

The Electrolyte and Solvent Influence upon the Reaction between Persulphate and Iodide

II. The Reaction Entropies and Heats of Activation

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The variation of the specific rate of a reaction in solution with temperature, provided that the temperature range is not wide, is represented by the Arrhenius equation

$$k = Ae^{-E/RT} \quad (1)$$

where E is the experimental activation energy and A is the frequency factor. According to the theory of absolute reaction rates by Eyring¹ this relationship is to be expressed, supposing the transmission coefficient to unity, by the equation

$$\begin{aligned} k &= \frac{kT}{h} e^{-\Delta G^\ddagger/RT} \\ &= \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \end{aligned} \quad (2)$$

where ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger are the free energy, heat content and entropy of activation, respectively. In comparing the Eqs. (1) and (2) with one another we obtain

$$\Delta H^\ddagger = E - RT \quad (3)$$

$$A = \frac{ekT}{h} e^{\Delta S^\ddagger/R} \quad (4)$$

In a previous investigation² I have derived, on the basis of Born's equation, expressions which give the dependence of the specific rate, experimental activation energy and frequency factor, respectively, on the dielectric constant of the solvent, referred to zero ionic strength. The equations are:

$$\log k^0 = \log k_{D\infty} - \frac{z_A z_B e^2}{2.3 k T \rho D} \quad (5)$$

$$E_D^0 = E_{D\infty} + \frac{z_A z_B e^2 R}{k \rho D} \quad (6)$$

$$\log A_D^0 = \log k_{D\infty} + \frac{E_{D\infty}}{2.3 RT} = \text{a constant at constant temperature} \quad (7)$$

$$\begin{aligned} E_C^0 &= E_D^0 + \frac{z_A z_B e^2 RT}{k \rho D^2} \cdot \frac{dD}{dT} \left(1 + \frac{D}{\rho} \frac{d\rho}{dD}\right) \\ &= E_{D\infty} + \frac{z_A z_B e^2 R}{k \rho D} \left(1 + \frac{T}{D} \frac{dD}{dT} + \frac{T}{\rho} \frac{d\rho}{dT}\right) \end{aligned} \quad (8)$$

and

$$\log A_C^0 = \log A_D^0 + \frac{z_A z_B e^2}{2.3 k \rho D^2} \cdot \frac{dD}{dT} \left(1 + \frac{D}{\rho} \frac{d\rho}{dD}\right) \quad (9)$$

By the subscripts *C* and *D* are designated the constants in a medium of fixed composition and in one of fixed dielectric constant, respectively. The terms with subscript D_∞ are those in the hypothetical solvent in which all the electrostatic effects vanish ($D = \infty$).

The Eq. (2) may be put in the form

$$\ln k^0 = \ln \frac{kT}{h} - \frac{\Delta G^\ddagger}{RT} \quad (10)$$

and the comparison with Eq. (5) gives

$$\Delta G^\ddagger = RT \left(\ln \frac{kT}{h} - \ln k_{D\infty} \right) + \frac{z_A z_B e^2 R}{k \rho D} \quad (11)$$

The two terms on the right-hand side may be identified with two types of free energy changes³, viz., ΔG_0^\ddagger for the non-electrical reaction and ΔG_D^\ddagger as the dielectric effect; thus,

$$\Delta G_0^\ddagger = RT \left(\ln \frac{kT}{h} - \ln k_{D\infty} \right) = \text{a constant at constant temperature} \quad (12)$$

and

$$\Delta G_D^\ddagger = \frac{z_A z_B e^2 R}{k \rho D} \quad (13)$$

The differentiation of these free energy terms with respect to temperature, and taking into account Eqs. (7) and (8), gives

$$\Delta S_0^\ddagger = - \left[\frac{\partial(\Delta G_0^\ddagger)}{\partial T} \right]_p = R \left(\ln A_D^0 - \ln \frac{ekT}{h} \right) = \text{a constant at constant temperature} \quad (14)$$

and

$$\Delta S_D^\ddagger = - \left[\frac{\partial(\Delta G_D^\ddagger)}{\partial T} \right]_p = \frac{z_A z_B e^2 R}{k_0 D^2} \left(\frac{\partial D}{\partial T} \right)_p \left(1 + \frac{D}{\rho} \frac{d\rho}{dD} \right) \quad (15)$$

or, according to Eq. (9),

$$\Delta S_D^\ddagger = R \left(\ln A_C^0 - \ln A_D^0 \right) \quad (15')$$

for the non-electrical and dielectric contributions to the entropy of activation at zero ionic strength.

The total entropy of activation ΔS^\ddagger is the sum of ΔS_0^\ddagger for the non-electrical reaction and of ΔS_D^\ddagger for the dielectric effect, hence it is seen that

$$\Delta S^\ddagger = R \left(\ln A_C^0 - \ln \frac{ekT}{h} \right) \quad (16)$$

as given by Eq. (4).

