Acknowledgment. R. B. D. was the recipient of a National Institutes of Health Postdoctoral Fellowship during the course of this work. We are grateful to the National Science Foundation (GP 8013) and the National Institutes of Health (GM 13468) for support of this research.

A Simple Model for Linear Salt Effects in Solvolysis Reactions

Charles L. Perrin[*1] **and Jeff Pressing**

Contribution from the Department of Chemistry, University of California, San Diego, La Jolla, California 92037.
Received January 28, 1971

Abstract: The rate-enhancing effect of added salts on solvolysis reactions in less polar solvents can be accounted for by a simple statistical-mechanical model, based on dipole-dipole interaction between the salt and the transition state. This model provides a satisfactory explanation for the concentration dependence. The calculated variations of the salt effect with solvent, salt, and temperature are in good agreement with experiment. Especially noteworthy is the ability of the model to rationalize the specificity of the various salts solely in terms of dipole-dipole interactions and to dissect the salt effect into enthalpy and entropy contributions. Two comments on the special salt effect are included, one concerning its origin and the other concerning its implication for the lifetimes of intermediates in solvolysis.

For many years chemists have been interested in the effects of salts on reaction rates.[2] Considerable effort has been devoted to understanding salt effects in polar solvents, but it is clear that there are many factors possibly operative—electrostatic and ion-atmosphere stabilization,[3-5] "drying" of solvent,[6-8] specific salt-induced medium effects,[5,9,10] and micelle formation.[11] Salt effects in less polar solvents have received less attention, although there have been interpretations involving specific interactions,[12,13] basicity,[14,15] and suppression of ion-pair return (the "special" salt effect).[16]

We now wish to present a new interpretation of a class of salt effects, namely, the "normal" salt effects in less polar solvents. In a series of papers, Winstein and coworkers have reported extensive studies of the dependence of solvolysis rates of arenesulfonates on the concentrations of added salts.[17] They consistently found that "normal" salt effects could be fit to the equation

$$k = k_0(1 + b[\mathrm{MY}]) \tag{1}$$

where k is the solvolysis rate constant in the presence of a concentration [MY] of added salt and b is a parameter varying with solvent, arenesulfonate, added salt, and temperature. Similar results have been reported by Salomaa[12] for the effects of added salts on alcoholysis rates of 1-halo ethers in various mixed solvents. Several qualitative and semiquantitative interpretations of such salt effects have been presented,[4,5,12,13,18] but none has been pursued very extensively. Nor has any satisfactory explanation of the concentration dependence, the effect of solvent, the specificity of salts, or the temperature dependence been offered. In view of the well-known success[3] of the Debye-Hückel theory in explaining salt effects on ionic reactions in aqueous solution, we thought that an analogous approach might explain the salt effects on solvolyses. However, in the less polar solvents employed, the salts are not dissociated to ions, but are present as ion pairs. (For example, the evidence for the state of $LiClO_4$ in acetic acid has been summarized.[16]) Also, the transition state is a dipole, rather than an ion. Therefore it is necessary to treat these salt effects on the basis of dipole-dipole interactions. In this paper it is shown that a simple statistical mechanical model for treating the interaction between the transition state and the added salt can provide a reasonable approach to the interpretation of b in terms of microscopic parameters.

Theory

According to the Brønsted rate law, k, the rate constant in the presence of added salt, is increased over k_0, the rate constant in the absence of salt, because salts decrease $\gamma_{\pm}$, the activity coefficient of the dipolar transition state (eq 2). Here we have neglected the

---

[1] Alfred P. Sloan Research Fellow, 1967–1969.

[2] For a recent review see L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, Chapter 7, pp 187–219.

[3] V. K. La Mer, *Chem. Rev.*, **10**, 179 (1932).

[4] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

[5] G. Kohnstam, *Chem. Soc., Spec. Publ.*, **No. 19**, 148 (1965).

[6] G. R. Lucas and L. P. Hammett, *J. Amer. Chem. Soc.*, **64**, 1928 (1942).

[7] C. G. Swain, T. E. C. Knee, and A. MacLachlan, *ibid.*, **82**, 6101 (1960).

[8] P. Beltramé, C. A. Bunton, A. Dunlop, and D. Whittaker, *J. Chem. Soc.*, 658 (1964).

[9] E. F. J. Duynstee, E. Grunwald, and M. L. Kaplan, *J. Amer. Chem. Soc.*, **82**, 5654 (1962).

[10] G. A. Clarke and R. W. Taft, *ibid.*, **84**, 2295 (1962).

[11] E. F. J. Duynstee and E. Grunwald, *Tetrahedron*, **21**, 2401 (1965).

