677. *The Interpretation of the Energies of Activation of some Reactions of Aromatic Nitro-compounds.*

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The factors influencing the energy of activation of bimolecular reactions in solution are reviewed, with special attention to the energy required for the reorganisation of solvent molecules. The conclusions are applied to the interpretation of the energies of activation of the reactions of ethoxide ion with various aromatic nitro-compounds; these reactions include proton-transfer, complex-formation, and addition-compound formation. It is concluded that the energy required to reorganise solvent molecules is considerable, and may account for the greater part of the observed activation energy, not only for complex-formation but for proton-transfer.

IN earlier papers the kinetics and mechanisms of the various reactions of ethoxide ion with a series of related aromatic trinitro-compounds have been considered.[1-4] These nitro-compounds are 2,4,6-trinitrotoluene (T.N.T.), 2,4,6-trinitroanisole (T.N.A.), and 1,3,5-trinitrobenzene (T.N.B.). The solvent was ethanol plus 1% of toluene by weight. The reactions, and the values found for the Arrhenius and other parameters, are summarised in Table 1. Most of the reactions are reversible; E_1 and A_1 denote the energy of activation and A-factor for the forward reaction, while E_{-1} and A_{-1} refer to the reverse reaction.

TABLE 1.

Reaction of ethoxide ion with	Mechanism	E_1 (kcal. mole^{-1})	$\log_{10} A_1$ (l. mole sec.$^{-1}$)	E_{-1} (kcal. mole^{-1})	$\log_{10} A_{-1}$ (sec.$^{-1}$)	ΔH (kcal. mole^{-1})	$\Delta S°$ (cal. deg.$^{-1}$ mole^{-1})
(*a*) T.N.T., " slow "	Proton-transfer	13·6	12·0	$10{\cdot}_0$	6·1	3·6	27
(*b*) T.N.A., " fast "	Complex-formation	10·4	10·7	13·7	12·3	—3·3	—8
(*c*) T.N.B.	Complex-formation?	11·7	13·3	11·4	9·9	0·3	16
(*d*) T.N.T., " fast "	Complex-formation?	12·4	12·3	$8{\cdot}_2$	$7{\cdot}_4$	4	22
(*e*) T.N.A., " slow "	Addition-compound formation	13·1	10·9	—	—	—	—

The mechanisms assigned in Table 1 are established most firmly for reactions (*a*), (*b*), and (*e*). In favour of the proton-transfer mechanism for reaction (*a*) is the evidence of the Brønsted relation for the reverse reaction with various acids.[1] In favour of the addition-compound mechanism for reaction (*e*) is the evidence that identical products are obtained from the reactions of ethoxide ion with trinitroanisole and that of methoxide ion with trinitrophenetole.[2] The view that the product of reaction (*b*) is some kind of complex (whether a charge-transfer complex or an ion-dipole complex) is the most obvious interpretation of the fact that the reaction occurs in the same mixture as reaction (*e*) but very much faster.[2] Reactions (*b*) and (*c*) are regarded as complex-formations [3,4] though the evidence does not exclude the formation of addition compounds as in reaction (*e*).[5]

All the values of $\log_{10}A_1$ lie in the range 10·7 to 13·3 when A_1 is in l. mole^{-1} sec.$^{-1}$. That some of these values are greater than the usual value of about 11·5 for ion-dipole reactions can be understood in general terms, since the charge which is originally mainly on the oxygen of the ethoxide ion will become distributed in the transition state, so that partial desolvation will occur and lead to a positive contribution to the entropy of activation.

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[1] Caldin and Long, *Proc. Roy. Soc.*, 1955, *A*, **228**, 263.
[2] Ainscough and Caldin, *J.*, 1956, 2528.
[3] Ainscough and Caldin, *J.*, 1956, 2540.
[4] Ainscough and Caldin, *J.*, 1956, 2546.
[5] Foster, *Nature*, 1959, **183**, 1042.

The considerable positive values of ΔS^0 for several of the reactions are in accord with this explanation.

The values found for the Arrhenius energy of activation E_1 all lie in the range 10·4 to 13·6 kcal. mole^{-1}. Since they refer to reactions of three different mechanisms, involving closely similar molecules, they give rise to some interesting comparisons. These must be prefaced by some general considerations about energies of activation.

Energies of Activation of Bimolecular Reactions in Solution.—Four different factors can contribute to the energy of activation E of a bimolecular reaction in solution: (i) The stretching of bonds in the reacting molecules, and the incipient formation of new bonds. (ii) Repulsion between unbonded atoms on close approach. (iii) Electrostatic interactions between the reactant molecules (ion-ion, ion-dipole, or dipole-dipole). (iv) Reorganisation of solvent molecules, first to allow the reactant molecules to come together, and then to form the solvated transition state. These factors have long been recognised;[6,7] their relative contributions, however, are still unknown for most reactions, and will probably depend markedly on the reaction. The present results call attention to factor (iv). Evidence on the contributions of these four factors may be briefly recalled.