If the thermodynamic relationship $\Delta H = \Delta G + T\Delta S$ is utilized, it follows from Eqs. (12)–(15) that the contributions to the heat of activation are

$$\Delta H_0^\ddagger = E_{D\infty} - RT = \text{a constant at constant temperature} \quad (17)$$

and

$$\Delta H_D^\ddagger = \frac{z_A z_B e^2 R}{k_0 D} \left(1 + \frac{T}{D} \frac{dD}{dT} + \frac{T}{\rho} \frac{d\rho}{dT} \right) \quad (18)$$

or, according to Eq. (8),

$$\Delta H_D^\ddagger = E_C^0 - E_{D\infty} \quad (18')$$

Hence,

$$\Delta H^\ddagger = E_C^0 - RT \quad (19)$$

From Eqs. (6) and (13) there follows the interesting result

$$E_D^0 = E_{D\infty} + \Delta G_D^\ddagger \quad (20)$$

which indicates the dependence of the experimental activation energy in media of fixed dielectric constants on the dielectric constant of these media. Thus the standard contribution $E_{D\infty} (= \Delta H_D^\ddagger + RT)$ designates the bond-stretching energy and the dielectric contribution ΔG_D^\ddagger the repulsion energy of Hinshelwood, Laidler and Timm⁴.

The abovementioned Eqs. (11), (13), (15) and (18) are valid only for reactions between two ions with charges $z_A e$ and $z_B e$. If one or both of the reactants are dipoles, $z_A e$ and $z_B e$ in these equations should be replaced with corresponding dipole expressions, in which case the Eqs. (15') and (18') are, however, still in force and can be applied to the measurement results. The $E_{D\infty}$ value should be obtained on extrapolating from the E_D values in regard to $1/D$ to zero, after which the non-electrical and dielectric contributions may be determined without a knowledge of the ρ values and their variation with the dielectric constant.

In the first part of this investigation there were derived also equations for the influence of ionic strength upon the Arrhenius parameters A_c and E_c . These equations (17 and 20 on page 23) are to be applied directly to Eq. (2) and we have

$$(\Delta G_D^\ddagger)_{\sqrt{\mu}} = (\Delta G_D^\ddagger)_{\mu=0} - 4.6RT \frac{z_A z_B A \sqrt{\mu}}{1 + a \sqrt{\mu}} + B \mu, \tag{21}$$

$$(\Delta H_D^\ddagger)_{\sqrt{\mu}} = (\Delta H_D^\ddagger)_{\mu=0} - 2.3RT \left(1 + \frac{T}{D} \frac{dD}{dT} \right) \frac{3z_A z_B A \sqrt{\mu}}{1 + a \sqrt{\mu}} \left(1 - \frac{a}{3} \frac{\sqrt{\mu}}{1 + a \sqrt{\mu}} \right) - B' \mu \tag{22}$$

and

$$(\Delta S_D^\ddagger)_{\sqrt{\mu}} = (\Delta S_D^\ddagger)_{\mu=0} - 2.3R \frac{z_A z_B A \sqrt{\mu}}{1 + a \sqrt{\mu}} \left[1 + 3 \frac{T}{D} \frac{dD}{dT} - \frac{a \sqrt{\mu}}{1 + a \sqrt{\mu}} \left(1 + \frac{T}{D} \frac{dD}{dT} \right) \right] - B'' \mu \tag{23}$$

or applied to the reaction under consideration in aqueous solution of 30° C:

$$(\Delta G_D^\ddagger)_{\sqrt{\mu}} = 5\,300 - \frac{2835 \sqrt{\mu}}{1 + 0.75 \sqrt{\mu}} + 88 \mu \tag{21'}$$

$$(\Delta H_D^\ddagger)_{\sqrt{\mu}} = -2\,400 + \frac{1638 \sqrt{\mu}}{1 + 0.75 \sqrt{\mu}} \left(1 - \frac{0.25 \sqrt{\mu}}{1 + 0.75 \sqrt{\mu}} \right) - 400 \mu \tag{22'}$$

$$(\Delta S_D^\ddagger)_{\sqrt{\mu}} = -25.4 + \frac{14.75 \sqrt{\mu}}{1 + 0.75 \sqrt{\mu}} \left(1 - \frac{0.092 \sqrt{\mu}}{1 + 0.75 \sqrt{\mu}} \right) - 1.61 \mu \tag{23'}$$

Table 1. The persulphate-iodide reaction in aqueous methyl alcohol solutions at zero ionic strength (30° C). The free energy, heat content, and entropy of activation and their non-electrical and dielectric contributions.

