[CONTRIBUTION FROM THE CHARLES E. COATES CHEMICAL LABORATORIES, LOUISIANA STATE UNIVERSITY]

Coulombic Energy of Activation

BY EDWARD S. AMIS

There are two ways of measuring the energy of activation of a reaction. In the usual case the temperature coefficient of a rate is measured in a solvent of constant composition, *e. g.*, pure water or water containing a constant percentage of some other solvent. The second method involves measuring the temperature coefficient of a rate in isodielectric solvents. In this method a given dielectric, *e. g.*, that of water at 45°, is chosen and at lower temperatures sufficient solvent of dielectric constant lower than that of water is added to keep the dielectric that of water at 45°.

When the composition of the solvent is held constant and the dielectric constant, therefore, varies, the measured temperature coefficient includes not only the increased energy of the reactants due to pure thermal effect, but the changed effect of the solvent on the reactants, due to the changed electrical forces in a different dielectric.

If we consider the effect of the solvent upon reactants (charged ions or dipoles) as mainly due to an influence upon the coulombic forces between the electrically unneutral particles, the picture for ionic reactants would be as follows. Suppose it were possible to hold all factors except the dielectric constant of the solvent constant; then for two oppositely charged particles the lower the dielectric constant of the solvent the greater would be the attraction between the particles and the more readily they would react. This follows from Coulomb's law. For reactants of like sign the repulsion would become greater at lower dielectric constants for the same reason, and hence a rate of reaction between them would be retarded. The opposite would hold true for an increase in dielectric constant. In the case of a polar liquid solvent, the change in force exerted by charged particles upon each other might be considered as a solvation effect whereby the polar molecules of the solvent orientate themselves around the reactants and in effect partially neutralize their charges; so that for a lower dielectric constant (less polar or less concentration of highly polar solvent) there is less orientation and hence less cancellation of electrostatic forces between the solute particles.

The measurement of energies of activation in isodielectric media gives an especially fortunate approach to the interpretation of the influences of electrostatic forces upon reaction rates as a function of the dielectric constant of the solvent. This is true because the determination of a particular temperature coefficient is free from the complication of changing dielectric constant. Hence if two temperature coefficients of a reaction are measured in two isodielectric solvents of the same solvent pair, the difference in the reaction rates should depend to a large extent only on the difference of electrostatic forces between the reactants in the different dielectrics, and the difference in temperature coefficients should be due to a large extent to a change in electrostatic energies.

If we assume the coulombic energy between two charged reactants is that part of the energy of activation which changes in isodielectric media, the effect can be calculated from the expression for the change of coulombic energy between the two electrically unneutral particles. E. A. Moelwyn-Hughes and Albert Sherman[1] give six classes of electrostatic forces between electrically unneutral particles. For the ion–ion pair the energy necessary to bring one of the ions from infinity to within the distance r of the other ion is given by the equation

$$E = Z_1Z_2e^2/Dr \qquad (1)$$

If the energy change necessary to bring the two ions together at two different constant dielectric constants of the same solvent pair is the change only of coulombic energy, this alteration of the energy of activation can be calculated from Eq. (1), as follows

$$\Delta E = \frac{-Z_1Z_2e^2}{D_1D_2r}\,\Delta D \qquad (2)$$

In these equations E is the coulombic energy between two ions, Z_1 and Z_2 are the valences of the ions, e is the electronic charge, D the dielectric of the media, and r the distance of approach of the ions.

For univalent ions in a vacuum and where r is 1 Å., E = 329.7 kcal./mole. Therefore for other values of valence dielectric constant and r (r is in Å.)

$$E = 329.7Z_1Z_2/Dr \qquad (3)$$

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[1] E. A. Moelwyn-Hughes and Albert Sherman, *J. Chem. Soc.*, 101 (1936).

and

$$\Delta E = -329.7 \frac{Z_1Z_2}{D_1D_2r} \Delta D \quad (4)$$

This equation indicates that for ionic reactants possessing charges of like sign, there will be an increase of energy of activation arising from coulombic effects, when the dielectric constant is lowered or *vice versa*. Likewise there will be a decrease in the energy of activation due to coulombic forces between reactants of unlike sign when the dielectric constant of the solvent is diminished and *vice versa*.

We will mention one of the five other coulombic energy types before discussing the experimental confirmation of the equations for the change of energy calculated from coulombic energies when the temperature coefficients of reaction rates are measured in isodielectric solvents. The interpretation of the equations for this charge type will be clear from what has been said in the case of the ion–ion type.

