reveal such a required variation in b. Furthermore, Braude's application of this treatment to his data for the activation energy variation in the rearrangement of unsaturated carbinols in ethanol–water mixtures reduced the minimum observed by 30% but did not remove it.

Svirbely and Warner[12] and Moelwyn-Hughes[14] have considered the dependence of activation energy on dielectric constant for ion–ion, ion–polar and polar–polar species reactions and in each case arrive at an expression of the type

$$\Delta E^* = A + Bf(D) \qquad (4)$$

Svirbely and Warner consider the function of D to be $-b/D$ while Moelwyn-Hughes used the function $(1 - bT)/D$ where b in these cases is given by $D = ce^{-bT}$. Neither of these functions, however, shows the necessary maximum–minimum variation with solvent composition for any of the binary solvent mixtures considered here.

A very persuasive illustration is presented in Fig. 5 of the essential validity of the claim that dielectric constant–temperature variation cannot account for the ΔE^* phenomena observed in mixed solvents. Here the ΔE^* for the solvolysis of *t*-butyl chloride[25c] is plotted against the $(1 - bT)/D$ function. A linear relationship should result if the isodielectric type of analysis is valid. Such a linear relationship is observed (solid line) when the dielectric constant is changed by a total change of solvent from water to methanol to ethanol. However, when the dielectric constant is varied from water to ethanol by changing the composition of the binary mixture, the relationship breaks down completely at both ends of the range. It should be noted, however, that between approximately 0.2 and 0.8 mole fraction of ethanol, the dependence of ΔE^* on the dielectric constant function is very similar to that for the pure solvents.

All of the above facts regarding the dependence of activation energy on dielectric constant or its temperature coefficient argue strongly against dismissing the maximum–minimum behavior of ΔE^* as the result of dielectric constant temperature dependence and strongly in favor of the specific solvation concept.

Conclusions.—The treatment offered in this paper has been restricted to solvolytic reactions for which kinetic data of sufficient accuracy and scope are available. Further substantiation of the essential validity of the specific solvation hypothesis must await more extensive precision measurements, but it is hoped that this treatment will serve as a guide to the choice of critical experiment. A detailed scrutiny of the literature has uncovered many examples of similar behavior in the activation energies of non-solvolytic reactions in mixed solvents,[32–34] many of which give every indication of being amenable to a similar type of treatment. It is hoped to discuss certain of these specific cases in subsequent papers of this series.

It is not the intention of this paper to imply that the observed behavior of the activation energy as a function of binary solvent composition is due solely to specific solvation effects. However, the facts as presented here do appear to constitute strong support for the belief that such a solvent-sorting phenomenon plays an important part in determining the observed activation energy behavior.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Diaryliodonium Salts. XV. Ultraviolet Absorption Spectra of Salts Bearing Functional Groups[1–3]

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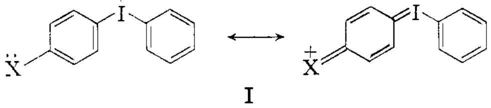
Ultraviolet absorption data on alkyl-, halogeno-, hydroxy-, alkoxy-, amino- and nitro-iodobenzenes and diphenyliodonium salts are presented and discussed in terms of the conjugative ability of iodine. It is concluded that in the unsubstituted diphenyliodonium cation, resonance interaction in which the iodine expands its valence shell to accommodate electrons is negligibly small but that such interaction may be made significant in the electronic excited state by the presence of electron-releasing *p*-substituents.

Introduction.—In iodonium salts iodine possesses both a positive charge and a rare-gas configuration. Because of the charge, iodine attracts electrons *via* an inductive or field effect. However, resonance would necessitate valence shell expansion of iodine with acceptance of the electrons into a 5d (or 4f) orbital.



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Evidence now indicates that some elements below the first row in the periodic table can indeed interact with adjacent unbonded electrons by expansion of their valence shells beyond the octet; this process has been termed d-orbital resonance.[5–7]

The effect of the substituent upon a functional group on a benzene ring has been evaluated by application of the Hammett equation[8,9] to acidity data and by examination and comparison of ultraviolet spectra.[10,11] These methods have been used to demonstrate the ability of sulfur,[12,13] silicon[14] and

[1] This paper is taken from the dissertation of Irving Lillien, submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

[2] For the synthesis of most of the salts bearing functional groups see F. M. Beringer and I. Lillien, THIS JOURNAL, **82**, 725 (1960).

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