(i) *Energies of bonds broken and formed in the reactant molecules.* That the breaking and making of covalent bonds in the reactant molecules is the main factor influencing E in many reactions has been commonly assumed on the basis of general chemical experience, supported by the moderate success of the London–Eyring–Polanyi method of calculating E for simple gas reactions. Experimental support is forthcoming from results on gas reactions of two classes: unimolecular reactions, for which E shows approximate agreement with independently-determined values of the dissociation energy D of the relevant bond; and radical reactions, which show a correlation between E and ΔH, so that Semenov has made extensive use of the assumption that E is to a first approximation a function of the difference between the energies of the bonds broken and formed.[8] For gas reactions between molecules, however, there are no satisfactory correlations with D or ΔH. Various authors have pointed out apparent parallelisms between E and D for relevant bonds,[9-12] but these relations are neither precise nor certain.[13] That a simple general relation between E and the various D's is not to be expected is shown by an investigation of the reactions between sodium and aryl halides, where the absence of such a relation is attributable to stabilisation of the transition state by resonance.[14] For reactions in solution, relations between E and D have not been reported. The Brønsted equation for acid–base catalysis can be derived from a potential-energy picture in which the activation energy is applied entirely to the stretching of a bond, but not all the consequences of this picture agree with experiment.[15] Nevertheless, the energy required to stretch bonds is clearly often an important contribution to E.

(ii) *Short-range repulsion.* The contribution to E arising from interpenetration of electron shells as atoms approach closely is not in general easy to estimate. It rises steeply as the distance r decreases, and has been expressed either as an exponential or as a term in r^{-12}. Some detailed calculations suggest that the contribution is important;[6,16] others, however, suggest that to a first approximation it can be omitted.[17] For proton transfer, $AH + B \longrightarrow A^- + BH^+$, the atom transferred has no valency electrons and so

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[6] Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 604.

[7] Evans and Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 11.

[8] Semenov, " Some Problems of Chemical Reactivity and Kinetics," Vol. I, Pergamon Press, London, 1958.

[9] Hirschfelder, *J. Chem. Phys.*, 1941, **9**, 645.

[10] Evans and Warhurst, *Trans. Faraday Soc.*, 1939, **35**, 593.

[11] Trotman-Dickenson, *Discuss. Faraday Soc.*, 1951, **10**, 111.

[12] Frost and Pearson, " Kinetics and Mechanism," Chapman & Hall, London, 1953, pp. 101, 102.

[13] Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955, p. 230.

[14] Riding, Scannell, and Warhurst, *Trans. Faraday Soc.*, 1956, **52**, 1364.

[15] Bell, " Acid-base Catalysis," Oxford, 1941, Ch. 8.

[16] Evans and Warhurst, *Trans. Faraday Soc.*, 1939, **35**, 593.

[17] Baughan and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 648.

is not subject to these short-range repulsive forces. Repulsion between the atoms A and B may still be appreciable, but Bell's calculations [18] make it unlikely that the contribution to E from repulsion will be greater than about 15% of the whole in a proton-transfer reaction.

(iii) *Electrostatic interactions.* The relatively long-range interactions between reactant ions or dipoles appear to have an important effect on E in certain reactions in solution. The most direct evidence is that in various series of related reactions the variations in E can be correlated with those of the dipole moments of the reactants, or with the known order of the inductive effects of substituents.[19,20]

(iv) *Reorganisation of solvent molecules.* In reactions in solution, there will generally be some reorganisation of the solvating molecules round the reactants. Two aspects of these solvation changes can be distinguished. (*a*) Solvated molecules cannot approach close enough to react unless at least one solvating molecule is detached from each; and if a molecule is charged, the energy required to remove a polar solvent molecule is considerable. (*b*) On forming the transition state there may be changes in the orientation of molecules in the solvation shell and in the restrictions on their motions. The evidence that these solvation changes affect E is as follows.