[12] P. Salomaa, *Ann. Univ. Turku., Ser. A*, **14**, (1953).

[13] (a) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763 (1956); (b) *ibid.*, **78**, 2780 (1956); (c) S. Winstein, E. C. Friedrich, and S. Smith, *ibid.*, **86**, 305 (1964).

[14] P. A. O. Virtanen, *Suom. Kemistilehti B*, **38**, 231 (1965).

[15] S. D. Ross, *Tetrahedron*, **25**, 4427 (1969).

[16] S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *J. Amer. Chem. Soc.*, **83**, 885 (1961).

[17] E. L. Allred and S. Winstein, *ibid.*, **89**, 4012 (1967), and previous papers.

[18] E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai, and Y. Pocker, *J. Chem. Soc.*, 1265 (1957).

$$\ln \frac{k}{k_0} = -\ln \gamma_\pm \qquad (2)$$

much smaller effect of added salt on the activity coefficient of the less dipolar reactant, since it will be seen that the magnitude of the effect increases very rapidly with dipole moment.

The effect of dipole–dipole interactions on the activity coefficient of a dipole was originally developed by Fuoss.[19] We present a more general derivation here so that we may refer to it in considering the concentration dependence. The activity coefficient $\gamma_\pm$ can be calculated theoretically as a virial series in powers of the concentrations of added solutes. It can be shown[20] that $\gamma_\pm$ is related to the concentrations of the m added solutes by

$$-\ln \gamma_\pm = \sum B_{\pm\{n_i\}} \prod_{i=1}^{m} \rho_i^{n_i} \qquad (3)$$

where ρ_i is the number density of the ith solute and the sum runs over all combinations (clusters) containing one transition-state molecule plus exactly $n_1, n_2 \ldots n_m$ molecules of the 1st, 2nd. . .mth solute. We have chosen the standard states to be the various pure solvents, without any added salts.[21] $B_{\pm\{n_i\}}$ is the virial coefficient corresponding to an integration over all spatial configurations of the transition state and the other Σn_i molecules in the cluster. The concentration of the transition state is vanishingly small, and hence no terms $B_{\pm\pm}\rho_\pm$, etc., need appear.

For a sufficiently dilute solution, only the second virial coefficients are important, and eq 3 may be truncated to

$$-\ln \gamma_\pm = \sum_{i=1}^{m} B_{\pm i}\rho_i \qquad (4)$$

where $B_{\pm i}$ is given explicitly by

$$B_{\pm i} = \lim_{V\to\infty} \frac{1}{V} \int\int \ldots \int (e^{-U(\mathbf{r},\Omega)/kT} - 1)\, d\mathbf{r}_1 d\mathbf{r}_2 \qquad (5)$$

V is the volume of the integration and

$$U(\mathbf{r},\Omega) = \frac{\mu_i\mu_\pm}{\langle\epsilon\rangle r^3} \cos\theta_i \sqrt{1 + 3\cos^2\theta_\pm} \qquad (6)$$

is the potential of average force (electrostatic potential energy) of two point dipoles of dipole moments μ_i and $\mu_\pm$, separated by a distance r in a medium of effective dielectric constant $\langle\epsilon\rangle$, and with relative orientations specified by the polar angles θ_i and $\theta_\pm$. Integrating over all positions and orientations of the two molecules is easy only if the dipoles are at the centers of two spheres, with the distance of closest approach of the dipoles equal to some value r_0. Power-series evaluation of the resulting integral gives

$$B_{\pm i} = {}^4/_3\, \pi r_0^3 \sum_{n=1}^{\infty} c_n x^{2n} \equiv {}^4/_3 \pi r_0^3 \phi(x) \qquad (7)$$

where

$$x = \frac{\mu_i\mu_\pm}{\langle\epsilon\rangle kT r_0^3} \qquad (8)$$

We have found that the coefficients are given explicitly by the relation

$$c_n = \frac{1}{(2n+1)!(2n-1)} \sum_{m=0}^{n} \frac{n!}{m!(n-m)!} \frac{3^m}{2m+1} \qquad (9)$$

Values of ${}^4/_3\pi\phi(x)$ are listed in Table I. It may be seen that ϕ is a very rapidly varying function of x. (Logarithmic interpolation is recommended.) As a result, ϕ, $B_{\pm i}$, and $-\ln \gamma_\pm$ are quite sensitive to the values of T, μ_i, $\mu_\pm$, $\langle\epsilon\rangle$, and (especially) r_0. Since the last three quantities cannot be estimated very reliably, it is not feasible to calculate $B_{\pm i}$ *a priori*. Therefore, we shall demonstrate the validity and the limitations of this model by holding all parameters but one fixed and determining whether the variation of $-\ln \gamma_\pm$ with that parameter is as expected.

