Solvent Participation in Nucleophilic Displacement Reactions. Part I. General Considerations.

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Attention is drawn to the inadequacy of the Born–Kirkwood theory of solvation as applied to reactions with polar transition states. The close similarity between the solvation of inorganic ions and organic transition states is discussed in terms of specific solvation. This leads to the conclusion that the solvation energy of the anion is generally much greater than that of the cation in agreement with the strong electrophilic catalysis observed in ionisation reactions.

The significance of activation entropy in liquid mixtures is discussed in terms of specific solvation, and under some conditions the entropy is shown to be related to the composition of the mixture. The influence of covalent-bond formation on the extent of solvent participation is briefly discussed.

ALTHOUGH the effect of structural changes on the rate of reactions leading to pseudo-ionic (or ionic) transition states has been studied extensively, the influence of changes of solvent has received comparatively little attention owing largely to the unsatisfactory state of theoretical knowledge of liquid structure. This is particularly serious as it is becoming increasingly evident that mechanism and environment are closely correlated. However, the prevalent theories of organic substitution reactions are largely empirical, and hence by analogy one might expect that semi-empirical treatments of solvent effects would be the most rewarding at present.

The experimental work described in the following papers was undertaken with this in mind, and the following discussion gives a brief critical survey of the present position.

The Born-Kirkwood Treatment.—The effect of changing the solvent on the rate of reaction involving a polar transition state has usually been investigated by considering the corresponding changes in the free energy of activation (see Glasstone, Laidler, and Eyring, " Theory of Rate Processes," New York, 1941, Chapter 8). If this is referred to a standard reference state, *e.g.*, the vapour phase, the general rate equation shows that

$$\log k = \log k_0 - \Delta F^*/\boldsymbol{R}T$$

where ΔF^* is the free-energy change on transferring the reacting system from vacuum to the medium under consideration. If long-range electrostatic forces only are considered, ΔF^* is given by the appropriate Born charging energy (Born, *Z. Physik*, 1920, **1**, 45), and hence it follows that

$$\log k = \log k^\circ - \mathrm{f}(D,r_a,r_b,r^*)$$

where D is the dielectric constant of the medium, and r_a,r_b, and r^* are the effective radii of reactants and transition state respectively.

This type of equation does not hold in media of low polarity owing to the failure of the necessary condition $\mu^2/DkTr^3 \ll 1$ (Bell, *Trans. Faraday Soc.*, 1935, **31**, 1557), and has therefore in general been applied to kinetic data in highly polar media (see Glasstone, Laidler, and Eyring, *op. cit.*).

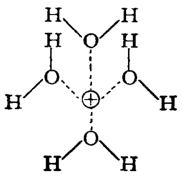
Any equation of this type requires the rate to be an increasing function of dielectric constant for reactions between neutral molecules, the transition-state structure being assumed to remain constant. Examination of the available data, however, shows a complete lack of correlation between these two quantities (*e.g.*, see Moelwyn-Hughes, " Kinetics of Reaction in Solution," Oxford, 1947; Le Fèvre and Northcott, *J.*, 1949, 944; Brown and Hudson, *J.*, 1953, 3352), and in many cases increases in dielectric constant lead to considerable decreases in reaction velocity, irrespective of the nature of the reaction (*e.g.*, whether it is an S_N1 or an S_N2 process). For example, Norris and Haines (*J. Amer. Chem. Soc.*, 1953, **75**, 1425) found that the rate of alcoholysis in 1M-alcohol solution is approximately constant in a large number of solvents (particularly if non-polar solvents are excluded). Fairclough and Hinshelwood have given several examples of unequal rates in isodielectric media (*J.*, 1937, 538).