(*a*) Taube's experiments on the rate of exchange of $H_2{}^{18}O$ with solutions of aluminium salts [21] have shown that the activation energy for the substitution reaction of $Al(H_2O)_6$ with $H_2{}^{18}O$ is of the order of 20 kcal. mole^{-1}. Thus, considerable energy is concerned in removing a water molecule from the ion. Calculations of solvation energies had previously pointed to this conclusion. For hydroxide ion in water, on the assumption that each OH^- is co-ordinated to six water molecules, and that its heat of hydration is equal to that of the fluorine ion which is known from thermal data, the energy required to remove one solvent molecule has been calculated as 20·7 kcal. mole^{-1}, equal to nearly the whole of the observed value of E for the hydrolysis of methyl halides by the hydroxyl ion in water. This led Moelwyn-Hughes and Glew [22] to consider the hypothesis that most of E represents work done in reorganisation of the solvent molecules which solvate the ion. That this energy is an important contribution to E is suggested also by the considerable magnitudes of the heats of solvation of halide ions [23] and of carbonium ions [24] in water and alcohols; these have been used by Franklin [24] in calculations of E for the solvolysis of alkyl halides, and the calculated values are within a few kcal. mole^{-1} of those determined experimentally. It seems, therefore, that, in some reactions at least, the process of desolvation before reaction can require considerable activation energy. Some further evidence suggesting a distinction between this preliminary desolvation and the overall change of solvation on forming the transition state is provided by the effect of pressure on the exchange reaction of $H_2{}^{18}O$ with the pentammino-aquo cobaltic ion.[25]

(*b*) The evidence for changes of solvation when the transition state is formed is well known. The A-factors of reactions in solution, especially those involving changes in magnitude or distribution of charge, can often be explained in these terms.[26] The changes in A when the pressure is increased,[27,28] and when the solvent is changed,[29,30] can often be interpreted in the same way. These solvation changes should contribute to E, as has been suggested by Libby [31] for electron-exchange reactions.

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[18] Bell, *Trans. Faraday Soc.*, 1944, **37**, 493.
[19] Hinshelwood, Laidler, and Timm, *J.*, 1938, 848.
[20] Moelwyn-Hughes, " Kinetics of Reactions in Solution," Oxford, 1947, Ch. 4, 5, 7.
[21] Hunt and Taube, *J. Chem. Phys.*, 1951, **19**, 602; Baldwin and Taube, to be published.
[22] Moelwyn-Hughes and Glew, *Proc. Roy. Soc.*, 1952, *A*, **212**, 260.
[23] Latimer, Pitzer, and Slansky, *J. Chem. Phys.*, 1939, **7**, 108.
[24] Franklin, *Trans. Faraday Soc.*, 1952, **48**, 443.
[25] Hunt and Taube, *J. Amer. Chem. Soc.*, 1958, **80**, 2642.
[26] Bell, *J.*, 1943, 629.
[27] Hamann, " Physico-chemical Effects of Pressure," Butterworths, London, 1957, Ch. 9.
[28] Burrell and Laidler, *Trans. Faraday Soc.*, 1955, **51**, 1497.
[29] Pearson, *J. Chem. Phys.*, 1952, **20**, 1478.
[30] Caldin and Peacock, *Trans. Faraday Soc.*, 1955, **51**, 1217.
[31] Libby, *J. Phys. Chem.*, 1952, **56**, 863.

The most direct evidence comes from solvent effects. The effect of change of solvent on E is often considerable; for several reactions the variations are greater than 5 kcal. mole^{-1}.[30, 35-42] These observed changes in E will reflect changes in the energy required for the reorientation of solvent molecules when the transition state is formed. Two factors seem to be concerned in the variations of E with solvent. First, a change of solvent will be expected to alter the electrostatic interactions considered in (iii), since they depend on the dielectric constant. Calculations from simple models indicate that E will be appreciably affected,[29, 30, 32] and that in a polar solvent of dielectric constant even as low as 5 the electrostatic contribution to E will be about double that in a non-polar solvent.[29] The experimental results do not always agree with these predictions, however, especially when the range of solvents is wide. A survey of reactions which involve a large change in polarity, such as Menschutkin reactions, led to the conclusion that, except perhaps for aliphatic solvents, the electrostatic picture is inadequate.[30] It has been pointed out [29] that the electrostatic contribution to E should be nearly the same for all solvents with even a moderate dielectric constant, so that the differences often found for water, ethanol, and acetone [30, 36-39, 42] are anomalous from the electrostatic point of view. Anomalies in infrared spectra [33] and equilibria [34] have also been reported. More specific interactions must therefore be considered as well. These may be solvent–solute or solvent–solvent interactions. As regards the first of these, we must expect a considerable contribution to E if solvent molecules are attached to one or both of the reactants, but not to the transition state, by hydrogen bonding or any other specific attraction which has to be overcome before the reactants can approach each other in the correct orientation. Specific solvation of this kind has been invoked to explain results on the nitramide reaction catalysed by dimethylaniline.[30] As regards the second type, we should expect that in hydroxylic solvents hydrogen bonding would affect E, since the rearrangement of solvent molecules will involve the breaking of solvent–solvent bonds. This may account for the much higher values for E often found in hydroxylic solvents compared with benzene or even with non-hydroxylic aliphatic solvents.[30]