Table I. The Function ϕ

x	${}^4/_3\pi\phi(x)$	x	${}^4/_3\pi\phi(x)$
1.00	1.454	6.00	532.0
2.00	6.638	7.00	2.122×10^3
3.00	19.24	8.00	9.481×10^3
4.00	52.16	9.00	4.588×10^4
5.00	154.5	10.00	2.351×10^5

In what follows, we shall restrict our consideration primarily to para methoxyneophyl systems. These have the advantage that ionization always leads to product. Therefore, we are guaranteed that the salt effects are operative on a single transition state, rather than on partitioning of ion-pair intermediates.

Finally, we point out that this model is necessarily limited to those pure solvents in which salts are present predominantly as ion pairs. It is well known that there is selective solvation in mixed solvents, so we have not attempted to interpret here the extensive data in such media. For the usual salts, concentrations, and solvents ($10 < \epsilon < 30$), the salts do seem to be present predominantly as ion pairs. For example, from the data for $LiClO_4$ in HOAc summarized by Winstein, Klinedinst, and Robinson,[16] we may calculate that at 10^{-4} *M*, 80% of the species are ion pairs, with the remainder free ions, and even at 0.1 *M* (beyond the range of fit to eq 1), 50% of the species are ion pairs, with the remainder principally ion quadrupoles. Even when a small but appreciable fraction of salt is present as free ions or as higher aggregates, we may still concentrate on the ion pairs, since whenever the forces are electrostatic, the stabilization due to a free ion or a higher aggregate is comparable to that due to a dipole. (See the comments on the special salt effect.)

Choice of Parameters. To test this model, it is necessary to choose values for the parameters that enter x of eq 8. We need never specify values for $\mu_\pm$ or $\langle\epsilon\rangle$ since we fit their ratio empirically.

Although a detailed consideration of the shapes of transition state and salt would be necessary in the integral of eq 5, we have chosen the simpler and roughly equivalent method of taking an average r_0 that gives more weight to shorter approach distances, where the attraction is considerably stronger (see Figure 1). Hence for the effective radius of the transition state we use the radius of a molecule whose cross-section is

---

(19) R. M. Fuoss, *J. Amer. Chem. Soc.*, **56**, 1027 (1934); **58**, 982 (1936).

(20) W. G. McMillan and J. E. Mayer, *J. Chem. Phys.*, **13**, 276 (1945).

(21) Since we are not attempting to treat the effect of solvent on solvolysis rate, we need not consider the effect of changing solvents on $\gamma_\pm$.

estimated to be the same as the cross-section of the transition state. In particular, we use the radius of $NaHSO_4$, as determined from the molar volume

$$V = \frac{\pi}{3\sqrt{2}}\frac{M}{Nd} = \frac{4}{3}\pi r^3 \tag{10}$$

where M is the molecular weight and d the density of the crystal. The factor $\pi/3\sqrt{2}$ corrects for the space left empty by close-packed spheres. This estimate of the radius of the transition state has the advantage of great simplicity and the further advantage that the same value is applicable to all the sulfonates discussed. We also use this value for the radius of toluenesulfonic acid. We estimate the radii of the other added salts in identical fashion, from the molar volume, under the approximation that the crystal is composed of close-packed spherical salt molecules.

The chosen radii of the transition state and of the various salts are listed in Table II. Also listed are the dipole moments of each of the salts. Finally, we take r_0 to be the radius of the salt plus the radius of the transition state.

Table II. Parameters Used in Calculations

	Radius, Å	Dipole moment, D[a]
$ROTs^{\ddagger}$	2.34	
HOTs	2.34	3.80[b]
$LiClO_4$	2.34	7.89[c]
LiBr	1.95	6.19[d]
Bu_4NClO_4	4.51[e]	14.2[f]
Bu_4NBr	4.37[g]	11.9[h]

[a] Values earlier than 1948 as corrected by A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963. [b] Value for benzenesulfonic acid in benzene (HOTs is not ionized in acetic acid either: I. M. Kolthoff and S. Bruckenstein, *J. Amer. Chem. Soc.*, **78**, 1 (1956)); E. N. Gur'yanova, *J. Phys. Chem. (USSR)*, **15**, 142 (1941); *Chem. Abstr.*, **36**, 305^9 (1942). [c] M. G. Malone and A. L. Ferguson, *J. Chem. Phys.*, **2**, 99 (1934). [d] A. Honig, M. Mandel, M. L. Stitch, and C. H. Townes, *Phys. Rev.*, **96**, 629 (1954). [e] By extrapolation of molar volume of the molten salt: P. Walden and E. J. Birr, *Z. Phys. Chem., Abt. A*, **160**, 57 (1932). [f] J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936). [g] A. K. R. Unni, L. Elias, and H. I. Schiff, *J. Phys. Chem.*, **67**, 1216 (1963). [h] W. R. Gilkerson and K. K. Srivastava, *ibid.*, **65**, 272 (1961).

