(1971).
(4) I. Tabushi and Y. Aoyama, J. Org. Chem., **38**, 3447 (1973).
(5) H. Stetter, M. Schwarz, and A. Hirschhorn, Chem. Ber., **92**, 1629 (1959).
(6) H. Koch and W. Haaf, Org. Synth., **44**, 1 (1964).
(7) P. Kovacic and P. D. Roskos, J. Am. Chem. Soc., **91**, 6457 (1969).
(8) G. A. Olah and H. C.-h. Lin, J. Am. Chem. Soc., **93**, 1259 (1971).
(9) G. W. Smith and H. D. Williams, J. Org. Chem., **26**, 2207 (1961).
(10) I. Tabushi, J. Hamuro, and R. Oda, J. Am. Chem. Soc., **89**, 7127 (1967).
(11) I. Tabushi, Z. Yoshida, and N. Takashashi, J. Am. Chem. Soc., **92**, 6670 (1970).
(12) I. Tabushi, J. Hamuro, and R. Oda, J. Org. Chem., **33**, 2108 (1968).
(13) D. S. Breslow, E. I. Edwards, R. Leone, and P. v. R. Schleyer, J. Am. Chem. Soc., **90**, 7097 (1968).
(14) I. Tabushi, S. Kojo, and Z. Yoshida, Tetrahedron Lett., 2329 (1973).
(15) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966, p 783.
(16) (a) C. A. Parker, Proc. R. Soc. London, Ser. A, 220, 104 (1953); (b) C. G. Hatchard and C. A. Parker, Proc. R. Soc. London, Ser A, 235, 518 (1956).
(17) P. D. Bartlett and R. R. Hiatt, J. Am. Chem. Soc., **80**, 1398 (1958).
(18) (a) K. Sandros and H. J. J. Bäckström, Acta Chem. Scand., **16**, 958 (1962); (b) K. Sandros, ibid., **18**, 2355 (1964).
(19) H. L. J. Bäckström and K. Sandros, Acta Chem. Scand., **12**, 823 (1958).
(20) B. Stevens and J. T. Dubois, J. Chem. Soc., 2813 (1962).
(21) H. Zeldes and R. Livingston, J. Chem. Phys., **47**, 1465 (1967).
(22) W. G. Bentrude and K. R. Darnall, Chem. Commun., **810** (1968).
(23) W. A. Urry and D. J. Trecker, J. Am. Chem. Soc., **84**, 118 (1962).

(24) For adamantyl, acetylation took place almost quantitatively as was cited.
(25) (a) For gas phase, see a review: W. A. Noyes, Jr., and G. B. Porter, Chem. Rev., **56**, 49 (1956). (b) For liquid phase: S. A. Greenberg and L. S. Forster, J. Am. Chem. Soc., **83**, 4339 (1961).
(26) W. G. Bentrude and K. R. Darnall, J. Am. Chem. Soc., **90**, 3588 (1968). The peroxide initiated (thermal) radical acetylation of cyclohexane with biacetyl was reported to afford acetylcyclohexane although the yield based on the hydrocarbon was very low. In our attempted free-radical (thermal) acetylation, the yield of acetyladamantane based on adamantane was too low to determine the BH to BR product ratio. A probable reason of this failure may be undesirable thermal condensations.
(27) G. J. Gleicher, J. L. Jackson, P. H. Owens, and J. D. Unruk, Tetrahedron Lett., 833 (1969).
(28) H. E. Zimmerman and D. I. Schuster, J. Am. Chem. Soc., **84**, 4527 (1962).
(29) L. B. Hunphrey, B. Hodgson, and R. E. Pincock, Can. J. Chem., **46**, 3099 (1968).
(30) The thermolysis condition for the product analysis was adjusted on the basis of the kinetic results. Rate was followed from the decrease in $\mu_{C=O}$ at 1762 cm$^{-1}$ by use of a solution cell in cumene (concentration of the perester was ca. 0.1 M). The first-order rate constants for the thermolysis of the perester were 1.64 × 10$^{-5}$ at 80 °C, 6.56 × 10$^{-5}$ at 90 °C, and 21.2 × 10$^{-4}$ s$^{-1}$ at 100 °C, giving the activation enthalpy (32.5 kcal/mol) and entropy (11.5 cal/deg) of the thermolysis, respectively, and the half-life at 80 °C was ca. 11 h.
(31) H. Stetter and E. Rausher, Chem. Ber., **93**, 2054 (1960).
(32) G. W. Smith and H. D. Williams, J. Org. Chem., **26**, 2207 (1961).

# Correlation of Rate–Solvent Effects in Ionogenic Reactions

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There is ample evidence that a relation of log k with some commonly employed solvent parameter at a given temperature is not always a reliable index of the polarity of the activated complex. Through study of the temperature dependence of log k as a function of an empirical solvent property, viz. $\Delta G^{\pm}$ vs. (say) $E_T$, some perception of the ionogenic character of a reaction can be gained. The principal objective of this report is to show in some instances that the same rate data may be correlated with a universal and directly measurable property of matter, namely the dielectric, to permit a more quantitative and informative comparison of reaction transition states with respect to their polarities. For ionogenic reactions, where the activated complex possesses a significant dipole moment, a simple electrostatic argument based on the model developed by Kirkwood[9] is used to derive relationships between the activation parameters and readily accessible functions of the solvent dielectric (eq 9 → 13). These relationships have been tested by data gathered for two well known cases, the thermolysis of α-chlorobenzyl alkyl ethers[1] and the cycloaddition of TCNE to enol ethers,[8,10] both in aprotic solvents. In both cases the linear relationship involving activation free energy is found to be relatively insensitive to the occurrence of "chemical" interactions between the solvent and zwitterionic activated complex. However, though this treatment predicts an inverse linear correlation of negative activation entropy and solvent polarity, it is shown that "chemical" contributions of this nature can destroy the linearity and steeply invert the relationship so that the most polar solvents appear to be associated with the most negative entropies of activation. But, for a transition state of sufficiently high dipole moment, the "chemical" contribution term tends to predominate over the solvent dielectric term and to influence the $\Delta S^{\circ \pm}$ in such a way as to restore the appearance of linearity for all cases except those in which the solvent has nearly zero polarizability.