These four terms contributing to E will be assumed as a first approximation to be independent and additive. Thus we write,

$$E = E\ (\text{bonding}) + E\ (\text{repulsion}) + E\ (\text{electrostatic}) + E\ (\text{solvation}) \quad . \quad (1)$$

Application to the Present Results.—Consider first the proton-transfer reaction between T.N.T. and ethoxide [reaction (*a*) of Table 1], which we can write as $\text{ArCH}_3 + \text{OEt}^- \longrightarrow \text{ArCH}_2^- + \text{EtOH}$. The observed energy of activation (13·6 kcal. mole^{-1}) will be shared among the four factors distinguished above. However, since the reaction is a proton-transfer, E (repulsion), will be small, probably not more than about 2 kcal. mole^{-1}. A value for the electrostatic contribution can be calculated on the assumptions that the negative charge of the ethoxide ion is concentrated on the oxygen atom, and that it interacts mainly with the C–H dipole. This will be an induced dipole modified by the permanent dipole; we can treat the corresponding energies as additive. The permanent dipole, if it can be assumed to be similar to that in methane, has a magnitude of about 0·4 D, probably with the hydrogen as negative end,[43] so that the ion will be repelled.

[32] Moelwyn-Hughes, " Kinetics of Reactions in Solution," Oxford, 1947, Ch. 7.

[33] Bellamy *et al.*, *Trans. Faraday Soc.*, 1959, **54**, 14, 220.

[34] Ross and Labes, *J. Amer. Chem. Soc.*, 1955, **77**, 4916.

[35] Cox, *J.*, 1921, 142.

[36] Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.

[37] Hinshelwood *et al.*, *J.*, 1936, 1353; 1937, 538, 1573.

[38] Brown and Hudson, *J.*, 1950, 3259.

[39] Brown and Hudson, *J.*, 1953, 3352.

[40] Syrka and Gladischev, *Acta Physicochim. U.R.S.S.*, 1935, **2**, 291.

[41] Alder and Leffler, *J. Amer. Chem. Soc.*, 1954, **76**, 1425.

[42] Sweet and Le Roux, *J.*, 1956, 2110.

[43] Smith, " Electric Dipole Moments," Butterworths, London, 1955, Ch. 5.

The energy associated with this repulsion is $e\mu/\varepsilon r^2$, where e is the electronic charge, μ the dipole moment, and ε the dielectric constant. When r is taken as about 2·8 Å (from Bell's calculations [18]), the energy becomes $3{\cdot}3/\varepsilon$ kcal. mole^{-1}. The induced dipole will be attracted by the ion; the energy is $\frac{1}{2}\alpha e^2/\varepsilon a^4$, where α is the polarisability of the C–H bond and may be taken [44] as $7{\cdot}9 \times 10^{-25}$ cm.^{3}, and a is the distance from the centre of the ion to the middle of the C–H bond. This gives $13/\varepsilon$ kcal. mole^{-1}. Thus the overall electrostatic effect is an attraction associated with an energy of about $10/\varepsilon$ kcal. mole^{-1}. The calculation has ignored the effect of the neighbouring dipoles, but is probably correct as regards order of magnitude. The contribution E(electrostatic) can therefore be taken as about $-10/\varepsilon$ kcal. mole^{-1}. It is not easy to decide what value to adopt for the dielectric constant ε. The bulk value is clearly inapplicable; a valve between 3 and 1 is probably correct.

The dielectric constant first being taken as 3, E(electrostatic) becomes about -3 kcal. mole^{-1}; with E(repulsion) $\simeq$ 2 kcal. mole^{-1}, this gives E(electrostatic) + E_{-}(repulsion) $\simeq$ -1 kcal. mole^{-1}. Since the experimental value of E is 13·6 kcal. mole^{-1}, eqn. 1 gives for the proton-transfer (*a*):

$$E(\text{bonding}) + E(\text{solvation}) \simeq 15 \text{ kcal. mole}^{-1}, \text{ if } \varepsilon = 3 \quad . \quad . \quad . \quad (2)$$

