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Activation Energies for Diffusion in Aprotic Solvents. Application to the Estimation of Kinetic Parameters for Diffusion Controlled Bimolecular Reactions

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The activation energies for the diffusion of a number of aromatic compounds were determined in acetonitrile (AN), *N*,*N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) by chronoamperometry. Although the diffusion coefficients in each solvent varied by about a factor of 2 for the series of compounds studied, the activation energies varied very little. The mean values of $(E_a)_{diff}$ were found to be 2.00 ± 0.06 (AN), 2.43 ± 0.22 (DMF) and 3.19 ± 0.19 (DMSO) kcal/mol (1kcal = 4.184 kJ). Use of $(E_a)_{diff}$ and encounter controlled second order rate constants estimated from the Smoluchowski equation resulted in apparent entropies of activation at 298 K ranging from -6 to -9 cal/K mol. Using $(E_a)_{diff}$ along with $\Delta S^{\dagger} = 4/3\ \Delta S_c$ in an equation resulting from transition state theory resulted in second order rate constants in close agreement with those from the Smoluchowski equation. The cratic entropy for the reversible encounter ΔS_c was estimated for each solvent. It was concluded that reliable encounter controlled second order rate constants can be estimated by this approach.

Activation energies for the diffusion of aromatic compounds in acetonitrile (AN) and *N*,*N*-dimethylformamide (DMF) have recently been determined by the measurement of the temperature dependence of the peak currents during linear sweep voltammetry.[1] Estimates of diffusion controlled bimolecular rate constants were made by assuming zero entropy of activation and applying transition state theory equations. The rate constants estimated in this manner were from 20 to 30 times larger than those estimated using the Smoluchowski equation (1).[2] It was concluded that if zero entropy of activation is to be assumed and eqn. (2) used to estimate the diffusion controlled rate constant that the activation energy for diffusion of a single species must be multiplied by some factor in order to give k_{diff} in reasonable agreement with that obtained from (1). Values of k_{diff} calculated using eqn. (2) with $2(E_a)_{diff}$ were of the order of 3 – 4 times smaller than those estimated from eqn. (1). Since experimental tests of eqn. (1) have indicated that k_{diff} is over-estimated by a factor of 2 – 3,[3] it appeared that using $2(E_a)_{diff}$ in eqn. (2) gave reasonable estimates of k_{diff}.

$$k_{diff} = 4\pi\kappa a f N_o/1000(D_A + D_B) \qquad (1)$$

$$\ln k_{diff} = (\ln ek/h + \ln T) + (E_a)_{diff}/RT + \Delta S^{\dagger}/R \qquad (2)$$

In this paper we show that reasonably good agreement between k_{diff} calculated from (1) and (2) is obtained using $(E_a)_{diff}$ in eqn. (2) if $\Delta S^{\dagger}$ for the formation of the encounter complex is taken into account. Diffusion activation energies are reported for a number of aromatic compounds in AN, DMF and dimethylsulfoxide (DMSO).

RESULTS AND DISCUSSION

The measurement of activation energies for diffusion. The initial measurements involved the temperature dependence of the linear sweep voltammetry (LSV) peak currents for reversible electrode processes (3).[1] The peak current is given by (4) where n is the number of electrons per mol transferred,

$$A \pm ne^- \rightleftarrows A^{\mp n} \qquad (3)$$

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$$i_p = 0.4463nFAC_A(nF/RT)^{1/2}v^{1/2}D_A^{1/2} \qquad (4)$$

F the Faraday, A the electrode area, C_A the substrate concentration, and D_A the diffusion coefficient. At a given sweep rate (v) and C_A (substrate concentration) at a particular electrode (4) at a particular electrode (4) reduces to (5) where c is a constant. Thus, the temperature dependence of D_A can be obtained by correlating $(i_p)^2T$ as a function of $1/T$.

$$D_A = c(i_p)^2T \qquad (5)$$

Values of $(E_a)_{diff}$ obtained in this manner had standard deviations as great as ±20 %. We therefore abandoned the LSV measurements.

We find that chronoamperometry[4,5] measurements result in $(E_a)_{diff}$ values which are more reproducible. The method is based upon the Cottrell equation (6) which describes the current-time response of the reversible charge transfer (3) to a potential step from a potential where reaction does not take place to the potential region where (3) is diffusion controlled. In practice the latter can be accomplished by stepping about 200 – 300 mV beyond the LSV peak potential. Since D_A is the only factor on the right hand side of (6) that depends upon the temperature, D_A is given by (7) where c' is a constant.

$$i(t) = nFAD_A^{1/2}C_A/\pi^{1/2}t^{1/2} \qquad (6)$$

$$D_A = c'(it^{1/2})^2 \qquad (7)$$

The term in parentheses, $it^{1/2}$, is conveniently measured. In this study we have measured the current at 1.0 *ms* intervals beginning 5 *ms* after the potential step until 10 *ms* after the step.

Measurement precision. The 6 $(it^{1/2})$ values obtained from each current-time curve typically had standard deviations of the order of ±0.2 %. Each relative D_A value, eqn. (7), involved three sets of 10 current-time curves. The standard deviation in the mean $(it^{1/2})$ value for the 30 curves was in general less than ±0.5 %.

