

The enormously higher rate of hydrolysis of BF_3O^{2-} (compared with the rate known for BF_4^-) is a consequence of both the inductive effect of the O atom and the increase of the negative charge of the anion being hydrolysed. Unfortunately our method could not be used to investigate the kinetics of the hydrolysis of BF_3O^{2-} at higher temperatures and the relative contributions of the reduced activation energy and increased activation entropy remain unknown.

Our data demonstrate that the communication of Ray and Mitra^{13,14}, who claim that salts containing the anion BF_3O^{2-} can be isolated by evaporating aqueous solutions, is erroneous; only the remark that the very sparingly soluble BaBF_3O and PbBF_3O are precipitated does not clearly contradict the properties of BF_3O^{2-} . The hydroxofluoro-complexes of germanium^{15,16}, arsenic¹⁷⁻¹⁹, and a number of other elements are known to undergo much faster alkaline hydrolysis than the corresponding fluoro-complexes. In all these cases the formation of conjugate bases probably plays a part.

The hypotheses that the high rate of hydrolysis of AsF_5OH^- is due to the migration of H from OH to F and the removal of HF¹⁸ or the insufficient screening of the As atom as a result of the asymmetric disposition of the ligands postulated by the authors¹⁹ have no physical justification. This can also be said about the attempt to account for the sharp differences in the rates of the alkaline hydrolysis of $\text{AsF}_4(\text{OH})_2^-$ and $\text{AsF}_4(\text{OCH}_3)_2^-$ by postulating¹⁷ that their hydrolysis is due to the addition of water molecules to the oxygen-containing ligand, which, according to these investigators, takes place to a greater extent in the first case.

SUMMARY

1. The kinetics of the alkaline hydrolysis of BF_3OH^- at 0°C have been investigated by measuring the variation of the specific conductance of the solutions with time. It has been shown that the equilibrium $\text{BF}_3\text{OH}^- + \text{OH}^- = \text{BF}_3\text{O}^{2-} + \text{H}_2\text{O}$ obtains in the solution with an equilibrium constant of 3130 ± 60 litre mole⁻¹; the pK value for the acid dissociation of BF_3OH^- at 0°C is 11.44.
2. The BF_3O^{2-} ion is hydrolysed by an S_N1 mechanism. The rate constant is $(2.00 \pm 0.04) \times 10^{-2}$ s⁻¹.
3. The rapid alkaline hydrolysis of the hydroxofluoro-complexes of germanium, arsenic, and a number of other elements can probably be accounted for by a similar mechanism. The reason for the sharp difference between the rates of the alkaline hydrolysis of the hydroxo- and fluoromethoxy-complexes of boron or arsenic may be that the conjugate base cannot form in the case of the fluoromethoxy-complexes.

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BRØNSTED'S RELATION AND THE PROPERTIES OF THE ACTIVATED COMPLEX

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Equations in the theory of rate processes usually contain the activity coefficient $\gamma^\ddagger$ of the activated complex. The present paper aims to show that this parameter of the transition state can be determined from the activity coefficients γ_i and γ_k of initial and final states if Brønsted's relation is used.

Brønsted's relation states that, for reactions of the same type, the variation in the standard free energy of activation $\Delta G^\ddagger$ is some fraction α (≤ 1) of the corresponding variation in the standard free energy of the elementary act in this reaction ΔG° :

$$\Delta \Delta G^\ddagger = \alpha \Delta \Delta G^\circ. \quad (1)$$

This relation is usually derived by the method of potential curves¹. The arguments underlying this proof are not completely rigorous, so that it is probably more correct to regard Brønsted's relation as semi-empirical. Equation (1) is satisfied quite strictly in some cases, e.g. the barrierless electrode processes which I have observed², for which the transition state is identical with the final state ($\alpha = 1$).