Discussion

Before we attempt to apply this model to kinetics, it is prudent to see whether it is applicable to the thermodynamics of stable species. Cohn[22] has used this model to calculate the activity coefficients of glycine and asparagine in aqueous solutions of glycine and diglycine. His calculations generally underestimated $-\ln \gamma$ by a factor of $\sim$2. However, for r_0, the distance of closest approach of two amino acids, he chose the average of their molecular diameters, obtained from molar volumes. This choice would be exact only if the molecules were spherical, and a more realistic estimate of the average distance of closest approach leads to good agreement between calculated and experimental activity coefficients.[23] Therefore, we are encouraged to extend this model to transition states and rate constants. We now proceed to consider, in turn, the dependence of $-\ln \gamma_{\ddagger}$ on concentration, on solvent, on added salt, on substrate, and on temperature.

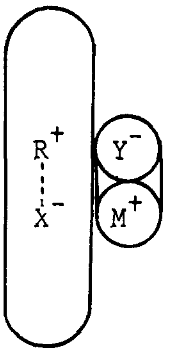

Figure 1. Approach of MY ion pair to transition state for RX solvolysis.

Concentration Dependence. For many years progress toward understanding normal salt effects in less polar solvents has been impeded by the discrepancy[13a,b] between the linear form of eq 1 and the logarithmic form implied by eq 2. We now demonstrate that this discrepancy results from truncating eq 3 and that the effect of including higher virial coefficients must be such as to improve the agreement with the empirical observations.

For a single added salt s, eq 2 and 3 reduce to

$$\ln \frac{k}{k_0} = -\ln \gamma_{\ddagger} = B_{\pm s}\rho_s = B_{\pm s}N\frac{[MY]}{1000} \tag{11}$$

where N is Avogadro's number, [MY] is the molar concentration of salt, and the units of $B_{\pm s}$ are cubic centimeters. Therefore we would conclude that ln k should increase linearly with [MY], contrary to observation. Instead, it is k that increases linearly (with only slight upward curvature) with [MY], as expressed by eq 1. And plots of log k *vs.* [MY] show downward curvature.[13a,b] Of course, eq 11 is valid only for low [MY] since it arises by truncating eq 3.

We therefore must consider the form that eq 11 would take were we to calculate higher terms. In principle it is possible to calculate higher virial coefficients to obtain coefficients of $[MY]^2$, etc., but such calculations are quite formidable. For example, $B_{\pm ss}$ is an integral over all configurations of three dipoles, and the value is very sensitive to the shape of the potential assumed.[24] Therefore, we have not attempted an explicit calculation of even $B_{\pm ss}$. Nevertheless, it can be shown that $B_{\pm ss}$ is negative whenever the repulsive configurations of two salt dipoles clustering about the transition state outweigh the attractive ones. This is the situation with an elongated transition state (Figure 2). Therefore the stabilization due to successive salt molecules diminishes and the plot of ln k *vs.* [MY] acquires a negative curvature, as observed. Furthermore, there are other higher order effects, such as the aggregation of added salt and the effect of salts on $\langle\epsilon\rangle$,[25] which also lead to downward curvature. Indeed, the activity coefficients of amino acids do show such a curvature.[22] Therefore, we conclude that the

---

(22) E. J. Cohn in "Proteins, Amino Acids, and Peptides as Ions and Dipolar Ions," E. J. Cohn and J. T. Edsall, Ed., ACS Monograph, Hafner Publishing Co., New York, N. Y., 1943, pp 231–234.

(23) J. Pressing, unpublished calculations.

(24) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1954.

(25) Y. Pocker and R. F. Buchholz, *J. Amer. Chem. Soc.*, **92**, 2075 (1970).

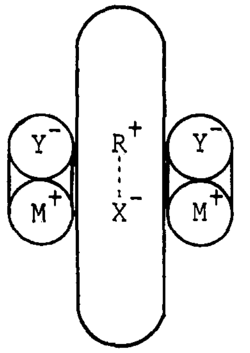

Figure 2. Repulsion of two salt dipoles clustering about a transition state.

observed concentration dependence is quite consistent with our model.