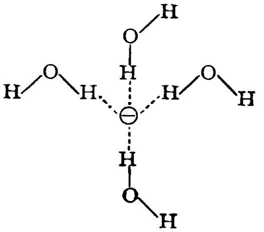
The cases where *k* is related quantitatively to *D* usually involve regular changes in a particular solvent mixture such that the concentration of the more polar constituent (and hence *D*) is varied. On the other hand, examples are known where such a regular change increases *k* but decreases *D* (Gelles, Hughes, and Ingold, *J.*, 1954, 2918). The rate is frequently determined fairly closely by the concentration of the more polar constituent; thus, Hudson and Brown (*J.*, 1953, 883) found the rate of hydrolysis of several acid chlorides to be almost equal in 95% aqueous acetone (v/v) and 95% aqueous dioxan in spite of the considerable difference in dielectric constant and similar conclusions may be drawn from the recent results of Cropper, Olsen, and Spieth (*J. Amer. Chem. Soc.*, 1954, **76**, 6248) for an ionisation reaction. However, the rate of reaction of *p*-nitrobenzoyl chloride in 5% aqueous formic acid (which has a very high value of *D and* solvating power—see p. 4116) is considerably less than in these solvents (Crunden and Hudson, unpublished work). This is attributed to the increased bond energy between water and formic acid, compared with the bond energy between hydroxyl groups and ketones, ethers, alcohols, etc. (see Davies, *Ann. Reports*, 1946, **43**, 15).

These examples are sufficient to show that the rates of reactions of this kind are determined primarily by specific solute–solvent interactions, and consequently the influence of long-range electrostatic forces is only a secondary factor. This has long been recognised in equilibrium processes, by attempted calculations of internal dielectric constants (*e.g.*, Debye, *Z. phys. Chem.*, 1927, **130**, 56; Webb, *J. Amer. Chem. Soc.*, 1926, **48**, 2589; Kirkwood, *J. Chem. Phys.*, 1939, **7**, 911; Oster and Kirkwood, *ibid.*, 1943, **11**, 175; Oster, *J. Amer. Chem. Soc.*, 1946, **68**, 2036), but in general the resulting expressions are too complex to be applied to kinetic data.

The Bernal–Fowler Method.—The effect of solvent on the rate of organic reactions raises essentially the same problems as in the solvation of inorganic ions, which has been treated fairly satisfactorily by Bernal and Fowler (*J. Chem. Phys.*, 1933, **1**, 515). This treatment leads to the important conclusion that the inner shell of solvent molecules determines most of the energy and entropy changes. Thus the Born charging energy contributes only about 30% of the heat and about 10% of the entropy of solvation of simple ions (Eley and Evans, *Trans. Faraday Soc.*, 1938, **34**, 1093). As shown later, the latter value is of the greatest significance in solvolytic reactions. It is convenient therefore to distinguish between the two types of interaction, termed interaction and environmental energy by Banks (*ibid.*, 1937, **33**, 215). This "freezing" of water molecules around the central ion has been discussed in considerable detail by Frank (*J. Chem. Phys.*, 1945, **13**, 793).

Complete theoretical estimations of the thermodynamic functions have been made only for simple salts in water, usually by the Bernal–Fowler method (*loc. cit.*), but it is of interest to consider solvation in aqueous mixtures in this way. According to this treatment, the water and ice structures are taken to be given by a tetrahedral arrangement of molecules around each central molecule. The heat of solvation is calculated by assuming this assembly to be removed to the gas phase, the central molecule replaced by an ion and returned to the liquid phase, and the four remaining molecules reorientating to the position of minimum energy:





Finally, the hydrated ion is returned to the liquid phase, and the enthalpy of Born charging taken into account. In calculating the interaction energy between the ion and the nearest solvent molecules the coulombic energy between the ion and each formal charge on the dipole was considered, as the usual ion–dipole relation cannot hold over such short distances. This leads to some uncertainty in the calculations, but the absolute magnitude of such charges is not important in the present discussion.

Entropies of solvation can be calculated by using the Sackur–Tetrode equation giving the standard gas entropy, then by assuming that all translational entropy is momentarily lost, the loss in entropy associated with the formation of the inner co-ordination shell is obtained. The resulting hydrated ion is finally allowed to move through the free volume of the liquid, thus creating entropy.