Ion–Dipole Type:

$$E = -Z_2e_2\mu_1 \cos\theta_1/Dr^2 \quad (5)$$

where Z_2e_2 is the charge on the ion, μ_1 is the dipole moment of the molecule, θ_1 is the angle formed by the line joining the centers of charge in the dipole and the line drawn from the ion to one of these centers of charge.[2] Then as above

$$\Delta E = \frac{Z_2e_2\mu_1 \cos \theta_1}{D_1D_2r^2} \Delta D \quad (6)$$

and for head-on alignment of the dipole and ion we get

$$\Delta E = \frac{Z_2e_2\mu_1}{D_1D_2r^2} \Delta D \quad (7)$$

The other four paired types may be calculated in a similar way. A thorough test of this theory would require that reactions between the various paired types of coulombic reactants mentioned above be studied in a variety of iso-dielectric solvent pairs.

In all the above equations, the parameter r occurs, and it is conceivable that the value of this parameter would not be the same for different pairs of reactants even of the same charge type. It is also possible that r might vary for the same reactant pair in different bisolvent mixtures. Nevertheless, any experimental confirmation of this theory must be based upon a reasonable value of r. Rice[3] has chosen 2 Å. as a value of r to use in a problem in the case of the ion–ion type as an illustration which gives roughly the expected value of the coulombic energy in this case. If kinetic values of molecular dimensions can be taken as reasonable values for r, then anywhere from 1 to 6 Å. would be acceptable for the magnitude of this parameter.

The only published data at present involve the ion–ion type of reaction in a number of solvent pairs, and for several constant dielectric constants of these pairs. Svirbely and Warner's[4] and Svirbely and Schramm's[5] data on the positive univalent ammonium ion and the negative univalent cyanate ion in ethyl alcohol–water isodielectric media, Lander and Svirbely's[6] work on the same reaction in glycol–water isodielectric media, Amis and LaMer's[7] study of the reaction between the negative bivalent tetrabromophenolsulfonphthalein ion and the negative univalent hydroxide ion offer an excellent opportunity for comparison of the theory with data in the ion–ion case for different charge types in different isodielectric solvent pairs.

In Table I is given a comparison of the change of energy of activation considered as a change of coulombic energy calculated from Eq. (4) and the actual experimental energy change between specified constant dielectric constants of the mixed solvents.

The calculated change of coulombic energy of activation for the negative bivalent brom phenol blue ion and the negative univalent hydroxide ion reaction, taking the parameter r equal to 2 Å., agrees with the observed energy change for this reaction in both the methyl alcohol–water and ethyl alcohol–water isodielectric solvents. The calculated coulombic energy changes of the reaction between the positive univalent ammonium ion and the negative univalent cyanate ion agree with the observed energy variations down to between dielectrics of 45 and 40, when the parameter is again 2 Å. The solvent in this case was also methyl alcohol–water.

For the dielectric ranges 63.5–40.0 and 63.5–30.0 the calculated values of the energies are progressively greater than the observed changes. This might have been expected from the fact that the logarithm of the specific reaction rate constant begins to depart, at low dielectrics, from being in-

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(2) See Oscar Knefler Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, pp. 462–468, for diagrams of these lines and angles.

(3) Oscar Knefler Rice, ref. 2, pp. 462–468.

(4) Svirbely and Warner, THIS JOURNAL, **57**, 1883 (1935).

(5) Svirbely and Schramm, *ibid.*, **60**, 330 (1938).

(6) Lander and Svirbely, *ibid.*, **60**, 1613 (1938).

(7) Amis and LaMer, *ibid.*, **61**, 905 (1939).

versely proportional to the dielectric constant of the solvent and this departure becomes more marked as the dielectric constant is continually decreased.[8] In the case of the ammonium ion–cyanate ion reaction in glycol–water solvent, the agreement between the calculated and observed changes of energy, taking r as 5 Å., are excellent down to a dielectric constant of 45, when again the calculated values become progressively larger than the observed values.

The fact that the parameter r can be taken as 2 Å. for the two distinct ion types of reactions in both methyl alcohol–water and ethyl alcohol–water, and that r takes a different value for the same reaction in going from mono-hydroxy alcohol–water to a poly-hydroxy alcohol–water solvent suggests that this parameter is more a function of the solvent than of the charge type or chemical nature of the reactants.