The use of empirical solvent parameters as a means of correlating solvent effects on rate has developed greatly since the introduction of the Winstein–Grunwald Y-value scale.[1a] Others such as the Kosower Z values[1b] and the Reichardt $E_T$ values[1c] have gained widespread application in probing the polarity of the activated complex. Such applications rely on the occurrence of a simple linear plot of log k vs. (say) $E_T$ at a given temperature, the steepness of the slope of the resulting line being accepted as a proportional measure of transition state polarity. But the information to be realized from this exercise is frequently of limited value; such factors in a polar transition state as charge separation and dipole moment do not emerge from the empirical solvent parameter relationship with rate.

Moreover, it is by no means unusual for an ionogenic reaction to display an inverse relationship between rate and an empirical measure of solvent polarity at a single temperature.

Under circumstances where this is close to the isokinetic temperature,[2,3a] a frequently undetected occurrence, plots of log k vs. (say) $E_T$ can be illusory. Two recent examples come to mind in which, at the given temperature, the observed inverse relationship of rate and solvent polarity suggested a non-ionogenic or a concerted process with an unpolarized transition state, namely, the thermolysis of trimethylsilylacetophenones to siloxyalkenes[2] and the corresponding rearrangement of aryl allyl sulfides[4] in aprotic solvents. Unequivocal evidence has subsequently been found to demonstrate the intervention of zwitterionic activated complexes in both of these cases.[3,4]

In a previous article[5] reporting on the thermolysis of α-chloro ethers in aprotic solvents, it was noted that the activation parameters $E_a$, $\Delta S^{\pm}$ and $\Delta G^{\pm}$ for the reaction in seven solvents showed a decreasing trend with increasing ionizing character of the solvent. These results in conjunction with

other considerations have been construed to support the classical Ingold picture[6] of a reaction process with an ion pair intermediate. However, the observation in such cases that greater negative values of $\Delta S^{\ddagger}$ occur with more polar solvents is not without exception; in fact a fairly extensive body of data has accumulated which does not fulfill this expectation.[7,8]

In order to avoid some of these pitfalls and to gain a greater perception of the charged structure of the transition state through application of a rate–solvent effect criterion it becomes necessary to reconsider the use of empirical solvent parameters. A return to correlations of rate with a direct, physical measure of solvent polarity, namely, the dielectric property, seemed to be recommended. Some well-trodden ground has been chosen as the foundation for an approach to interpreting solvent–rate effects in ionogenic reactions; it is based on a well-established treatment[9,10] which has previously provided sound guidance in the understanding of electrostatic interactions in solution.

## Discussion of Results

Before considering the specific problem associated with $\alpha$-chloro ether thermolysis[5] it is useful to review in a qualitative way the molecular basis for the effect of solvent on reaction rates. Given the reaction expressed by the equation

$$A \rightleftharpoons \ddagger \xrightarrow{k} \text{products} \tag{1}$$
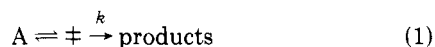
where A and $\ddagger$ denote reactant and activated complex, respectively, and applying the transition state theory of reaction rates,[11] the rate constant $k$ for this process is obtainable from the equation

$$\ln k = \ln (KT/h) - \Delta G^{\circ\ddagger}/RT \tag{2}$$

where $h$, $K$, and $T$ have their usual meanings and $\Delta G^{\circ\ddagger}$ is the difference between the standard state chemical potentials of the activated complex and the reactants expressed by the equation

$$\Delta G^{\circ\ddagger} = \mu^{\circ\ddagger} - \mu^{\circ}A \tag{3}$$

The standard state chemical potential refers to the species at infinite dilution in the particular solvent under consideration. It is constituted from contributions which depend upon the structure of the solute species (intrinsic effects) and contributions arising from species–solvent interactions (extrinsic effects). Although it is convenient to visualize the chemical potential as being composed of contributions from these two sources, strictly speaking they are not completely independent and separable. The molecular situation for a given solute species, i, can be represented diagrammatically[12,13] as follows.
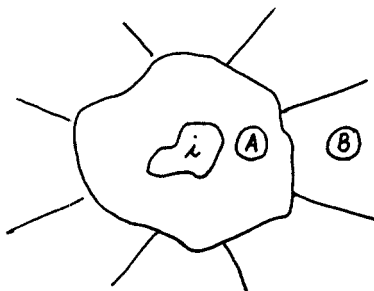


The region A corresponds to solvent adjacent to solute species i and having properties which differ to a greater or lesser extent from the properties of bulk solvent represented. by the region B. The difference in properties of these two solvent regions stem from the presence of the solute species perturbing the solvent in its immediate vicinity. Expectedly,

also, the solvent should modify the solute molecule to some extent and cause a lack of additivity of intrinsic and extrinsic contributions to the solute chemical potential. However, in all probability this effect is small and can be neglected in most of the following considerations. We may, therefore, assume[14] that the standard state chemical potential of a species can be represented as the sum of two contributions as given by the equation

$$\mu^{\circ} = \mu^{\circ}_{\text{int}} + \mu^{\circ}_{\text{ext}} \tag{4}$$

where $\mu^{\circ}_{\text{int}}$ depends on the molecular nature of the species, and $\mu^{\circ}_{\text{ext}}$ reflects the extrinsic interaction stemming from the specific interaction of the species with the solvent.