Partition functions for radial motion of n water molecules vibrating (1) in the field of a water molecule and (2) in the field of an ion are assumed to take the form $\phi = \boldsymbol{h}\nu/\boldsymbol{k}T$ per vibrator, where ν is the vibration frequency calculated from a likely value of the force field f of the quasi-harmonic vibration $\nu = \frac{1}{2\pi} \cdot \left(\frac{f}{\mu}\right)^{\frac{1}{2}}$ where μ is the reduced mass. Similar partition functions may be calculated to allow for lateral movement of water molecules on the surface of the ion, and for restricted rotation (libration) of the dipoles in symmetrical force fields associated with water on the one hand and with the ion on the other. The entropy contributed by the more distant water molecules is given by the standard thermodynamic relation $\Delta S = (\partial \Delta F/\partial T)_p$, where ΔF is the free energy of Born charging (see Pearson, *J. Chem. Phys.*, 1952, **20**, 1478).

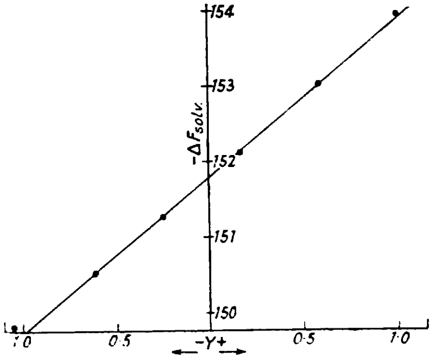
This type of treatment may in principle be extended to ionic reactions, as there is considerable evidence to show that solvent influences are similar to the solvation of inorganic ions. Thus the free energy of ionisation of alkyl halides in the gas phase is of the same order of magnitude as the compensating free energy of solution of inorganic salts in aqueous media (Evans, *Trans. Faraday Soc.*, 1946, **42**, 719). By taking into account the radius of the cation, which is normally inversely proportional to the solvation energy (Latimer, Pitzer, and Slansky, *J. Chem. Phys.*, 1939, **7**, 108), rates of solvolysis can be estimated approximately by assuming the transition state of the ionisation reaction to be in the form of an ion-pair (Franklin, *Trans. Faraday Soc.*, 1952, **48**, 443). Moreover, the change in rate on changing from water to methanol is given closely by the corresponding change in free energy of solvation of inorganic ions of similar dimensions (Brown and Hudson, *loc. cit.*).

This close similarity can be demonstrated by applying Grunwald and Winstein's empirical equation (*J. Amer. Chem. Soc.*, 1948, **70**, 846) relating the rate of S_N1 solvolysis to solvating power, Y, as evaluated from experimental data on a "calibration" reaction, to the solvation of inorganic ions. This equation takes the form $\log k_1 = \log k^\circ + mY$, where m is a specific constant for each reaction, unity in the case of the "calibration" reaction. Comparison with the general rate equation shows that

$$-(\Delta F_1 - \Delta F_2) = 2{\cdot}3\boldsymbol{R}Tm\ (Y_1 - Y_2)$$

The changes in the parameters of Grunwald and Winstein's equation may therefore be identified with the differences in free energy of ionic solvation in different media.