We also consider in more detail the origin of eq 1. The obvious way of explaining a linear concentration dependence is to suppose that a salt-assisted second-order reaction occurs simultaneously with the unassisted first-order reaction

$$\mathrm{RX} \xrightarrow{k_1} \mathrm{product(s)}$$

$$\mathrm{RX} + \mathrm{MY} \xrightarrow{k_2} \mathrm{product(s)}$$

Yet there is no reason why assistance should be restricted to only one salt molecule. If any number is possible, then the observed first-order rate constant would be a sum, $\Sigma_{n=0}^{\infty} k_{n+1}[\mathrm{MY}]^n$, and a plot of k *vs.* [MY] would curve upward, as observed. It is readily shown that eq 11 would arise in an idealized situation in which salt molecules assist solvolysis but do not interact with each other. However, as indicated above, repulsion between salt dipoles makes the first salt molecule more effective than subsequent ones. In the limit that the repulsion is infinite, it can be shown that $B_{\ddagger n\mathrm{s}}$ equals $(-1)^n B_{\ddagger\mathrm{s}}{}^n/n$. In this limit only the first salt molecule is effective, and eq 1 would be followed exactly. Of course, the actual situation must lie between the two extremes of zero repulsion and infinite repulsion. We therefore conclude that both our model and the empirical equation represent limiting forms of the true concentration dependence. Also, we note that according to eq 4, the effects of several added salts are additive in the low concentration range, as has frequently been assumed and occasionally observed.[26]

Finally, for the purpose of comparing calculated and observed b values we substitute eq 1 into eq 11, expand the logarithm, and keep only the first term, to obtain

$$b = \frac{B_{\ddagger\mathrm{s}}N}{1000} = \frac{4}{3}\pi N r_0{}^3 \frac{\phi(x)}{1000} \tag{12}$$

Solvent Effects. It has long been recognized that salt effects are more pronounced in less polar solvents. The extensive study of Winstein, Smith, and Darwish[27] shows that in solvolysis of *p*-methoxyneophyl tosylate, $b_{\mathrm{LiClO_4}}$ correlates well with ionizing power. According to our electrostatic model, b should depend strongly on dielectric constant. However, the exact dependence of eq 12 is not followed by the data, because bulk dielectric constant is not an adequate measure of the effective dielectric constant in the neighborhood of the transition state. Also, the range of polarities included in their study is so large that the salt is not always present primarily as ion pairs. Nevertheless, we note the remarkable identity of $b_{\mathrm{LiClO_4}}$ in acetone and acetic anhydride (47.0 and 47.1, respectively), whose dielectric constants, extrapolated to the temperature of the solvolysis, are 16.3 and 16.2, respectively.[28]

Specificity of Salt Effects. One of the most puzzling features of salt effects has been the specificity of the various salts.[13a,29] Table III lists some examples, along with the values of b calculated according to this model. In each of the two solvents $b_{\mathrm{LiClO_4}}$ was used to determine $\mu_{\ddagger}/\langle\epsilon\rangle$, so that only dipole moments and molecular radii were needed to calculate the remaining b values. Despite the paucity of comparisons (many more b values have been determined, but the dipole moments of the salts are not known; nevertheless, those b values are consistent with the dipole moment to be expected for the salt), it is clear that the agreement is good. The small discrepancies presumably may be attributed to inaccuracies in the parameters $\mu_{\ddagger}$ and r_0.

Table III. Salt Effects on *p*-Methoxyneophyl Tosylate Solvolysis

Salt	b_{obsd}	b_{calcd}
$\mathrm{LiClO_4}$[a]	15.4	
HOTs[a]	1.1	0.8
$\mathrm{LiClO_4}$[b]	47	
$\mathrm{Bu_4NClO_4}$[b]	3.4	6.8
$\mathrm{Bu_4NBr}$[b]	4.8	4.3
LiBr[b]	31	44

[a] In HOAc at 25°; ref 13b. [b] In acetone at 75.1°; ref 13c.

The quantitative success of this model permits us to look more closely at the origin of the specificity. Toluenesulfonic acid is less effective than $\mathrm{LiClO_4}$ because the dipole moment of the former is only half as great. A twofold increase in dipole moment produces a greater than tenfold increase in b; this is evidence that b is a rapidly varying function of $\mu_{\ddagger}$. In contrast, the tetrabutylammonium salts are less effective than $\mathrm{LiClO_4}$ because they are much larger, even though their dipole moments are greater. Lithium bromide is almost as effective as $\mathrm{LiClO_4}$ because the decrease in dipole moment is nearly compensated for by the decrease in size.