As a consequence, the standard free energy change (eq 2) for the reaction (eq 1) is given by the equation

$$\Delta G^{\circ\ddagger} = (\mu^{\circ}_{\ddagger,\text{int}} - \mu^{\circ}_{A,\text{int}}) + (\mu^{\circ}_{\ddagger,\text{ext}} - \mu^{\circ}_{A,\text{ext}}), \text{ or}$$

$$\Delta G^{\circ\ddagger} = \Delta G^{\circ\ddagger}_{\text{int}} + \Delta G^{\circ\ddagger}_{\text{ext}} \tag{5}$$

It is apparent from this that a solvent effect on the rate of reaction should generally be expected since, although the first term on the right hand side of eq 5 would be essentially solvent independent, the second term should depend to a greater or lesser extent upon the solvent nature.

Applying the usual thermodynamic manipulations to eq 5 leads to the equations

$$\Delta G^{\circ\ddagger} = \Delta H^{\circ\ddagger} - T\Delta S^{\circ\ddagger}$$

$$\Delta G^{\circ\ddagger} = (h^{\circ}_{\ddagger,\text{int}} - h^{\circ}_{A,\text{int}}) + (h^{\circ}_{\ddagger,\text{ext}} - h^{\circ}_{A,\text{ext}})$$
$$- T[(s^{\circ}_{\ddagger,\text{int}} - s^{\circ}_{A,\text{int}}) + (s^{\circ}_{\ddagger,\text{ext}} - s^{\circ}_{A,\text{ext}})] \tag{6}$$

As before, we would expect the changes in intrinsic enthalpy and entropy to be solvent independent, while the remaining terms would not be. Thus, the basic formulation of the effect of solvents on free-energy changes and reaction rate constants, within the context of transition state theory, is apparently quite straightforward. The problem, however, is to arrive at expressions for the extrinsic contributions based on the physical properties of the solvents considered.

There have been many discussions of this matter[2] all of which foster the conclusion that no single approach can be applied for all types of reactions. In certain situations, by making rather drastic assumptions, it is possible to derive expressions for rate dependence on solvent. For instance, in reactions involving the formation of ions from a covalency, a simple expression results by assuming that the solvent is a continuous dielectric. This relationship, the Born equation, describes the dependence of the extrinsic free-energy change on the dielectric constant. There is a considerable body of evidence,[15] however, which indicates that the Born equation[16] estimates the free-energy changes of real chemical processes only in a semiquantitative way at best. On the other hand, it is clearly preferable[14] to designate the extrinsic contribution to the chemical potential of a given ionic process as the sum of two terms, one arising from electrostatic effects and the other from what one might call "chemical" effects. The latter would include contributions from (say) solvent reorganization and packing effects and such specific interactions between solvent and solute as hydrogen bonding. It would seem eminently reasonable, therefore, to represent in an analogous way the contributions to the free-energy change which occur when completely isolated ionic charges are not formed, i.e., by transforming eq 5 into

$$\Delta G^{\circ\ddagger} = \Delta G^{\circ\ddagger}_{\text{int}} + \Delta G^{\circ\ddagger}_{\text{elec}} + \Delta G^{\circ\ddagger}_{\text{chem}} \tag{7}$$

where the last two terms on the right hand side correspond to $\Delta G^{\circ\ddagger}_{\text{ext}}$. Though it cannot be stated categorically, it may be supposed that $\Delta G^{\circ\ddagger}_{\text{chem}}$ would be smaller the less structured and idiosyncratic the solvent species is. If, for example, the

**Table I. Solvent Dielectrics and Dielectric Functions**

| Solvent | $\epsilon^a$ | $-d\epsilon/dT^a$ | $(\epsilon-1)/(2\epsilon+1)$ | $-(d\epsilon/dT) \cdot [1/(2\epsilon+1)^2]$ |
|---|---|---|---|---|
| Acetonitrile | 36.75 | 0.186 | 0.4799 | $3.35 \times 10^{-5}$ |
| Sulfolane | 43.32 | | 0.4829 | |
| Chloroform | 4.72 | 0.0177 | 0.3563 | $1.62 \times 10^{-4}$ |
| Chlorobenzene | 5.62 | 0.0168 | 0.3775 | $1.12 \times 10^{-4}$ |
| Toluene | 2.38 | 0.00243 | 0.2396 | $7.32 \times 10^{-5}$ |
| Carbon tetrachloride | 2.23 | 0.00200 | 0.2253 | $6.71 \times 10^{-5}$ |
| Nitrobenzene | 34.82 | 0.1804 | 0.4788 | $3.62 \times 10^{-5}$ |
| Cyclohexane | 2.02 | 0.00160 | 0.2030 | $6.30 \times 10^{-5}$ |
| Tetrahydro-furan | 7.39 | | 0.4050 | |
| Ethyl acetate | 6.02 | 0.0150 | 0.385 | $8.82 \times 10^{-5}$ |
| Methylene chloride | 9.08 | 0.0373 | 0.422 | $1.016 \times 10^{-4}$ |
| Acetone | 20.7 | 0.0977 | 0.465 | $5.43 \times 10^{-5}$ |
| Benzonitrile | 25.19 | | 0.471 | |

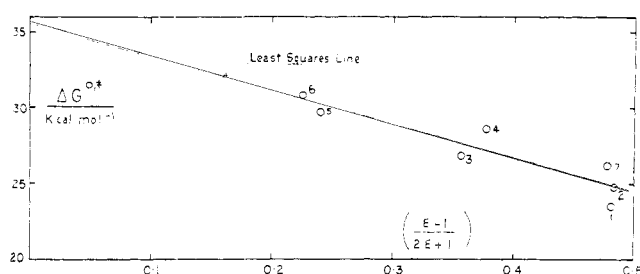$^a$ These data are taken or computed from data in ref 17 and 18.



