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THE QUESTION OF SOLVENT EFFECT ON THE RATES OF IONIC REACTIONS THAT HAVE LITTLE CHARGE DEVELOPMENT IN THE TRANSITION STATE

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Abstract—A relationship, $\alpha_{E_T} = (\beta/1000)(d\Delta S^{\neq}/dE_T)$, is proposed where α_{E_T} may represent an indication of transition state structure in ionic reactions. The relationship suggests a reactant-like transition state for the Menshutkin reaction, in agreement with conclusions reached by other methods, and it is concluded that the absence of a large solvent effect on the rate of a reaction does not necessarily constitute evidence of a non-ionic mechanism.

Since the observation by Hughes and Ingold in 1935, that the rates of reactions involving formation of charge should be, and are, accelerated by an increase in the ion-solvating power of the medium,[1] the effect of solvent polarity on reaction rates has become a widely used test for distinguishing ionic from non-ionic mechanisms. Rules have been developed, such as a rate spread of 10^3 or 10^5 being indicative of an ionic mechanism, but smaller spreads being considered inconcistent with an ionic reaction.[2] An aggravating point, however, in using these rules, is the generally overlooked matter that the correctness of the rule demands that the *transition state* (as opposed to the intermediate or product) in the rate-controlling step has substantial charge development. A reaction producing ions and yet proceeding through a highly reactant-like transition state (for example[3] an exothermic ionization) will presumably have little rate dependency on solvent and the rule will be expected to fail. It is clear that to probe this matter further it is required that the relation between the magnitude of the solvent induced rate spread and the position of the transition state along the reaction coordinate be considered, and this communication represents an effort in this direction.

The solvent induced rate spread is caused mainly by solvent electrostriction which manifests itself in the activation entropy, and, therefore, a desirable relationship in order to probe the question posed above is that between the magnitude of the activation entropy and the degree of charge development in the transition state. Despite recent controversy arising out of studies on the deprotonation of nitroalkanes,[4] one widely used experimental method of obtaining information on transition state structure has been the free-energy rate-equilibrium relationship (1), with the interpretation that the slope α_G implies a reaction-like transition

$$\alpha_G = d\Delta G^{\neq}/d\Delta G^0 \qquad (1)$$

state if near zero and a product-like transition state if near unity.[5] The question of which of the free-energy rate-equilibrium relationship and the enthalpy rate-equilibrium relationship (2) is the more fundamental is one which has been discussed both originally and more

$$\alpha_H = d\Delta H^{\neq}/d\Delta H^0 \qquad (2)$$

recently[6] without a firm decision having been reached, although the free-energy relationship is by far the more common, owing in part to the ready availability of equilibrium data at one temperature. The use of the entropy rate-equilibrium relationship (3) appears to have been extremely limited. It would seem to be an interesting question as

$$\alpha_S = d\Delta S^{\neq}/d\Delta S^0 \qquad (3)$$

to whether the magnitude of α_S would represent a useful guide to transition state structure in a reaction that is predominantly entropy controlled.

The obvious way to test this question would be to select an entropy-controlled reaction for which entropies of reaction and of activation were known in a variety of solvents together with independent measurements on the nature of the transition state so that the transition state prediction from α_S could be tested against those from other methods. Unfortunately no such reaction exists, mainly because of the difficulty of obtaining, and consequent scarcity of entropy of reaction data. The reaction which comes closest and which was selected for investigation was the Menshutkin reaction,[7] (the quaternization of tertiary amines by alkyl halides), $R_3N + RX \rightarrow R_4\overset{\oplus}{N}\overset{\ominus}{X}$. For this reaction there already exist studies on the nature of the transition state based on chlorine isotope effects and on free energies of transfer (vide infra), and activation parameters in different solvents have been measured. The only omission preventing analysis is a set of values of ΔS^0 in various solvents, and thus attention was given to generating a new relationship replacing ΔS^0 with a parameter more tangible, not only from the point of view of analysis in the Menshutkin reaction, but also for application to other reactions. In equation (3) applied to ionic reactions, the ΔS^0 term is basically functioning as a measure of solvent polarity and this suggests that a possible simple substitute might be the widely-used empirical parameter E_T.[8] Although reasonable correlation is, in fact, found between $\Delta S^{\ddagger}$ and E_T (vide infra), their direct relationship is not interpretatively useful as E_T does not represent an entropy term; furthermore it is not experimentally appropriate to plot $\Delta H^{\ddagger}$ vs E_T as the changes in ΔH^{-} as a function of solvent in ionic reactions are small. This problem can however be overcome by the use of the isokinetic relationship (4),[9]

$$\delta \Delta H^{\ddagger} = \beta \delta \Delta S^{\ddagger} \qquad (4)$$

where β is the isokinetic temperature, which suggests equation (5) as a possibly useful relationship where all terms are reasonably tangible and

$$\alpha_{E_T} = \frac{\beta}{1000} \frac{d\Delta S^{\ddagger}}{dE_T} \qquad (5)$$

αE_T is a dimensionless parameter. The magnitude of this parameter should depend on the degree of charge development in the transition state and can be tested in this connection.