It is instructive to note the values of x involved. For the common solvolysis solvents ethanol, acetic acid, and acetone, x ranges from 4 to 6.25. Comparison of eq 6 and 8 shows that x is the ratio of the maximum electrostatic attraction to the thermal energy. Therefore we may conclude that the transition state is rather tightly complexed with added $\mathrm{LiClO_4}$, with an interaction energy of several kilocalories per mole. We note that tight dipole–dipole complexes have been detected previously in nonpolar solvents.[30,31]

---

(26) Reference 12, but see ref 13b.

(27) S. Winstein, S. Smith, and D. Darwish, *J. Amer. Chem. Soc.*, **81**, 5511 (1959).

(28) A. A. Maryott and E. R. Smith, *Nat. Bur. Stand. (U.S.) Circ.*, No. 514 (1951); through "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio.

(29) S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Lett.*, No. 22, 12 (1960).

(30) C. D. Ritchie, B. A. Bierl, and R. J. Honour, *J. Amer. Chem. Soc.*, **84**, 4687 (1962).

(31) R. W. Taft, G. B. Klingensmith, and S. E. Ehrenson, *ibid.*, **87**, 3620 (1965).

This model for the specificity of salt effects is thus not so different from the usual one. Ordinarily the specificity of salts has been rationalized in terms of a salt-assisted second-order reaction occurring simultaneously with the unassisted first-order reaction.[12,13c] The second-order term thus arises from a 1:1 complex between transition state and added salt. We have not assumed that such a complex is formed. Instead we have calculated $B_{\pm s}$ by integrating the electrostatic dipole-dipole interaction over all distances and orientations. Of course, the dipole-dipole interaction is short range, so the major contribution to $B_{\pm s}$ arises from configurations with the dipoles close together, that is to say, tight complexes. Thus, we conclude that our model does not contradict the usual approach. However, it does go further in that the stabilization of the complex between transition state and added salt is attributed solely to the electrostatic interaction.

One exceptional case has been reported.[4g] For a cyclohexanespirohexadienyl *p*-nitrobenzoate in acetone, $b_{\mathrm{Bu_4NClO_4}} = 12$ and $b_{\mathrm{Bu_4NOPNB}} = 7$ are normal, but $b_{\mathrm{LiClO_4}} = 20{,}000$ and $b_{\mathrm{NaClO_4}} = 2100$ are unusually large. Winstein, Friedrich, and Smith[4g] have already attributed these very large accelerations to specific electrophilic assistance to ionization, presumably *via* coordination of $\mathrm{Li^+}$ or $\mathrm{Na^+}$ at the carbonyl oxygen. Here we see the limitations of our model, since in these two examples dipole-dipole interactions are not dominant. Nevertheless, that these examples of specific interaction lead to very large accelerations suggests that the "normal" salt effects are not so very specific, so that they can be accounted for by a purely electrostatic model.

Variation with Substrate. Winstein and coworkers have determined $b_{\mathrm{LiClO_4}}$ for more than 25 substrates,[17] but with little rationale apparent for the values observed. Yet the general range of $b_{\mathrm{LiClO_4}}$—from ~10 to ~30—corresponds to only a 20% variation in $\mu_{\pm}$, so that we ought not expect this model to interpret such subtle differences quantitatively. However, we can propose a qualitative interpretation for one feature, namely, that $b_{\mathrm{LiClO_4}}$ is larger for neophyl tosylate than for either neophyl brosylate or *p*-methoxyneophyl tosylate.[13a] One might have expected the reverse, since the substituents should increase the dipole moment of the latter two transition states (because of the C–Br dipole and because of the delocalization of positive charge onto methoxyl). However, dipole-dipole interactions seem to involve only localized polar groups,[30,31] so that substituents do not affect $\mu_{\pm}$ directly. The observed order results because the effect of the substituents is to decrease $\mu_{\pm}$; the latter two solvolyze faster, so there is *less* charge separation developed when these transition states are attained.[32]

We may also consider the salt effect on formation of solvent-separated ion pairs. For *threo*-3-*p*-methoxyphenyl-2-butyl and 2-*p*-methoxyphenyl-1-propyl systems, $b_{\mathrm{LiClO_4}}$ is smaller for the initial ionization to the intimate ion pair than it is for the formation of the solvent-separated ion pair.[33] Fainberg and Winstein[13b] have explained such results in terms of a reduction of ion-pair return by added salt. Our model provides an equivalent viewpoint for this phenomenon. Since the alkyl cation and the leaving anion are more distant in the solvent-separated ion pair, the dipole moment of the transition state leading to this ion pair must be greater than that of the transition state for ionization to intimate ion pair. Therefore, we may also attribute this difference in b values to a difference in $\mu_{\pm}$ for the two transition states involved. However, we do not expect this model to be quantitatively successful when applied to the transition states leading to solvent-separated ion pairs, for which the point-dipole approximation of eq 6 becomes quite poor.