This linear relation holds for the solvation energy of salts in alcohol–water mixtures (Latimer and Slansky, *ibid.*, 1940, **62**, 2020), Y values determined experimentally from rate measurements (see Fig.) being used. The value of m for potassium chloride is 1·505 compared with 1·00 for *tert.*-butyl chloride. This difference may be attributed to the difference in size of the K^+ and Bu^{t+} ions, or to internal assistance to ionisation in the case of the organic halide. This comparison indicates that the energy of ionisation of a covalent molecule is given by the same type of solvation forces as are involved in the solvation of inorganic ions. Further support for this view may be obtained by comparison of changes in energies of activation of ionisation reactions as the medium changes with the corresponding changes in the heats of solvation of inorganic ions (Askew, Bullock, Smith, Tinkler, Gatty, and Wolfenden, *J.*, 1934, 1368). For simple salts $-\Delta H$ in alcohols is slightly greater than in water (see Table), which is probably due to an increase in solvation energy of the cation * as a result of the electron release R ⟶ OH. As the size of the cation increases, however, this order is reversed (see Table). The solvation energy of the halide ion thus becomes more important than that of the cation, as solvation energy is inversely proportional to size (Latimer *et al.*, *loc. cit.*). Similarly, an increase in the size of the anion from chloride to bromide increases the relative importance of the cation solvation energy, with a corresponding increase in the solvation energy in alcohol relative to that in water. In further agreement with this explanation it is observed that the effect is more pronounced in ethanol than in methanol both for small and for large cations. The activation energy for the solvolysis of the *tert.*-butyl halides changes in a similar way to the heat of solvation of tetramethylammonium halides, in agreement with the general explanation. It is well known that carbonium ions are much more readily formed in acidic solvents, *e.g.*, carboxylic acids and phenol, than in basic solvents, *e.g.*, ethers and tertiary amines (see Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1955, **51**, 481) which supports the conclusion that ionisation is produced largely by electrophilic action.



" *Solvating power* " (Y) *plotted against free energy of ionic solvation* ($-\Delta F_{solv.}$) *for* K^+Cl^- *in methanol–water at 25°.*

Change in heat of solvation ($-\Delta H$) *on change of solvent.*

	$H_2O \longrightarrow MeOH$	$H_2O \longrightarrow EtOH$
LiCl	+3·8	+4·3
NaCl	+3·5	—
KCl	+2·9	—
NMe_4Cl	−2·06	−2·40
NEt_4Cl	−3·92	−4·75
NEt_4Br	−2·78	−3·66
Bu^tCl *	−2·10	−3·10
Bu^tBr *	—	−2·20

* From activation energy on the assumption that the change is due to the change in solvation energy only.

Bernal–Fowler Theory applied to Mixtures.—In many liquid mixtures, the activation energy is found to be relatively insensitive to changes in composition (see, *e.g.*, data compiled

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* The direction of this change is in agreement with the predictions of Born's treatment.

by Grunwald and Winstein, *loc. cit.*). This may be attributed to the specific nature of the solvation (by the more polar constituent), subject to the following conditions: (*a*) No change in transition-state structure (Brown and Hudson, *loc. cit.*). (*b*) The energy of association between solvent molecules A and B is approximately equal to that between 2A molecules (where A is the more polar). This condition may be satisfied in solvolysis where hydrogen-bonding liquids are employed, as hydrogen-bond energies in alcohols, ketones, ethers, and water are probably very similar (see Davies, *loc. cit.*).

In media of this kind, therefore, the rate is determined largely by entropy changes (a fact which is not always recognised). The solvent effect may therefore be calculated in principle by assuming that the ions are solvated specifically by the co-ordination * of n (hydroxylic) molecules, and estimating the entropy differences as the solvent composition changes. As the entropy change on co-ordinating n water (or alcohol) molecules from some standard condition in the gas phase on to the transition state may be taken to be almost independent of the solvent composition, the change in entropy on change of solvent will be related to the entropy of the solvating component in the mixture.

For kinetic purposes the free-volume theory of liquids seems to be the most suitable for estimating the entropy. The entropy of a molecule undergoing classically excited motions is calculated on the basis that its equivalent translational movement in a volume v_x accessible to the centre of gravity of the molecule completely determines entropies of phase change. It is appreciated that, in a refined treatment, fluctuation factors to allow for variation of cell size with temperature, communal entropy, etc., should be considered, but some idea of the significance of activation entropy in terms of specific solvation may be obtained from the following simplified approach.