**Figure 1.** Activation free-energy change with solvent dielectric function in thermolysis of $\alpha$-chlorobenzyl methyl ether. Least-squares computation: slope = −21.6; intercept = 35.4; correlation coefficient $R = -0.92$.

| Solvent | Graph index | $\Delta G^{\circ \ddagger}$, kcal mol$^{-1a}$ |
|---|---|---|
| $CH_3CN$ | 1 | 23.6 |
| Sulfolane | 2 | 24.8 |
| $CHCl_3$ | 3 | 26.8 |
| $C_6H_5Cl$ | 4 | 28.6 |
| $C_6H_5CH_3$ | 5 | 29.7 |
| $CCl_4$ | 6 | 30.8 |
| $C_6H_5NO_2$ | 7 | 26.2 |

$^a$ Data from ref 5.

solvent was capable of hydrogen bonding with either the reactant or the activated complex, this interaction would presumably drive $\Delta G^{\circ \ddagger}{}_{chem}$ toward a large value.

Bearing in mind the above deductions, we may now turn to consideration of the specific problem of the thermolysis of $\alpha$-chloro ethers in aprotic solvents shown[1] to take place via an ion-paired intermediate. This develops from an activated complex possessing a high dipole moment. For such circumstances it is plausible to use a simple electrostatic argument based upon a model developed some years ago by Kirkwood[9] to explain some of the thermodynamic properties of amino acids. The solvent dependence of the electrostatic contribution to the free energy of zwitterionic species has been considered in the Kirkwood treatment.[9] The model he used corresponded to a spherical solute species in the continuous dielectric solvent. For such a system the electrostatic contribution to the chemical potential is given by the equation

$$\mu^{\circ \ddagger}{}_{elec} = \frac{L\bar{\mu}^2}{b^3}\left(\frac{1-\epsilon}{2\epsilon+1}\right) \tag{8}$$

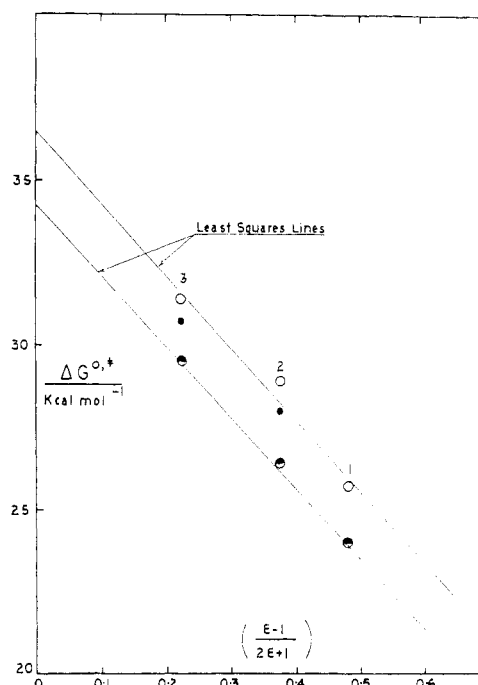where $L$, $\mu$, $b$, and $\epsilon$ are Avogadro's constant, the dipole mo-



**Figure 2.** Activation free-energy change with solvent dielectric function in thermolysis of para-substituted $\alpha$-chlorobenzyl methyl ethers.

| Solvent | Graph index | $\Delta G^{\circ \ddagger}$, kcal mol$^{-1a}$ | | |
|---|---|---|---|---|
| | | $p$-Cl | $p$-F | $p$-CH$_3$ |
| Sulfolane | 1 | 25.7 | | 24.0 |
| $C_6H_5Cl$ | 2 | 28.9 | 28.0 | 26.4 |
| $CCl_4$ | 3 | 31.4 | 30.7 | 29.5 |
| Symbol | | $\odot$ | $\bullet$ | $\ominus$ |
| Least Squares Computations | | | | |
| $R$ | | −0.985 | | −0.998 |
| Slope | | −21.7 | | −21.4 |
| Intercept | | 36.5 | | 34.2 |

$^a$ Data from ref 5.

ment, and the radius of the zwitterionic species, respectively, and the dielectric constant of the solvent. Equation 8 and modifications of it have been used successfully to explain the behavior of peptides in solution.[17]

If we assume for the specific examples to be analyzed here that the reactant species has no significant dipole moment, the combination of eq 7 and 8 results in the equation

$$\Delta G^{\circ \ddagger} = \Delta G^{\circ \ddagger}{}_{int} + \left(\frac{L\bar{\mu}^2}{b^3}\right)\left(\frac{1-\epsilon}{2\epsilon+1}\right) + \Delta G^{\circ \ddagger}{}_{chem} \tag{9}$$

The simplest situation which could possibly arise is when the "chemical" term makes no contribution. We then obtain a direct link between the standard free-energy change and the solvent dielectric constant, viz. the equation

$$\Delta G^{\circ \ddagger} = \Delta G^{\circ \ddagger}{}_{int} - \frac{L\bar{\mu}^2}{b^3}\left(\frac{\epsilon-1}{2\epsilon+1}\right) \tag{10}$$

The solvent dielectric data[2,18] and the quantities computed therefrom are listed in Table I. The plot according to eq 10, delineating the solvent effect on activation free energy, $\Delta G^{\circ \ddagger}$, for the solvolytic rearrangement of $\alpha$-chlorobenzyl methyl ether, is given in Figure 1. The plots in Figure 2 (along with the data from which they were constructed) are presented as a correlation of the effect of the para substituent on the parameters of eq 10. Clearly, all substituted cases in Figures 1 and 2 are correlated by lines of the same slope, i.e., $L\bar{\mu}^2/b^3$ = 21.6, because their activated complexes have about the same
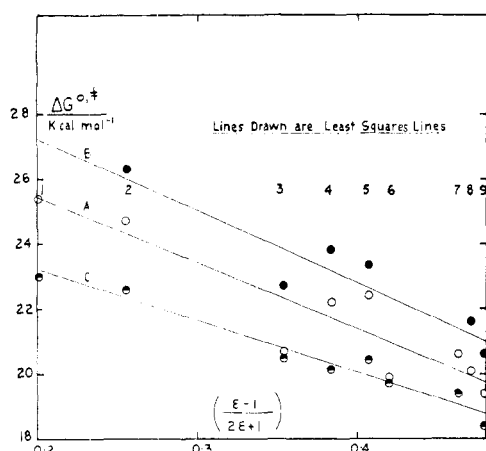
**Figure 3.** Activation free-energy change with solvent dielectric function in cycloaddition of TCNE with various vinylic ethers.