Let us consider the occurrence of a reaction firstly in an ideal solution (with all the $\gamma = 1$) and then in a real solution. These two cases can be regarded as two reactions of the same type but with somewhat different values of ΔG° , and we can apply Brønsted's relation to them. The variation in the standard free energy of the elementary act in the

process on passing from an ideal to a real solution is determined by the activity coefficients of initial and final substances:

$$\Delta\Delta G^\circ = RT \ln \Pi\gamma_k / \Pi\gamma_i. \quad (2)$$

Similarly for the variation in the free energy of activation

$$\Delta\Delta G^\# = RT \ln \gamma^\# / \Pi\gamma_i. \quad (3)$$

Substituting from Eqns. (2) and (3) for $\Delta\Delta G^\circ$ and $\Delta\Delta G^\#$ in the Brønsted relation (1), we obtain

$$\gamma^\# = \Pi\gamma_k^\alpha \Pi\gamma_i^\beta, \quad (4)$$

where $\beta = 1 - \alpha$.

I have obtained Eqn. (4) previously² for the cathodic evolution of hydrogen, but it was not strictly proved, being obtained by generalising the two self-evident limiting cases: if the process requires no activation energy, the activated state is identical with the initial state, and $\gamma^\# = \Pi\gamma_i$ (this follows from Eqn. (4), since in this case it is easy to show that $\alpha = 0$); if, however, activated and final states are identical (barrierfree process, $\alpha = 1$), we have $\gamma^\# = \Pi\gamma_k$. We shall show in the present paper that Eqn. (4) is a direct consequence of the Brønsted relation in the form (1).

It has already been remarked above that Brønsted's relation is usually derived by means of potential curves. However, this method leads directly not to Eqn. (1)[†] but to a link between the variations in internal energy

$$\Delta\Delta U^\# = \alpha\Delta\Delta U. \quad (5)$$

The transition from Eqn. (5) to (1) can be effected only provided that $\Delta S^\#$ does not vary or else that all variations in entropy are proportional to the corresponding heat effects,

$$\Delta\Delta S^\circ = m\Delta\Delta U, \quad \Delta\Delta S^\# = m\Delta\Delta U^\#. \quad (6)$$

It follows from Eqns. (5) and (6) that

$$\Delta\Delta G^\# = \alpha \frac{1-nT}{1-mT} \Delta\Delta G^\circ = \alpha' \Delta\Delta G^\circ. \quad (7)$$

With α , n , and m constant (or, more precisely, with α' constant) Eqn. (7) is identical with Eqn. (1).

A relation between the entropy and the energy of activation of the type of Eqn. (6) has been noted repeatedly (so-called compensation effects³). It is especially significant for us that in many cases Eqn. (6) is satisfied as a good approximation for the departure of the thermodynamic properties of solutions from ideality⁴. It can be strictly proved for solutions of electrolytes within the framework of the Debye-Hückel theory. Therefore the deduction of the expression for the activity coefficient of the activated complex given above can be regarded as soundly based.

Temkin was the first to suggest that a change from one temperature to another could be regarded as a change from one solution to another having a different activity coefficient⁵. It is evident from the above that this implies the hypothesis that the relation (1) is valid also for variations in $\Delta G^\#$ and ΔG° caused by variation in the temperature. Dividing $\Delta\Delta G$ by ΔT and passing to the limit as $\Delta T \rightarrow 0$, we obtain

$$\Delta S^\# = \alpha \Delta S^\circ. \quad (8)$$

Substituting $\Delta S^\# = S^\# - \Sigma S_i^\circ$ and $\Delta S^\circ = \Sigma S_k^\circ - \Sigma S_i^\circ$ yields

$$S^\# = \alpha \Sigma S_k^\circ + \beta \Sigma S_i^\circ \quad (9)$$

a relation which I have also used previously². However, the hypothesis that Eqn. (1) is applicable to temperature changes in ΔG , used in its deduction, seems too distant an extrapolation.