Consider the partition function Q_x for a water molecule in a solvent containing x mols. of water and $(1 - x)$ mols. of inert solvent. Q_x may be factorised into Q_{ix} and $v_f(2\pi m_x \boldsymbol{k}T/\boldsymbol{h}^2)^{3/2}$ where Q_{ix} is the partition function of x due to molecular vibrations, librations, etc., and is approximately independent of environment of the water, and the other factor is the partition function due to translational motion in three degrees of freedom within the free-volume box v_f. Since

$$Q_x = Q_{ix} v_f (2\pi m_x \boldsymbol{k}T/\boldsymbol{h}^2)^{3/2} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

and

$$S = \partial(\boldsymbol{R}T \ln Q)/\partial T \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$S = \boldsymbol{R}[\ln Q_{ix}(2\pi m_x \boldsymbol{k}T/\boldsymbol{h}^2)^{3/2} + T\partial(\ln Q_{ix} \cdot 2\pi m_x \boldsymbol{k}T/\boldsymbol{h}^2)^{3/2}/\partial T + \ln v_f + T\partial \ln v_f/\partial T] \quad (3)$$

Eqn. (3) can be simplified at constant temperature to

$$S = \boldsymbol{R}(a + \ln \gamma\, v_f) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3a)$$

where γ is used to absorb into v_f the effect of the last term in (3). If v_{fx} is the free volume of water and $v_{f(1-x)}$ that of the other component of the binary liquid mixture, then the total free volume of the solution can be represented (Eyring, Hirschfelder, and Stevenson, *J. Chem. Phys.*, 1937, **5**, 896) by

$$v_f = v_{fx}^{x}\, v_{f(1-x)}^{(1-x)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

The free volume per water molecule is therefore,

$$v_f/x_v = \{v_{fx}^{x} v_{f(1-x)}^{(1-x)}\}/x_v \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

From (3*a*) the entropy of water in the binary solvent is given by

$$S = \boldsymbol{R}[a + \ln \gamma + x \ln v_{fx} + (1 - x) \ln v_{f(1-x)} - \ln x_v] \quad . \; . \; . \quad (6)$$

It follows from this equation that the volume composition is related stoicheiometrically to the entropy, *i.e.*,

$$\frac{\partial(\Delta S)}{\partial x_v} = \frac{\boldsymbol{R} \ln v_{fx}}{v_{f(1-x)}} \cdot \frac{\partial x}{\partial x_v} - \frac{\boldsymbol{R}}{x_v}$$

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* This term is used to denote the operation of short-range electrostatic forces, and not necessarily the formation of dative bonds.

where x_v is the volume fraction of water. If the free volumes of water and the other component are not too different, (6) reduces to the simple relation

$$S = \boldsymbol{R}(\text{const.} - \ln x_r) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If we assume that n water molecules co-ordinate around an ion or ion-pair, the entropy change on solvating an ion from a liquid having a volume fraction of x_v is

$$\begin{aligned} \Delta S &= n(-\Delta S_1 + S) \\ &= n(-\Delta S_1 + \text{const.} - \boldsymbol{R} \ln x_r) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8) \end{aligned}$$

where ΔS_1 is the entropy change of solvating an ion with one water molecule from standard conditions in the gas phase.

According to the absolute rate equation,

$$k_0 = (\boldsymbol{k}T/\boldsymbol{h}) \exp(\Delta S^*/\boldsymbol{R}) \exp(-\Delta H^*/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad (9)$$

where ΔH^* and ΔS^* are the heat and entropy of activation. The entropy of the gaseous transition state will be reduced by an amount given in equation (8) on undergoing solvation; *i.e.*,

$$\begin{aligned} \Delta S^* &= \Delta S_g{}^* - n(-\Delta S_1 + \text{const.} - \boldsymbol{R} \ln x_r) \\ &= \text{constant} + n\boldsymbol{R} \ln x_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10) \end{aligned}$$

thus from equation (9),

$$2{\cdot}3 \log_{10}k_0 = 2{\cdot}3 \log_{10} [(\boldsymbol{k}T/\boldsymbol{h}) \exp(-\Delta H/\boldsymbol{R}T)] + \Delta S^*/\boldsymbol{R} \quad . \quad . \quad (11)$$