Finally, we wish to make a recommendation concerning corrections for salt effects in solvents where salts are present predominantly as ion pairs. A classic technique in kinetics is the use of added salts for diverting intermediates, but it is necessary to take into account the salt effect on the rate of formation of those intermediates. Often such salt effects have been estimated from model systems. But the difficulty is that b is quite characteristic of both the salt and the transition state. Of course, it is possible to calculate b semiempirically, as in Table III. Alternatively, we may simply note that b depends on dipole moments and, more strongly, on a distance of closest approach. Therefore, model systems should be chosen to reproduce these parameters. We note further that it is rather difficult to find model salts, but that it is easier to find model transition states. Sneen and Larsen[34] seem to have reached this same conclusion.

Temperature Dependence. Fainberg and Winstein[13a] have noted that b generally decreases with increasing temperature. Indeed, since x, $\phi(x)$, and b depend inversely on T, it seems as though this should be a general phenomenon. Yet among all of Winstein's data there is one exception.[35] For 2-(*p*-methoxyphenyl)ethyl tosylate in ethanol, $b_{\mathrm{LiClO_4}}$ increases from 2.6 at 50° to 3.6 at 75°. But of course it is necessary to take into account the variation of dielectric constant with temperature.[28] For ethanol, as for most solvents, not only does ϵ decrease with increasing temperature, but even $\mathrm{d}(\epsilon T)/\mathrm{d}T < 0$. If we use b at 50° to determine $\mu_{\mathrm{LiClO_4}}\mu_{\pm}/r_0^3$, and if we use the known variation of ϵ_{EtOH} with temperature, we may calculate that b at 75° should be 3.61. We consider this agreement remarkable, although further testing is certainly desirable. Also, we conclude that b is a more rapidly varying function of $1/\epsilon T$ than the $(\epsilon T)^{-2}$ required by a previous theory.[4,13a]

The "general" decrease of b with increasing T is thus seen to be a result of the unusual temperature dependence of ϵ_{HOAc}, which increases with increasing T. However, if we use the known variation of ϵ_{HOAc} with T, we always calculate a greater variation of b with T than is observed. On the basis of this discrepancy, we conclude that in the neighborhood of a dipolar transition state, acetic acid behaves normally, with $\mathrm{d}\langle\epsilon_{\mathrm{HOAc}}\rangle/\mathrm{d}T < 0$.

Winstein and his coworkers[36] have further noted that in acetic acid the increase of rate by added salt may be attributed to a decrease in $\Delta H^{\ddagger}$, with $\Delta S^{\ddagger}$

---

(32) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

(33) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958); S. Winstein and A. H. Fainberg, *ibid.*, **80**, 459 (1958). However, for *threo*-3-phenyl-2-butyl tosylate, b_{NaOAc} and b_{NaOTs} show the opposite behavior.[13b] We cannot rationalize this behavior.

(34) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 362 (1969).

(35) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2767 (1956).

(36) A. H. Fainberg, G. C. Robinson, and S. Winstein, *ibid.*, **78**, 2777 (1956).

nearly unchanged. From our model it is readily shown that in acetic acid the effect of salts is to decrease both $\Delta H^{\neq}$ and $T\Delta S^{\neq}$, with the effect on $\Delta H^{\neq}$ greater. On the other hand, in normal solvents, where $d(\epsilon T)/dT < 0$, the effect of salts is to *increase* both $\Delta H^{\neq}$ and $T\Delta S^{\neq}$, with the effect on $T\Delta S^{\neq}$ greater. Such behavior has been noted by Salomaa.[12]

Some Comments on the Special Salt Effect. Hughes, Ingold, Mok, Patai, and Pocker[18] have suggested that the special salt effect is due to dissociated ions. Winstein, Klinedinst, and Robinson[16] have demonstrated that their observed kinetics are inconsistent with this explanation and consistent with a mechanism involving scavenging of solvent-separated ion pairs by added salts. We wish to add further evidence that dissociated ions are not responsible for the special salt effect. There seems to be an implicit assumption in the interpretation of Hughes, *et al.*, that free ions are far more effective at promoting ionization than are ion pairs. For example, $\sim 10^{-3}$ *M* Bu_4NClO_4 produces a fourfold increase in the rate of methanolysis of trityl chloride in benzene containing 0.1 *M* methanol.[37] But even at this low concentration most of the Bu_4NClO_4 is present as ion pairs and fewer than 1 in 10^6 are present as free ions.[38] Since the normal salt effect shows that the ion pairs give only about a onefold rate increase, it is necessary to assume that free ions are more than 10^6 times as effective as ion pairs.