It appears more correct to use as starting point the relation

$$\Delta G^\# = \Delta G^{*\circ} + \alpha \Delta G^\circ \quad (10)$$

(where $\Delta G^{*\circ}$ is the free energy of activation when $\Delta G^\circ = 0$), which follows directly from Eqn. (1). Differentiating Eqn. (10) with respect to temperature and making appropriate substitutions for $\Delta S^\#$ and ΔS° , we obtain

$$S^\# = \alpha \Sigma S_k^\circ + \beta \Sigma S_i^\circ + \Delta S^{*\circ} - \frac{d\alpha}{dT} \Delta G^\circ \quad (11)$$

in which $\Delta S^{*\circ} = -d\Delta G^{*\circ}/dT$. No additional barrier is present when $\Delta G^\circ = 0$ with either barrierfree ($\alpha = 1$) or activationfree ($\alpha = 0$) processes, so that $\Delta G^{*\circ} = 0$ at all temperatures. Hence for these processes (for which α cannot depend on the temperature) we obtain from (11) Eqn. (9). The latter simplifies to $S^\# = \Sigma S_k^\circ$ when $\alpha = 1$, and to $S^\# = \Sigma S_i^\circ$ when $\alpha = 0$. These equations are self-evident, since the activated state coincides with the final state in the former case, and with the initial state in the second case.

In general, however, Eqn. (11) does not simplify to Eqn. (9), even on the assumption that α is independent of temperature. In terms of statistical thermodynamics, Eqn. (9) is equivalent to

$$F^\# = \Pi F_k^\alpha \Pi F_i^\beta, \quad (12)$$

where the F are the corresponding partition functions. It is easy to see that in general the product of translational and rotational partition functions for the activated complex does not conform to the relation (12), very considerable departures being possible, so that Eqn. (9) is not satisfied for reactions in the gas phase. But approximate observance of Eqn. (12) is probably entirely possible for vibrational, including intermolecular, degrees of freedom. It may therefore be supposed that Eqn. (9) can be used in several cases to estimate the entropy of the activated complex for reactions in condensed phases.

SUMMARY

The properties of the activated complex are discussed for reactions obeying Brønsted's relation. It is shown that the activity coefficient $\gamma^\#$ of the activated complex is linked in this case with the activity coefficients γ_i and γ_k of starting materials and reaction products by the relation $\gamma^\# = \Pi\gamma_k^\alpha \Pi\gamma_i^\beta$, where $0 \leq \alpha \leq 1$ is the transfer coefficient (the coefficient in Brønsted's relation) and $\beta = 1 - \alpha$. In some cases Eqn. (9) may also hold.

[†] Brønsted's empirical rule links rate constants with equilibrium constants: i.e. it corresponds to Eqn. (1).

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DEPENDENCE OF SELECTIVITY ON STRUCTURE OF SOLVENTS AND OF COMPONENTS TO BE SEPARATED. I. APPLICABILITY OF HAMMETT'S EQUATION TO THE ESTIMATION OF THE SELECTIVITY OF AROMATIC SOLVENTS

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Dipole moments have been shown¹⁻³ to be inadequate as measures of the selective action of solvents. The selectivity of solvents can be approximately assessed by means of their dielectric constants³, but this attempt at correlation also cannot be accepted as satisfactory. Correlation equations have been obtained⁴⁻⁶ enabling activity coefficients to be calculated for various members of a homologous series from a few experimental data, but these equations are unreliable⁷ in the case of multifunctional solvents.

The selectivity of a solvent is made up of physical and chemical components. Anderson and his coworkers^{8,9} have suggested an equation for calculating the physical component of selectivity, but it uses a homomorphous method¹⁰, which makes the equation approximate in character.

In the present paper an attempt is made to isolate the chemical component of the selectivity of aromatic solvents, and to correlate it with the Hammett constants. Owing to the difficulty of allowing for physical effects, it was not possible to estimate the chemical component of selectivity from the difference between the overall selectivity and its physical component. However, Anderson's equation shows that the polar physical effect can be eliminated by choosing for the separation pairs of components having equal collision volumes (or with equal molar volumes).