| Solvent | Graph index | $\Delta G^{\circ\ddagger}$ kcal mol$^{-1a}$ | | |
|---|---|---|---|---|
| | | A | B | C |
| Cyclohexane | 1 | 25.4 | | 23.0 |
| CCl$_4$ | 2 | 24.7 | 26.3 | 22.6 |
| THF | 3 | 22.4 | | 20.4 |
| EtOAc | 4 | 22.2 | 23.3 | 20.1 |
| CHCl$_3$ | 5 | 20.7 | 22.8 | 20.5 |
| CH$_2$Cl$_2$ | 6 | 19.9 | 22.7 | 19.7 |
| Acetone | 7 | 20.6 | | 19.4 |
| C$_6$H$_5$CN | 8 | 20.1 | 21.6 | |
| CH$_3$CN | 9 | 19.4 | 20.6 | 18.4 |
| Symbol | | $\odot$ | $\bullet$ | $\ominus$ |
| Least-Squares Computations | | | | |
| R | | −0.916 | −0.956 | −0.978 |
| Slope | | −20.2 | −22.3 | −15.7 |
| Intercept | | 29.4 | 31.7 | 26.3 |

*a* Data from ref 8.
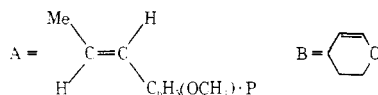


degree of charge separation as suggested previously by the linearity of their Hammett free-energy plot.[1] The differences in intercept suggests that the substitutent effect is exerted only on the $\Delta G^{\circ\ddagger}{}_{int}$ term, varying with the polar nature of the substituent in an expected way. It is therefore apparent from these plots that the linear relation encompassed by eq 10 is obeyed to an acceptable approximation, implying that the "chemical" contributions to the standard free-energy change are relatively unimportant. Moreover, it can be shown that the slopes of the lines in Figures 1 and 2 are of the proper magnitude for reactions of the type under consideration (see Appendix).

Further confirmation of the correctness of this approach is to be found in studies reported by Steiner and Huisgen[8] on the solvent dependence of the rate of reaction of tetracyanoethylene (TCNE) with enol ethers, which is characterized by a zwitterionic transition state. The data obtained by these authors for the cycloaddition of TCNE to anethole, 2,3-dihydro-4H-pyran and butyl vinyl ether are listed in the table accompanying the plot in Figure 3, constructed in accordance with the variables of eq 10.

The general trend of these data is satisfactorily correlated with the terms of the electrostatic treatment outlined above, although the scatter of points about the linear relationships encompassed by eq 10 is such as to suggest that "chemical contributions" are not insignificant for some of the systems investigated. Nonetheless, it can be seen that these systems

still show significant differences in slope which reflect the expected differences in transition-state charge separation, as well as differences in intercept indicative of differences in their $\Delta G^{\circ\ddagger}{}_{int}$ terms.
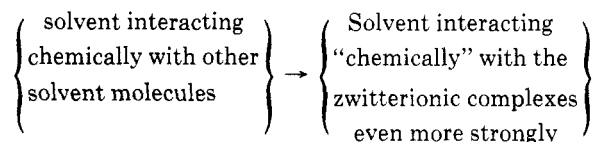
The general approach applied here for the change of standard activation free energy can be readily extended to other activation parameters. For example, the entropic analogues of eq 7, 9, and 10 are obtained by partial differentiation with respect to temperature at constant pressure.

$$\Delta S^{\circ\ddagger} = \Delta S^{\circ\ddagger}{}_{elec} + \Delta S^{\circ\ddagger}{}_{chem} \tag{11}$$

$$\Delta S^{\circ\ddagger} = \Delta S^{\circ\ddagger}{}_{int} + \frac{3L\bar{\mu}^2}{b^3}\frac{1}{(2\epsilon+1)^2}\left(\frac{d\epsilon}{dT}\right) + \Delta S^{\circ\ddagger}{}_{chem} \tag{12}$$

$$\Delta S^{\circ\ddagger} = \Delta S^{\circ\ddagger}{}_{int} + \frac{3L\bar{\mu}^2}{b^3}\frac{1}{(2\epsilon+1)^2}\left(\frac{d\epsilon}{dT}\right) \tag{13}$$

Since the $d\epsilon/dT$ terms are negative, the primary equation (eq 12) anticipates that the activation entropy becomes more negative with lower values of the solvent dielectric, providing the $\Delta S^{\circ\ddagger}{}_{chem}$ term is negligible, i.e., the circumstances under which the simplifying equation (eq 13) would prevail. Where the $\Delta S^{\circ\ddagger}{}_{chem}$ term is not negligible the entropic changes originating in "chemical contributions" would be greatest for the more polar and structured solvents and may even exceed in magnitude the second term involving the dielectric function. These contributions can be estimated in a qualitative way to be possibly more negative in value the greater the degree of chemical interaction between solute and solvent, since under these circumstances the reaction thermodynamics would include the process:

$$\left\{\begin{array}{l}\text{solvent interacting} \\ \text{chemically with other} \\ \text{solvent molecules}\end{array}\right\} \rightarrow \left\{\begin{array}{l}\text{Solvent interacting} \\ \text{"chemically" with the} \\ \text{zwitterionic complexes} \\ \text{even more strongly}\end{array}\right\}$$

Thus, the entropic change would be much more negative for the more polar solvents than is predicted by the simplified equation (eq 13) deduced from the electrostatic model.