Substituting (10) into (11), we have

$$\log_{10} k_0 = 2{\cdot}3 \log_{10} \text{const.} + n \log_{10} x_r \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

This treatment shows that the entropy of solvation, and hence the reaction rate, are related simply to the volume composition of the liquid mixture under certain conditions. Such a relation will hold most satisfactorily when the two components of the mixture differ considerably in solvating power, but also requires random distribution of the two kinds of solvent molecule. The first requirement is readily satisfied in most liquid mixtures, but the distribution of the molecules in a solvent is a complex function of interaction energies, molecular size, and free volume. As already pointed out, however, strong hydrogen-bonding between the two components of a mixture will tend to distribute the molecules at random.

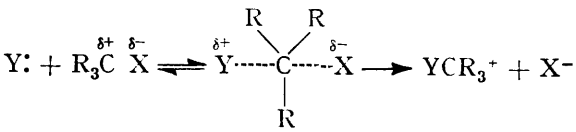
A relation of this kind has been found to hold over a fairly wide concentration range in acetone–water mixtures for several ionisation reactions (Brown and Hudson, *loc. cit.*). Olsen and Cropper (*loc. cit.*) have adduced a relation between the velocity of ionisation reactions and mole-fraction of water over a wide range of solvent composition. In these cases n is roughly constant ($n = 4{\cdot}0$—$4{\cdot}7$), which again may be explained by the greater solvation energy of the halide ion (see p. 4117) than of that of the cation.

It follows from the above discussion that reactions involving ionisation will in general occur in the electrostatic field of a specific number of molecules (which may of course vary with the solvent composition), and hence the order of reaction with respect to molecules of a particular kind will be related closely to the kinetic order of the solvation process, *i.e.*, to the number of molecules of a certain species participating in the solvation of the transition state. This will be investigated further by analysing the experimental data recorded in Parts II and III (following papers).

Influence of Covalent-bond Formation.—So far the discussion has been concentrated on reactions which proceed by a rate-determining ionisation process (S_N1 type). It is of interest to apply the above principles to reactions in which the rate is determined partly by bond formation between the two reactants (S_N2 type). Again, solvation is necessary to reduce the activation energy to permissible values, but the effect of solvent changes on rate is generally smaller than in the case of an ionisation reaction, at least under solvolytic conditions (Dostrovsky, Hughes, and Ingold, *J.*, 1946, 167). This is a consequence of the different driving forces in the two cases, as may be shown by the following simple argument. In the case of an S_N1 ionisation, a considerable increase in C–X polarity is essential in order to reach the potential-energy maximum, as the process is fundamentally a single-bond stretching with simultaneous charge transfer. Ingold and Hughes have assumed a transition state structure corresponding to " half ionisation," and a bond extension of *ca.* 0·1 Å. Approximate calculations of the activation energy, however, indicate that the transition state resembles the final state closely (Evans, *loc. cit.*; Franklin, *loc. cit.*), and it seems likely that the transition state resembles an " intimate ion-pair " (Winstein *et al.*, *Chem. and Ind.*, 1954, 664). The process may then be represented as follows:

$$R_3\overset{\delta+}{C}\cdot\ \overset{\delta-}{X} \rightleftharpoons R_3\overset{\Delta+}{C}\cdot\ \overset{\Delta-}{X} \rightleftharpoons R_3C^+X^-$$

In the case of an S_N2 process, however, an increase in charge is not *essential* in the formation of the transition state, since a transfer of electrons from substituting atom Y to the carbon atom causes a weakening of the C–X bond:



$$Y\colon + R_3\overset{\delta+}{C}\ \overset{\delta-}{X} \rightleftharpoons \overset{\delta+}{Y}\cdots\cdots \underset{R}{\overset{R\ \ R}{C}}\cdots\cdots\overset{\delta-}{X} \longrightarrow YCR_3^+ + X^-$$