Yet there is no reason to expect that free ions are vastly more effective than ion pairs at promoting ionization. Indeed, simple electrostatic considerations show that the effects of ions and ion pairs should be quite similar. For example, the magnitude of the interaction of the transition-state dipole with a point charge is identical with that with a suitably oriented dipole of dipole moment $\sim$10 D. A more extensive treatment,[23] analogous to that presented here but for point charge–dipole interactions, also leads to the conclusion that the electrostatic stabilizations due to ions and ion pairs are comparable. Thus, the special salt effect cannot be attributed to acceleration by the small fraction of free ions present, but must be attributed to scavenging of ion pairs by the added salts.

We also wish to point out an interesting implication concerning the lifetimes of intermediates in solvolysis. Winstein and coworkers[17] have shown that at a $LiClO_4$ concentration reported as $[LiClO_4]_{1/2}$—10^{-3}–10^{-5} *M*, depending on substrate—half of the solvent-separated ion-pair intermediates that would otherwise return to reactant are scavenged by $LiClO_4$ and diverted to product. In the notation of Solvolysis Scheme II of ref 16, $k_{ex}^{III}[LiClO_4]_{1/2} = k_{sx} + k_{-2}k_{-1}/(k_{-1} + k_2)$; the left-hand side is the rate constant for reaction of solvent-separated ion pairs with $LiClO_4$ and the right-hand side is the rate constant for the destruction of solvent-separated ion pairs in the absence of $LiClO_4$. But since it is also found experimentally that $1/b_{\text{titrimetric}} \gg [LiClO_4]_{1/2}$, we may now draw the further conclusion that almost all of these intermediates are formed *via* transition states that have not been appreciably stabilized by a $LiClO_4$ dipole.[39] Therefore, the rate constant $k_{ex}^{III}[LiClO_4]_{1/2}$ is not a rate constant for reaction of a solvent-separated ion pair with a $LiClO_4$ molecule that is already in its vicinity. The lifetime of the ion pairs must be sufficiently long that even at a $LiClO_4$ concentration of $[LiClO_4]_{1/2}$, half of them can encounter a $LiClO_4$ ion pair and enter into a metathesis reaction before reacting with solvent or returning to reactant. And if we assume that the metathesis reaction is diffusion controlled, with a second-order rate constant k_{ex}^{III} of 10^{10} $M^{-1}sec^{-1}$, we may conclude that for those solvolyses that show the special salt effect, the lifetime of a solvent-separated ion-pair intermediate is $10^{-10}/[LiClO_4]_{1/2} \sim 10^{-5}$–$10^{-7}$ sec, depending on substrate.

Conclusions

We consider that this model is quite a satisfactory one for interpreting salt effects in solvolysis reactions. First, it is a "reasonable" model, one that might be expected, *a priori*, to be applicable to such systems. Second, it permits semiempirical calculation of *b* values that are in good agreement with experiment. Third, it provides an intuitively simple framework for understanding the nature of these salt effects. A further advantage is that the input variables—dipole moments and molecular radii—are readily available. Admittedly, the model is quite crude and oversimplified. We may therefore ask why the model is at all successful. It seems to us that the success depends on the fact that the transition state and the added salts have such large dipole moments. As a result, the dipole–dipole forces are dominant and other forces are negligible (or cancel in the ratio $\gamma_{RX}/\gamma_{\pm}$). Of course, further testing of this model is necessary, and we hope that more data are forthcoming. Nevertheless, we expect this approach to be of general utility for reactions where dipole–dipole forces predominate.

Acknowledgments. We wish to acknowledge enlightening discussions with Dr. Joseph E. Mayer and Mr. John Lett. This research was supported in part by Atomic Energy Commission Grant No. At(1-11)-34 Project 65.

---

(37) E. D. Hughes, C. K. Ingold, S. F. Mok, and Y. Pocker, *J. Chem. Soc.*, 1238 (1957).

(38) E. D. Hughes, C. K. Ingold, S. Patai, and Y. Pocker, *ibid.*, 1206 (1957).

(39) This conclusion follows immediately if eq 1 is interpreted as arising from two simultaneous reactions, one independent of salt and the other first order in salt. Alternatively, if the lowering of $\gamma_{\neq}$ is interpreted in terms of an uncomplexed transition state in equilibrium with one stabilized by association with $LiClO_4$, the same conclusion follows.