Figure 4 has been plotted according to the variables of eq 13 from the data of Kwart and Silver[5] (which is listed in the accompanying table). Clearly the correlations are much less satifactory than those obtained for the corresponding activation free-energy changes. The slope to be expected (the "theoretical lines") has been drawn in the Figure 4 plot; it should have a value 3000 times greater (for $\Delta S^{\circ\ddagger}$ expressed in cal K$^{-1}$ mol$^{-1}$) than the corresponding free-energy plot in Figure 1 based on eq 10.

It is obvious from the Figure 4 plot that the more structured solvents such as acetonitrile and nitrobenzene deviate most from the simple relationship of eq 13. Such deviation is to be expected where the zwitterionic activated complex has a moderate dipole moment. For low and average polarity solvents the slope tends to become more horizontal (than if eq 13 was applicable), since the normal direction of change of the dielectric function term is being opposed by a $\Delta S^{\circ\ddagger}{}_{chem}$ term arising from proportionately moderate chemical contributions. A sudden, large contribution to this term can therefore be correlated with a highly structured solvent, producing a degree of interaction which is extraordinary among the members of the solvent series. This seems to be the case for acetonitrile and nitrobenzene in Figure 4, where these higher dielectric solvents drive the reaction steeply toward more negative $\Delta S^{\circ\ddagger}$ values.

The converse might also be found for a zwitterionic transition state with a larger dipole moment. Here the $\Delta S^{\circ\ddagger}{}_{chem}$ may be very large and dominate the right-hand side of eq 12 for most members of the solvent series having more than a threshold degree of polarity. For such cases, in fact, the
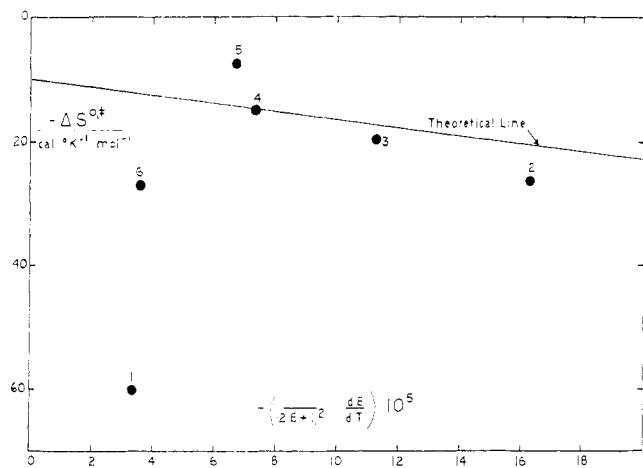
**Figure 4.** Activation entropy change with solvent dielectric function in thermolysis of $\alpha$-chlorobenzyl methyl ether. Slope drawn is that calculated from the experimental value of Figure 1 in accordance with eq 13.

| Solvent | Graph index | $-\Delta S^{\circ\ddagger}$, cal $K^{-1}$ mol$^{-1}$[a] |
|---|---|---|
| $CH_3CN$ | 1 | 60.1 |
| $CHCl_3$ | 2 | 26.1 |
| $C_6H_5Cl$ | 3 | 19.5 |
| $C_6H_5CH_3$ | 4 | 15.0 |
| $CCl_4$ | 5 | 7.5 |
| $C_6H_5NO_2$ | 6 | 26.9 |

[a] Data from ref 5.

$\Delta S^{\circ\ddagger}_{chem}$ term would tend to parallel solvent properties such as polarizability,[19] which come into play most importantly when the solvent is introduced into a sufficiently strong field. That is to say, a $\Delta S^{\circ\ddagger}_{chem}$ term based largely on polarizability interactions will tend to eclipse the dielectric function term of eq 12 for transition states of higher dipole moment. However, for solvents which lack any structure and are nonpolarizable we could expect strong deviation from the line correlating the more polarizable members of the solvent series. This appears to be the case for the TCNE–enol ether cycloaddition reaction studied by Huisgen[8,10] where the transition state dipole moment (~14 D) is some 50% greater than that characterized for the $\alpha$-chlorobenzyl methyl ether (~9 D). As is evident from Figure 5 and the accompanying table of data, only the very inert, nonpolarizable cyclohexane stands away from the correlation line of the five other solvents, ranging from acetonitrile to the highly polarizable carbon tetrachloride.

Since $\Delta G^{\circ\ddagger}$ has been assumed in this treatment to be linearly related to $\Delta S^{\circ\ddagger}$, it may be surprising to observe an acceptable linear correlation of $\Delta G^{\circ\ddagger}$ and the appropriate dielectric function from eq 10 in Figure 1, and a nearly complete lack of correlation of the $\Delta S^{\circ\ddagger}$ data accordirg to Figure 4. But this is not an unprecedented experience; rather it is another example of the operation of the "compensation law" wherein a reaction factor bringing about a significant change in the entropy is simultaneously effecting a compensatory change in enthalpy.[20] As a consequence, the $\Delta G^{\circ\ddagger}$ may respond to the influence of this reaction factor with no significant deviation from linear behavior.

An analogous treatment could be applied to the volumes of activation[19,20] ($\Delta V^{\circ\ddagger}$), but in terms of an electrostatic model the appropriate physical property, viz., $d\epsilon/dP$ (see eq 15), is generally not available for the sorts of solvents which might be expected to obey the predicted electrostatic relationships.