Application of equations (3) *and* (5) *to the Menshutkin reaction*

Activation parameter data as a function of solvent have been published on the reactions of ethyl iodide with triethylamine,[10] and of aniline with phenacyl bromide.[11] Values of $\Delta S^{\ddagger}$ are generally in the range −30 to −50 entropy unit, consistent with a bimolecular reaction producing charge. Table 1 summarizes these data in terms of their application to equation (5). Data have also been reported on the reaction of pyridine with methyl iodide,[12] however, although these apparently give a value of α_{E_T} in the same range, the correlation between $\Delta S^{\ddagger}$ and E_T is poor ($r < 0{\cdot}8$). No data apparently exist to permit the use of equation (3) with solvent being the variable: however Rossell has reported both entropy of activation and entropy of reaction data for the reaction $RC_6H_4NR'R'' + R'''X$ in nitrobenzene[12] which permit the use of equation (3) with structural rather than solvent variation. Omitting the *meta*-substituted anilines, 7 examples are linearly correlated (correlation coefficient 0·92) giving a value of α_s of 0·22.

From these data a number of encouraging points appear evident (a) application of experimental data to equations (3) and (5) give sensible values of α_s and α_{E_T} respectively (i.e. values lying between 0·0 and 1·0); (b) values of α_{E_T} and α_s obtained are in reasonable agreement with each other; and (c) interpretation of the values of α_s and α_{E_T} in the same way as that for α_G[5] suggests that the transition state for the Menshutkin reaction is approximately a quarter of the way along the reaction co-ordinate (i.e. has significant N–C bonding but resembles reactants rather than products). This conclusion is in agreement with conclusions drawn from chlorine isotope effect studies[14] and from free energy of transfer studies.[15] For these reasons we put forward equation (5) as a possible, easily accessible, guide to transition state structure for ionic reactions.

Solvent induced rate increases as a function of E_T

If the value of α_{E_T} represents a measure of the degree of charge development in the transition state, then the original question of relating this to the solvent induced rate acceleration may be returned to, since the relationship between $\Delta S^{\ddagger}$ and rate constants is well established. Indeed, whether or not the above interpretation of α_{E_T} is strictly correct, the magnitude of solvent induced rate increases can certainly be calculated from values of α_{E_T}, provided a value of α_{E_T} exists for the reaction under consideration by virtue of a linear $\Delta S^{\ddagger}$ vs E_T relationship. From the Eyring equation one can write the ratio of two rate constants as in equation (6).

$$\log k_1/k_2 = \frac{-(\Delta H_1^{\ddagger} - \Delta H_2^{\ddagger})}{2.303RT} + \frac{(\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger})}{2.303R} \qquad (6)$$

In an entropy controlled reaction, the compensating effect of enthalpy change can be incorporated by means of the isokinetic relationship[9] (4), equation (6) thus becoming

$$\log k_1/k_2 = \frac{(\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger})(1 - \beta/T)}{2.303R} \qquad (7)$$

From equation (5), the value of $(\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger})$ can be substituted with

$$\delta \Delta S^{\ddagger} = \alpha_{E_T} \cdot \frac{1000}{\beta} \cdot \delta E_T \qquad (8)$$

Table 1. Values of α_{E_T} from $\alpha_{E_T} = \frac{\beta}{1000} \frac{d\Delta S^{\ddagger}}{dE_T}$

Reaction	Solvent range	Correlation coefficient	α_{E_T}
$Et_3N + EtI$ (50°)[10]	Bromobenzene (E_T 37·5) to acetone (E_T 42·2)	0·89 (7 solvents)	0·18
Aniline + Phenacyl bromide[11] (28°)	Benzene (E_T 34·5) to methanol (E_T 55·5)	0·83 (6 solvents)	0·22

and substitution of equation (8) into (7) gives

$$\log k_1/k_2 = \frac{1000}{2.303RT}(\Delta E_T)(\alpha_{E_T})(T/\beta - 1) \qquad (9)$$

giving an expression of solvent induced rate acceleration as a function of solvent polarity difference, the value of α_{E_T}, and the isokinetic temperature. The correctness of equation (9) will, of course, depend on the degree of linearity to which the reaction obeys the isokinetic relationship and equation (5), but the value predicted by equation (9) does *not* hinge on the interpretation of α_{E_T}. Table 2 lists some calculated rate accelerations using equation (9); the value of $\beta = 210°$ is used as the data[11] indicate this to be the isokinetic temperature for the Menshutkin reaction. Clearly the rate accelerations will be smaller the higher the value of β.

From Table 2 it is clear that, depending on the values of ΔE_T and α_{E_T} (and β), a very wide range of solvent induced rate accelerations may be expected. Whilst it is easy to see that the figures of 10^3–10^5 may frequently arise, an extremely small rate acceleration (<10) can be expected for a reaction with a small value of α_{E_T} (0·1) (which may correspond to an early transition state), even for a very wide (n-hexane → water) solvent polarity change. Thus, whilst a large solvent effect on rate may indicate an ionic mechanism, the converse is not necessarily true, i.e. *the absence of a large, or even medium solvent effect on rate does not constitute unambiguous evidence of a non-ionic mechanism, with rate ratios as low as* 10 *apparently being quite possible for an ionic mechanism with an early transition state.*

Table 2. Calculated rate accelerations depending on ΔE_T and α_{ET}[a]

Solvent change	α_{E_T}	k_1/k_2
n-hexane → water	1	$7{\cdot}9 \times 10^9$
$\Delta E_T = 32{\cdot}2$	0·5	$8{\cdot}9 \times 10^4$
	0·3	$9{\cdot}3 \times 10^2$
	0·1	9·8
toluene → methanol	1	$4{\cdot}3 \times 10^6$
$\Delta E_T = 21{\cdot}6$	0·5	$2{\cdot}1 \times 10^3$
	0·3	98
	0·1	4·6
Benzene → nitrobenzene	1	200
$\Delta E_T = 7{\cdot}5$	0·5	14
	0·3	4·9
	0·1	1·7

[a] For $\beta = 210°$; $T = 298°$.

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