Wt. % alcohol	D_{30°	ΔG_0^\ddagger kcal/ mole	ΔH_0^\ddagger kcal/ mole	ΔS_0^\ddagger E. U.	ΔG_D^\ddagger kcal/ mole	ΔH_D^\ddagger kcal/ mole	ΔS_D^\ddagger E. U.	ΔG^\ddagger kcal/ mole	ΔH^\ddagger kcal/ mole	ΔS^\ddagger E. U.
0	76.7	12.2	14.5	+ 7.6	5.3	- 2.4	- 25.4	17.5	12.1	- 17.8
10.2	72.3	12.2	14.5	+ 7.6	5.7	- 1.5	- 23.6	17.9	13.0	- 16.0
20.7	67.3	12.2	14.5	+ 7.6	6.0	- 0.7	- 22.1	18.2	13.8	- 14.5
26.6	64.5	12.2	14.5	+ 7.6	6.2	+ 0.4	- 19.0	18.4	14.9	- 11.4
31.7	62.0	12.2	14.5	+ 7.6	6.3	+ 1.1	- 17.1	18.5	15.6	- 9.5
43.1	56.6	12.2	14.5	+ 7.6	6.6	+ 2.3	- 14.1	18.8	16.8	- 6.5
57.5	49.8	12.2	14.5	+ 7.6	6.8	+ 3.8	- 9.9	19.0	18.3	- 2.3

EXPERIMENTAL RESULTS

Table 1 presents the contributions of free energy, heat content, and entropy of activation for reaction between persulphate and iodide ions in various aqueous methyl alcohol solutions containing 0—57.5 weight per cent alcohol. The non-electrical contributions ΔG_0^\ddagger , ΔH_0^\ddagger and ΔS_0^\ddagger are fundamental values for the reaction under consideration. It would be of interest to know the corresponding values for other reactions of different types. However, only few reactions in solution have hitherto been measured with such an accuracy and with such an extensive variation of the temperature and dielectric constant that a determination of $E_{D\infty}$, especially, either making use of Eq. (6) or graphically, is possible. However, after my calculations according to experimental results of several authors, it seems that ΔH_0^\ddagger has a value of the same

Table 2. The effect of ionic strength μ (KNO_3) on the free energy, heat content, and entropy of activation.

$\sqrt{\mu}$	$(\Delta G_D^\ddagger)\sqrt{\mu}$ kcal/ mole	$(\Delta H_D^\ddagger)\sqrt{\mu}$ kcal/ mole	$(\Delta S_D^\ddagger)\sqrt{\mu}$ E. U.	ΔG^\ddagger kcal/ mole	ΔH^\ddagger kcal/ mole	ΔS^\ddagger E. U.
0	5.3	- 2.4	- 25.4	17.5	12.1	- 17.8
0.05	5.2	- 2.3	- 24.7	17.4	12.2	- 17.1
0.1	5.0	- 2.3	- 24.0	17.2	12.2	- 16.4
0.2	4.8	- 2.2	- 23.0	17.0	12.3	- 15.4
0.3	4.6	- 2.1	- 22.2	16.8	12.4	- 14.6
0.5	4.3	- 2.1	- 21.1	16.5	12.4	- 13.5
0.7	4.0	- 2.1	- 20.3	16.2	12.4	- 12.7
1.0	3.8	- 2.2	- 19.6	16.0	12.3	- 12.0
1.2	3.6	- 2.2	- 19.3	15.8	12.3	- 11.7
1.5	3.5	- 2.3	- 19.2	15.7	12.2	- 11.6

order as for the reaction under consideration, *viz.* 14—15 kcal, for a number of reactions of different types, as for fading of bromphenolblue ⁵, hydrolysis of ethyl benzoate ⁶, dealdolization of diaceton alcohol ⁷, Cannizzaro reaction ⁸ and for reaction between ethylene chlorhydrin and hydroxyl ion ⁹, wherein ΔS_0^\ddagger also, at least for the three first mentioned reactions, has the value appr. + 7 E. U. (cal/degree · mole).

Table 2 gives the dependence of the various contributions on the ionic strength of the solution. The heat of activation is, as is perceivable from these values, only slightly dependent on the ionic strength, and the variation of the free energy change with the ionic strength is to a great extent caused by the variation of the entropy change.

SUMMARY

Provided that the specific rate of a reaction has been measured in different solvents by varying the temperature and dielectric constant of the solvent, the parameters of the Arrhenius equation can be calculated both for solvents of constant composition or of fixed dielectric constant. If the measurements furthermore, have been performed in sufficiently dilute solutions or by variation of the ionic strength, the values of these parameters referred to zero ionic strength can be calculated. According to the expressions derived above, the non-electrical and dielectric contributions to the free energy, heat content, and entropy of activation then can be determined without a knowledge of the radii of the reactants, or of their variation with solvent, or of any other conceptions.

The equations giving the influence of the ionic strength of the solution on the free energy, heat content, and entropy of activation of ionic reactions have been derived on the basis of the Debye-Hückel theory.

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