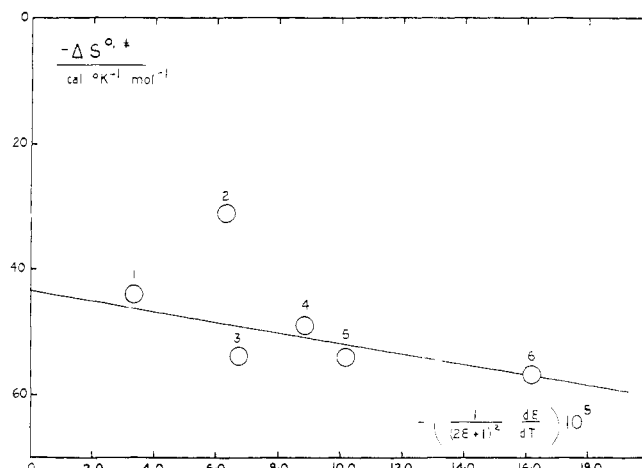**Regarding the Correlation of $\Delta S^{\circ\ddagger}$ and $\Delta G^{\circ\ddagger}$ with**



**Figure 5.** Activation entropy change with solvent dielectric function in cycloaddition of TCNE to anethole.

| Solvent | Graph index | $-\Delta S^{\circ\ddagger}$, cal $K^{-1}$ mol$^{-1}$[a] |
|---|---|---|
| Acetonitrile | 1 | 44 |
| Cyclohexane | 2 | 31 |
| $CCl_4$ | 3 | 54 |
| Ethyl acetate | 4 | 49 |
| $CH_2Cl_2$ | 5 | 54 |
| $CHCl_3$ | 6 | 57 |

[a] Data from ref 8.

**Solvent Polarity as an Index of Charge Separation in the Activated Complex.** A basis for the expectation that reactions which give rise to zwitterionic intermediates should show more negative activation entropies in less polar solvents stems from many kinetic studies at high pressures,[21,22] which yield estimates of the activation volume $\Delta V^{\circ\ddagger}$. This conclusion apparently is deduced from two considerations: (a) $\Delta V^{\circ\ddagger}$ values for such ionogenic reactions as solvolysis are very much more negative in nonpolar solvents,[21] and (b) $\Delta S^{\circ\ddagger}$ tends to parallel $\Delta V^{\circ\ddagger}$ since both are derivative functions of $\Delta G^{\circ\ddagger}$. What is implicit in the latter assumption is that $\Delta S^{\circ\ddagger}$ is determined largely by solvent electrostriction. The $\Delta V^{\circ\ddagger}$ is taken as a *direct measure* of electrostriction on the basis of the Drude–Nernst equation (eq 15), which expresses the volume change resulting from immersion of a *discrete ion* into a continuous, structureless dielectric $\epsilon$.[16] The Drude–Nernst equation, in turn, is a derivative of the classical Born equation.[16]

The Born equation (eq 15) is analogous to eq 10 which we derived above for zwitterions, but it applies *only* to species with a discrete charge, i.e., $+$ rather than $+-$. Thus, if we consider a process where discrete charge rather than a zwitterion or ion pair is created (A $\rightarrow$ A$^+$ rather than A $\rightarrow$ $^-$A$^+$), in a solvent of dielectric $\epsilon$, the free-energy change on forming a mole of charged species A$^+$ from *electrostatic sources only* is

$$\Delta G^{\circ\ddagger} = \frac{-LZ^2e^2}{2r}(1 - 1/\epsilon) \qquad (14)$$

where $L$ is Avogadro's number, $Z$ is the valence, $e$ is the electron charge, and $r$ is the charge radius. The volume change corresponding to this is given by

$$\Delta V^{\circ\ddagger} = \left(\frac{\partial \Delta G^{\circ\ddagger}}{\partial P}\right)_T = -\frac{LZ^2e^2}{2r\epsilon^2}\left(\frac{d\epsilon}{dP}\right) \qquad (15)$$

Comparison of eq 14, which expresses the free energy of activation involved with formation of a discrete charge within a dielectric $\epsilon$, with eq 10, which expresses the analogous rela-

tionship in cases of zwitterion formation, conveys a measure of understanding as to why the Drude–Nernst equation and derivatives thereof cannot ordinarily be applied as criteria for ionogenic reaction processes.

Finally, the results discussed here suggest that correlation of $\Delta G^{\circ\ddagger}$ and solvent dielectric expressed in eq 10 provides a reasonably reliable index of a zwitterionic or ion pair structured transition state. Evidently, the effects of "chemical"contributions arising from the solute zwitterions interacting with the solvent are generally cancelled out and appear to be insignificant compared to their influence on the entropy of activation. Thus, it would appear that any given attempt to establish a relation between entropy of activation and some solvent polarity parameters, depending on the range of solvents employed, may lead to results which are contrary to expectation.[3] This is particularly so where a large degree of charge separation is developed in the activated state and a high extent of solvent polarization and other kinds of interaction with solvent can occur as a consequence.

## Appendix: Estimation of Charge Separation in the Transition State

Equation 10 can be rewritten as:

$$\Delta G^{\circ\ddagger} = \Delta G^{\circ\ddagger}{}_{int} + 14.40 \left(\frac{\bar{\mu}^2}{b^3}\right) \left(\frac{1-\epsilon}{2\epsilon+1}\right) \qquad (16)$$

$$(\text{kcal mol}^{-1}) = (\text{kcal mol}^{-1})$$

if the dipole moment of the zwitterion is expressed in debye units and the radius is in angstrom units. Similarly, eq 13 may be written as

$$\Delta S^{\circ\ddagger} = \Delta S^{\circ\ddagger} + 0.0432 \left(\frac{\bar{\mu}^2}{b^3}\right) \left(\frac{1}{(2\epsilon+1)^2}\right) \left(\frac{d\epsilon}{dT}\right) \quad (17)$$

$$(\text{cal deg}^{-1} \text{ mol}^{-1}) = (\text{cal deg}^{-1} \text{ mol}^{-1})$$