TABLE I

CALCULATED CHANGES OF COULOMBIC ENERGIES OF ACTIVATION AS A FUNCTION OF DIELECTRIC CONSTANT OF THE SOLVENT COMPARED WITH OBSERVED CHANGES OF ENERGY OF ACTIVATION

The observed changes are the averages for the following temperature ranges: Amis and LaMer, 5–45°; Svirbely and Warner, 30–70°; Svirbely and Schramm, 30–70°; Lander and Svirbely, 30–60°.

$\sqrt{\mu}$	r	Dielectric range (ΔD = diff.)	ΔE = change of coulombic energy	ΔE obsd.	
Amis and LaMer, $B\phi B^{=} + OH^-$, $MeOH-H_2O$					
0.300	2	71.42–64.86	470	390	
Amis and LaMer, $B\phi B^{=} + OH^-$, $EtOH-H_2O$					
.300	2	71.42–64.86	470	560	
Svirbely and Warner, $NH_4^+ + CNO^-$, $MeOH-H_2O$					
.0	2	63.5–55.0	−400	− 340	
.194	2	63.5–55.0	−400	− 530	
Svirbely and Schramm, $NH_4^+ + CNO^-$, $MeOH-H_2O$					
.0	2	63.5–55	− 400	− 340	Calcd. by their Eq. (5)
.0	2	63.5–50	− 700	− 730	
.0	2	63.5–45	−1070	−1000	
.0	2	63.5–40	−1520	−1250	
.0	2	63.5–35	−2110	−1470	
.194	2	63.5–55	− 400	− 290	Av. from their Eqs. (5) and (9)
.194	2	63.5–50	− 700	− 610	
.194	2	63.5–45	−1070	− 860	
.194	2	63.5–40	−1520	−1070	
.194	2	63.5–35	−2110	−1250	
Lander and Svirbely, $NH_4^+ + CNO^-$, $Glycol-H_2O$					
.0	5	63.5–60	− 60	− 80	Calcd. by their Eq. (3)
.0	5	63.5–55	− 160	− 90	
.0	5	63.5–50	− 280	− 160	
.0	5	63.5–45	− 430	− 160	
.0	5	63.5–40	− 610	− 140	
.194	5	63.5–60	− 60	− 80	Av. from their Eqs. (3) and (6)
.194	5	63.5–55	− 160	− 70	
.194	5	63.5–50	− 280	− 160	
.194	5	63.5–45	− 430	− 150	
.194	5	63.5–40	− 610	− 210	

TABLE II

Substance	Type of compound	Viscosity[a] 0°C.	Dipole moment
MeOH	Monohydroxy	0.817	1.68 (25°)[b]
EtOH	Monohydroxy	1.790	1.69 (25°)[b]
H_2O	Monohydroxy	1.792	1.84 (25°)[b]
Glycol	Dihydroxy	2.18	2.3 (20°)[c]

[a] "Handbook of Chemistry and Physics," 23rd Edition, Chemical Rubber Publishing Co., 1900 West 112th St., Cleveland, Ohio, 1939, pp. 1324–1327. [b] Duncan A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, 1939, p. 409. [c] Pierre Girard and P. Abadie, *Compt. rend.*, **197**, 146 (1933).

Table II gives some of the physical, chemical and electrical properties of the solvents concerned in this discussion and which conceivably may be pertinent to the effect of a solvent upon reaction rates. Even in the case of the glycol–water solvent, r taken as 2 Å. will give calculated coulombic energies of the right sign and magnitude when compared with observed energy changes, but the agreement is much better when r is taken as 5 Å.

It should be borne in mind that to check this theory requires utmost precision, since the energies involved amount to only a few hundred calories. Furthermore, for the five charge types other than the ion–ion type the checking of this theory will be more difficult, since there are more parameters than r involved and the magnitudes of the energies are less than for the ion–ion types. Nevertheless we have forthcoming from these laboratories data on a reaction between ion-dipole reactants which bear out the conclusions of this paper. In this case r is again taken as 2 Å. and head-on alignment is chosen as the relative positions of the ion and dipole in order to estimate the order of magnitude.

Conclusions

1. The change of energy of activation between the different ionic type reactants in the various solvents discussed above when the reaction rates are measured in different constant dielectric constant media is a change in the coulombic energies of the ions down almost to a dielectric constant of 40.