As an example close to this ideal case, we have investigated the selectivity of aromatic solvents towards the cyclohexane-toluene system (difference in molar volume $v_{\text{chx}} - v_{\text{tol}} = 2.7 \text{ cm}^3$ at 65°C). A parallel examination was made, for comparison, of the corresponding solvent-n-hexane-benzene systems, for which the polar physical effect could not be neglected owing to the considerable difference between the molar volumes of n-hexane and of benzene: $v_{\text{hex}} - v_{\text{bz}} = 47 \text{ cm}^3$ at 65°C . The measure of selectivity used was the logarithm of the ratio of the limiting activity coefficients for the hydrocarbons to be separated.

EXPERIMENTAL

Gas-liquid chromatography¹²⁻¹⁴ was used to determine the activity coefficients of cyclohexane, toluene, n-hexane, and benzene at infinite dilution in the aromatic solvents at

TABLE 1.

Solvent	M.p., °C	Solvent	M.p., °C
Nitromesitylene	44.0	<i>o</i> -Nitrophenol	43.5
Acetophenone	185	<i>o</i> -Chloronitrobenzene	31.5
<i>o</i> -Anisidine	4.6	<i>m</i> -Phenylenediamine	62.0
<i>p</i> -Nitrotoluene	51.0	2,4-Dinitrotoluene	70.0
Nitrobenzene	5.6	Chloro-2,4-dinitrobenzene	52.0
<i>m</i> -Nitroanisole	37.5	Ethyl-2,4,6-trinitrobenzene	38.0

65° and 80°C . The melting points of the solvents (Table 1) were close to published values¹¹. Aniline ($d_4^{20} = 1.0212$ and $n_D^{20} = 1.5851$) and *o*-nitrotoluene (1.1627 and 1.5470) were also investigated as solvents. All the solvents were applied, to the extent of 20 mass %, to the solid carrier INZ-600. The columns used were U-tubes of length 150 cm and internal diameter 5 mm. The temperature of the column was maintained constant to $\pm 0.25^\circ\text{C}$.

Helium was used as carrier gas. Its pressure measured with mercury manometers was 1100–1200 mmHg at the entrance to the column, and the barometric pressure at the outlet. Under these conditions the rates of flow, determined by means of soap-film meters, were 2.5–3.6 litres h^{-1} . The maximum quantity of hydrocarbon introduced into the column was 1 mg.

The ratio of the activity coefficients of the two components was determined from the relation¹²⁻¹⁴

$$\frac{\gamma_1}{\gamma_2} = \frac{p_1^0 v_1^0}{p_2^0 v_2^0} \quad (1)$$

where p_1^0 and p_2^0 are the vapour pressures of the components at the experimental temperature, and v_1^0 and v_2^0 the specific retention volumes of the components in the given solvent. With the rate of flow of the carrier gas, the quantity of solvent in the column, and the temperature all constant, the ratio of the specific retention volumes can be replaced by the relative retention time.

DISCUSSION

To correlate the selectivities of the solvents use was made of the Hammett constants of the corresponding substituents¹⁵.

The position in the aromatic ring, with respect to which the absolute sum of the Hammett constants was a maximum, was arbitrarily regarded as the reaction centre for each of the solvents. This arbitrary approach permitted the selectivities of all the solvents investigated, containing not only electrophilic but also nucleophilic substituents, to be correlated in one equation (in the case of the solvent-cyclohexane-toluene systems).

The possibility of using the absolute sum of the Hammett constants for solvents having nucleophilic substituents is probably due to the fact that the higher the electron density at the arbitrary reaction centre, i.e. the higher is $(\Sigma\sigma)_{\text{max}}$, the lower it is at the true reaction centre. Thus the maximum electron density on one of the carbon atoms in the aniline molecule indirectly characterises the magnitude of the positive charge at the true reaction centre—on the amino-nitrogen atom.

Application of the method of least squares to the results obtained at 65°C yields the following correlation equation (correlation coefficient $r = 0.98$).

$$\lg \frac{\gamma_{\text{chx}}^0}{\gamma_{\text{tol}}^0} = 0.210 \left| \Sigma\sigma \right|_{\text{max}} + 0.238 \quad (2)$$