Consider next the complex-formation between T.N.A. and ethoxide ion [reaction (*b*) of Table 1], which we can write: T.N.A. + $\text{OEt}^- \longrightarrow (\text{T.N.A.,OEt})^-$. Here no bond is broken, and the activation energy for the formation of the " bond " in the complex will be low, whether it is due to charge-transfer [45] or to ion-dipole interaction; thus E(bonding) $\simeq$ 0. It is difficult to estimate E(repulsion) and E(electrostatic), since the relative positions of the ethoxide ion and the T.N.A. molecule are not known, but it seems reasonable to assume that for this relatively loose complex-formation their joint contribution to E will be even less than for the proton-transfer (*a*). In that case, the major contribution to E will be from factor (iv), the reorientation of solvent molecules. Thus for reaction (*b*) and with the observed value of E (10·4 kcal. mole^{-1})

$$E(\text{solvation}) \simeq 10 \text{ kcal. mole}^{-1}, \text{ if } \varepsilon = 3 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Reactions (*c*) and (*d*) will have, on the same assumptions, similar values for E(solvation), namely about 11 and 12 kcal. mole^{-1}. Thus it appears that the contribution to E for these reactions from the solvent reorganisation is in the region of 10 kcal. mole^{-1}—a considerable amount—and this for an ion-dipole reaction involving no change of charge.

This conclusion is confirmed if we take account also of the results for the reverse reactions, *i.e.* the unimolecular dissociations of the complexes formed in reactions (*b*), (*c*), and (*d*). Consider first reaction (*b*). For the reverse dissociation, the terms E(repulsion) and E(electrostatic) will be equal to those for the complex-formation but of opposite sign, while E(bonding) will again be small. The sum of the energies of activation for the forward and back reactions will therefore, by eqn. 1, be nearly equal to the sum of the two E(solvation) terms, and their mean will give the mean value of E(solvation) for the forward and reverse reactions. From the values given in Table 1, the mean E(solvation) comes to 12 kcal. mole^{-1} for reaction (*b*). The corresponding value for reaction (*c*) is 12, and that for reaction (*d*) is 10 kcal. mole^{-1}. The separate values for the forward and reverse reactions cannot be found from this argument, but it would seem that the order of magnitude given in eqn. 3 is correct.

We may next compare the results for the proton-transfer and complex-formation reactions of T.N.T. [reactions (*a*) and (*d*)]. We might expect E(solvation) to be about the same for the two reactions, and this expectation is confirmed by the fact that the A-factors are equal within experimental error (Table 1). Then, if the value given above for reaction (*d*) is used, E(solvation) for reaction (*a*) will be not far from 12 kcal. mole^{-1}. Eqn. 2 then

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[44] Denbigh, *Trans. Faraday Soc.*, 1940, **36**, 936.

[45] Mulliken, personal communication, and *J. Phys. Chem.*, 1952, **56**, 801.

implies that E(bonding) is small for the proton-transfer (*a*)—not more than a few kcal.—and that E(solvation) is the main contribution to E for this reaction.

It is difficult to draw detailed conclusions about the addition reaction (*e*), for which $E = 13{\cdot}1$ kcal. mole^{-1}. If the desolvation energy is about the same as for the other reactions, it accounts for most of E, so that E(bonding) + E(repulsion) + E(electrostatic) $\simeq 0$. If E(electrostatic) can be assumed to be small compared with the other terms, this gives E(repulsion) $\simeq -E$(bonding). But it would be difficult to assign a numerical value to either of these terms.

If we take the dielectric constant as 1 instead of 3, the numerical values are different but we still reach the conclusions that E(solvation) is considerable and that it forms at least a considerable fraction of E for the proton-transfer. For this reaction, E(electrostatic) becomes about -10 kcal. mole^{-1}, whence E(electrostatic) + E(repulsion) $\simeq -8$ kcal. mole^{-1}, and eqn. 2 becomes:

$$E(\text{bonding}) + E(\text{solvation}) \simeq 23 \text{ kcal. mole}^{-1}, \text{ if } \varepsilon = 1 \quad . \quad . \quad . \quad (2')$$

For the complex-formation, if we suppose that E(electrostatic) + E(repulsion) lies between 0 and the above value of -8 kcal. mole^{-1}, eqn. 3 becomes:

$$E(\text{solvation}) \simeq 10 \text{ to } 18 \text{ kcal. mole}^{-1}, \text{ if } \varepsilon = 1 \quad . \quad . \quad . \quad . \quad (3')$$

Comparing eqn. 2′ and 3′, we see that if E(solvation) has similar values for the two reactions, it is a considerable contribution to the total energy of activation for the proton-transfer.

The main conclusions are that in this set of reactions in ethanol: (*a*) The contribution to E of the energy required to reorganise solvent molecules appears to be considerable, of the order of 10 kcal. mole^{-1} or more, and (*b*) that it accounts for the greater part of E, not only in complex-formation but in proton-transfer.

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