2. At 40 and below the calculated changes of coulombic energies are progressively greater than the observed changes in energies of activation

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[8] LaMer, *J. Franklin Inst.*, **225**, 709 (1938).

as the dielectric constant is continually lowered.

3. The parameter r always has a reasonable value, but is more a function of the properties of the solvent than of the charge type or chemical properties of the reactants.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

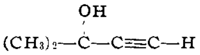
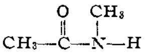
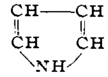
Hydrogen Bonds Involving the C–H Link. XIV.[1] Solubility of Donor Solutes in Hydrogen Bonding Solvents

BY C. S. MARVEL, JAMES HARKEMA AND M. J. COPLEY[2]

Following the methods previously described[3] we have measured the solubilities of a number of polymeric materials in a variety of hydrogen bonding solvents. The results of the solubility determinations are collected in Table I.

TABLE I

SOLUBILITY OF VARIOUS POLYMERIC SUBSTANCES IN HYDROGEN BONDING SOLVENTS

	Grams of solute per 100 g. of solvent indicated						
Solute	$C_6H_5C{\equiv}CH$	C_6H_5SH	$CH_3(CH_2)_4C{\equiv}CH$	CH_3NO_2	 $(CH_3)_2{-}\overset{OH}{C}{-}C{\equiv}C{-}H$	 $CH_3{-}\overset{O}{\overset{\Vert}{C}}{-}\overset{CH_3}{\overset{\vert}{N}}{-}H$	
1 Polyvinyl acetate	93	85	109	93	71	53	81
2 Polymethyl vinyl ketone	40	24	0.036	35	19	<0.2	25
3 Polymethyl methacrylate	46	33	0.73	19	27	< .3	41
4 Cellulose triacetate	0.018	0.032	.01	0.017	5.4	...	13
5 Polyvinyl chloride	0.085	0.048	.106	.004	0.007	...	0.115
6 "Vinylite" (34.1% Cl)	110	99	.053	2.1	.504	...	86

Discussion of Results

It should be mentioned again that low solubilities could be checked readily to about 10%, whereas the high solubilities are approximated by the scheme previously described.[3] The solvents were commercial or laboratory samples which boiled over a 2° range. The polymers were those used in the earlier work except the "Vinylite" which was a copolymer of vinyl chloride and vinyl acetate containing 34.1% chlorine, and was given to us by Mr. H. B. McClure of Carbide and Carbon Chemicals Corporation.

The high solubilities of the donor type polymer in phenylacetylene and thiophenol agree with predictions based on heats of mixing measurements which have been reported with these solvents.[4,5] Likewise the low solvent power of 1-heptyne agrees with heat of mixing data.[6] Heat of mixing data on nitromethane[5] and hydrogen bonding solvents indicate that it is associated. Yet it has hydrogens sufficiently active to make it a good solvent for donor materials. It is not possible to say whether the acetylenic hydrogen or the alcohol hydrogen in dimethylethylcarbinol is the effective one but it seems logical that it is a combined effect since an aliphatic acetylene is ineffective and a simple alcohol is a much less effective solvent than this acetylene alcohol.

The high solubility of these donor molecules in pyrrole is striking and illustrates the strong tendency for the formation of —N—H ← O bonds. Pyrrole seems to be an exceptionally good solvent for cellulose triacetate. The poor solvent properties of *n*-methylacetamide are apparently due to its very complete association with itself by virtue of strong donor and strong acceptor properties.

The high solubility of polyvinyl acetate in all solvents tried indicates that hydrogen bonding is not playing a very important role in this case.

Summary

Phenylacetylene, thiophenol, nitromethane, dimethylethynylcarbinol and pyrrole have been shown to be good solvents for donor molecules of high molecular weight.

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(1) For the thirteenth paper see THIS JOURNAL, **63**, 254 (1941).

(2) Present address: Eastern Regional Laboratory, U. S. Department of Agriculture, Chestnut Hill Station, Philadelphia, Pennsylvania.

(3) Marvel, Dietz and Copley, THIS JOURNAL, **62**, 2273 (1940).

(4) Copley and Holley, *ibid.*, **61**, 1599 (1939).

(5) Copley, Marvel and Ginsberg, *ibid.*, **61**, 3161 (1939).

(6) Holley, private communication, has found that mixing 1-heptyne with ethyl ether gives only 113 mole cal. and with acetone no heat effect.