**Sample Calculation.** To consider the effective radius of $\alpha$-chlorobenzyl methyl ether we may assume to a fair approximation that the densities of inert substances in the liquid phase are nearly unity. That is to say, assuming the density of the ether to be $1.0 \pm 0.1$, this structure of mol wt 157, having a packing density[23] $= 0.9$, is deduced to have a molar volume of $(157 \times 0.9) = 141$ cm$^3$ mol$^{-1}$. Therefore, the molecular volume (of 141/Avogadro's number) is calculated to be 253 Å$^3$ per molecule. Consequently, the cube of the molecular radius, equal to $b^3$ in eq 10, becomes 56.1 Å$^3$. Since the slope of the Figure 1 graph gives us 21.6 kcal mol$^{-1}$, then

$$21.6 = 14.4 \ \bar{\mu}^2/56.1$$

and

$$\bar{\mu}^2 = 84.2 \ \text{D}^2$$

$$\bar{\mu} = 9.2 \ \text{D}$$

and since $\bar{\mu} = e{\cdot}d$, the electron charge times the separation, the charge separation in the transition state is

$$d = 9.2/4.8 = 1.9 \ \text{Å}$$

Bearing in mind the approximations[23] which have been made throughout, the error is not significant.

## References and Notes

(1) (a) S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 846 (1948); (b) E. M. Kosower, *ibid.*, **80**, 3253 (1958); (c) C. Reichardt, *Angew, Chem., Int. Ed. Engl.*, **4**, 29 (1965); "Chemische Taschenbucher", Vol. 4, 1969, pp 142–145; (d) The University of Sheffield, Sheffield, England.
(2) (a) A. G. Brook, D. M. MacRae, and W. W. Limburg, *J. Am. Chem. Soc.*, **89**, 5493 (1967); (b) A. G. Brook, *J. Organomet. Chem.*, **86**, 185 (1975); (c) G. L. Larson and Y. V. Fernandez, *ibid.*, **86**, 193 (1975).
(3) (a) H. Kwart, and W. E. Barnette, *J. Am. Chem. Soc.*, **99**, 614 (1977); (b) H. Kwart and J. J. Stanulonis, *ibid.*, **98**, 4009 (1976); (c) H. Kwart and T. J. George, *ibid.*, **99**, 5214 (1977).
(4) (a) H. Kwart and N. Johnson, *J. Am. Chem. Soc.*, **92**, 6064 (1970); (b) H. Kwart and N. Johnson, *ibid.*, **99**, 3441 (1977).
(5) H. Kwart and P. A. Silver, *J. Org. Chem.*, **40**, 3019 (1975).
(6) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1969.
(7) (a) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2nd ed, Wiley, New York, N.Y., 1959, pp. 181–183; (b) E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, N.Y., 1959, pp 181–183.
(8) G. Steiner and R. Huisgen, *Tetrahedron Lett.*, 3769 (1973).
(9) (a) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934); (b) J. Jadzyn and J. Malecki, *Acta. Phys. Pol.*, **A38**, 57 (1972). These authors have shown the model works for one-component solvents but not for mixed solvents of high dielectric constant. The problem of mixed solvents introduces other problems associated with "solvent sorting" in the vicinity of the solute-species. Aspects of this problem are discussed in ref 14 and are not dealt with in the work under consideration here.
(10) R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, **95**, 5056 (1973).
(11) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, N.Y., 1941.
(12) See for further discussion, T. H. Lilley in "Water, A Comprehensive Treatise", Vol. 3, F. Franks, Ed., Plenum Press, New York, N.Y., 1973.
(13) H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 141 (1958).
(14) A. K. Covington, K. E. Newman, and T. H. Lilley, *J. Chem. Soc., Faraday Trans. 1*, **69**, 973 (1973).
(15) R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).
(16) For further discussion see R. W. Gurney, "Ionic Processes in Solution", Dover Press, New York, N.Y., 1962, Section 15.
(17) (a) R. M. Roberts and J. G. Kirkwood, *J. Am. Chem. Soc.*, **63**, 1373 (1941); (b) E. E. Schrier and R. A. Robinson, *J. Biol. Chem.*, **246**, 2870 (1971); (c) C. C. Briggs, T. H. Lilley, J. Rutherford, and S. Woodhead, *J. Solution Chem.*, **3**, 649 (1974); (d) T. H. Lilley and R. P. Scott, *J. Chem. Soc., Faraday Trans.*, **72**, 184, 197 (1976).
(18) (a) A. K. Covington and T. Dickinson, "Physical Chemistry of Organic Solvent System", Plenum Press, London, 1973; (b) G. J. Janz and R. P. T. Tompkins, "Non-aqueous Electrolytes Handbook", Vol. I, Academic Press, New York, N.Y., 1972.
(19) J. W. Smith, "Electric Dipole Moments", Butterworth, London, 1955.
(20) (a) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955); (b) R. Lumry and S. Rajender, *Biopolymers*, **9**, 1125 (1970).
(21) F. K. Fleischman and H. Kelm, *Tetrahedron Lett.*, 2773 (1973).
(22) See also for further illustrations and references to the application of this approach, W. J. Le Noble and R. Mukhtar, *J. Am. Chem.Soc.*, **97**, 4938 (1975).
(23) In a condensed phase only a fraction of the space is taken up by molecules, there being some dead space arising from packing effects. It is difficult to estimate what this dead space contribution would be for other than hard spherical molecules. Under those conditions we can estimate that the fraction of the total volume taken up by the molecules is 0.637 (this corresponds to dense, randomly packed spheres: see, e.g., K. Gotoh and J. L. Finney, *Nature (London)*, **252**, 202 (1974)). This must be very much a lower limit and as soon as one has mixtures of spheres of different sizes (corresponding more closely to our experimental situation) the number rises. For unlike-sized spheres W. M. Vischeer and M. Bolsterli [*Nature (London)*, **239**, 504 (1972)] found that it could rise to a value of 0.868. Not withstanding these points it would seem that with the molecules we consider, which are much "flatter" than spheres, the packing fraction would be considerably higher than results with the hard spheres. A value of 0.9 would thus seem not unreasonable.