If the C–X bond is weak, the transition-state structure may resemble that given in the above equation, but in general, further charge separation occurs. In this case, the additional energy required for the further stretching of the C–X bond is given largely by the increasing Y–C bond energy, and consequently the contribution of solvation energy will be considerably less than in a direct ionisation. This argument depends on a close correlation between the extent of bond stretching and electron transfer to X, and is similar to that of Marshall and Winstein (*J. Amer. Chem. Soc.*, 1952, **74**, 1120) who describe the transition state as a mixture of the canonical structures:

$$\underset{\text{(I)}}{Y\colon\ RX} \qquad \underset{\text{(II)}}{\overset{+}{Y}\colon R\ \overset{-}{X}} \qquad \underset{\text{(III)}}{Y\colon\ \overset{+}{R}\ \overset{-}{X}}$$

The gradual change from an S_N1 to an S_N2 process may be regarded as a gradual decrease in the contribution of structure (III). Quite recently, Hammond (*ibid.*, 1955, **77**, 334) has discussed in some detail the generalisation that the transition state of an ionisation reaction resembles that of the products, whereas that of an S_N2 process will tend to resemble the reactants more closely.

If the Born–Kirkwood treatment is applied to reactions with these two kinds of transition states, it readily follows that the solvent effect is greater for the S_N1 process. Suppose the charges εe are localised at particular positive and negative poles in the system, and reaction involves the same charge increases in the two cases. Then the magnitude of the solvent effect for a given change in D will be given by $\sum(\varepsilon^2e^2/r)$. The radius of the transition state, r, is greater for the S_N2 than for the S_N1 process (if the charge is supposed to be localised along the C–X bond in this case), and moreover the sum term includes an additional term for the nucleophilic reagent in the case of the S_N2 reaction. Consequently $\sum(\varepsilon^2e^2/r)$ and hence the solvent effect are greater for the S_N1 process. This interpretation is analogous to the view of Hughes and Ingold (*J.*, 1935, 252; Cooper, Dhar, Hughes, Ingold, Macnulty, and Woolf, *J.*, 1948, 2043) that the charge is more dispersed in an S_N2 transition state, thus leading to reduced solvent interaction.

As already shown, however, the solvation energy calculated by the Born–Kirkwood treatment is only a fraction of the total interaction energy. The short-range interactions of the nearest solvent molecules with the two poles of the dipole provide the greater part of the interaction energy whether dipoles (see Le Fèvre and Northcott, *loc. cit.*) or ions are under consideration. Accordingly, the greater solvent effect usually observed in S_N1 reactions is more probably due to the greater formal charges in the transition state, and in particular, for the reasons already discussed, to the magnitude of the negative charge on the halogen atom. This view, as already mentioned, requires the assumption that the charge remains in the C–X bond in an ionisation reaction. Although the position of the negative charge in the reactant and transition state is known, the position of the positive charge in either system is uncertain. Thus the stability of the carbonium ion is attributed to conjugation involving the participation of a large number of canonical structures (Baughan, Evans, and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 385; Butler and Polanyi, *ibid.*, 1943, **39**, 19). This necessarily requires considerable delocalisation of the charge in the positive radical. On the other hand, the positive charge in the corresponding S_N2 process is likely to be shared between atoms Y and C, and hence may be more localised :

$$\overbrace{\mathrm{Y}\text{---}\mathrm{C}}^{\delta+}\text{---}\overset{\delta-}{\mathrm{X}}$$

We conclude, therefore, that the greater solvent effect in an S_N1 process is due primarily to the greater negative charge on the leaving group, thus resulting in the specific interaction of a greater number of electrophilic solvent molecules in the transition state. This will be reflected in the kinetic order of the reaction under suitable conditions, and this relation is investigated in some detail in the following papers.

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