Table 1. Relative diffusion coefficients and activation energies for diffusion of aromatic compounds in DMF.[a]

Compound	$10^5D/\mathrm{cm^2\,s^{-1}}$ [b]	$(E_a)_{diff}$ [c]
4-Cyanopyridine	1.14	2.55(0.01)
Nitrobenzene	1.08	2.38(0.16)
Anthracene	0.891	2.46(0.21)
Phenazine	0.758	2.38(0.04)
Nitromesitylene	0.727	2.01(0.06)
Fluoren-9-one	0.671	2.75(0.01)
9-Phenylanthracene	0.521	2.50(0.03)

[a] Determined by chronoamperometry. [b] Values at 298 K. [c] Based on measurements at 0, 20 and 40 °C in solvent containing Bu_4NBF_4 (0.1 M). Measurements with nitrobenzene were made on both mercury and platinum electrodes, mercury electrodes were used for 9-phenylanthracene and anthracene, and platinum electrodes were used for all other compounds. The numbers in parentheses refer to the standard deviations in two or more measurements.

Activation energies for diffusion of aromatic compounds in DMF, AN and DMSO. The data obtained from measurements made at 0° and about 20 and 40 °C are summarized in Table 1 (DMF), Table 2 (AN) and Table 3 (DMSO). The temperatures were known in all cases to ±0.2 °C. The numbers in parentheses refer to the standard deviations, usually with 3 or more determinations. More detail of a particular determination is given in Table 4 for measurements during the reduction of nitromesitylene in DMSO. In this case $(E)_{diff}$ was observed to be equal to 3.29 kcal/mol with a standard deviation of ±0.09. The coefficients for the Arrhenius correlations were in all cases greater than 0.999.

The diffusion coefficients listed in Tables 1 – 3 are from relative values obtained from relative i^2

Table 2. Relative diffusion coefficients and activation energies for diffusion of aromatic compounds in AN.[a]

Compound	Process	$10^5D/\mathrm{cm^2\,s^{-1}}$ [b]	$(E_a)_{diff}/\mathrm{kcal\,mol^{-1}}$
Nitrobenzene	Reduction	1.983	1.99(0.01)
Nitromesitylene	Reduction	1.607	2.04(0.06)
Fluoren-9-one	Reduction	1.581	1.95(0.08)
Thianthrene	Oxidation	1.415	1.95(0.13)
4,4′-Dimethoxybiphenyl	Oxidation	1.386	2.10(0.10)
Tris-*p*-tolylamine	Oxidation	0.936	1.98(0.15)

[a] For conditions see Table 1. Measurements were made on platinum electrodes. [b] At 298 K.

Table 3. Relative diffusion coefficients and activation energies for diffusion of aromatic compounds in DMSO.[a]

Compound	$10^5 D/\mathrm{cm^2\,s^{-1}}$[b]	$(E_a)_{\mathrm{diff}}$/kcal mol^{-1}
Nitrobenzene	0.471	3.02(0.22)
Nitromesitylene	0.367	3.29(0.09)
Phenazine	0.315	3.39(0.05)
Fluoren-9-one	0.279	3.44(0.02)

[a] For conditions see Table 1. Measurements were made on platinum electrodes. [b] At 298 K.

values according to eqn. (6). The values reported were obtained using the value reported[6] for nitrobenzene in DMF at 298 K, *i.e.* 1.08×10^{-5} cm^2/s.

Comparison of diffusion parameters in AN, DMF and DMSO. The diffusion coefficients measuremed in each solvent encompassed about a 2-fold variation. However, it is interesting to note that in DMF and AN there does not appear to be any relationship between D and $(E_a)_{\mathrm{diff}}$. In fact, in AN $(E_a)_{\mathrm{diff}}$ appears to be independent of the particular compound upon which measurements were made. The mean value was 2.00 kcal/mol with a standard deviation of only ±0.06 kcal/mol. The variations were greater in DMF and the mean value was 2.43 ± 0.22 kcal/mol. On the other hand. decreases in D were accompanied by increases in $(E_a)_{\mathrm{diff}}$ in DMSO. In this case a reasonably good correlation of ln D *vs.* $(E_a)_{\mathrm{diff}}$ was obtained as would be expected from the Arrhenius-like equation (8).

$$D=(\mathrm{constant})\exp(-E_a)_{\mathrm{diff}}/RT \tag{8}$$

Measurements were made on nitrobenzene (NB), nitromesitylene (NM) and fluoren-9-one (FL) in all three solvents. The relative viscosities of the solvents are 1.00:2.33:5.75 (AN – DMF – DMSO). According to the Stokes-Einstein relationship (9), in which k is Boltzmann's constant and r is the radius of the molecule, D^{-1} should be linearly related to the viscosity η. The relative D^{-1} for FL were 1.00:2.36:5.67 (AN – DMF – DMSO) in almost exact agreement with the prediction based on eqn. (9). For NB and NM the correspondence was not as good. The ratios of relative D^{-1} were 1.00:1.73:4.21 and 1.00:2.21:4.38, respectively.

$$D=kT/6\pi\eta r \tag{9}$$

Table 4. Activation energy determinations for the diffusion of nitromesitylene in DMSO.[a]

Run	$(E_a)_{\mathrm{diff}}$/kcal mol^{-1}	r[b]
1	3.16	−1.0000
2	3.34	−1.0000
3	3.33	−0.9998
4	3.23	−0.9998
5	3.21	−1.0000
6	3.39	−0.9999
7	3.36	−0.9990

[a] For conditions see Table 1. Measurements were made on platinum electrodes. [b] The linear regression correlation coefficient for data obtained at 0, 20, and 40 °C.

The activation energy for diffusion and the rate constants for bimolecular diffusion controlled reactions. It has been proposed that during the process of diffusion the motion of one molecule past another demands a free energy lying between those required by the two molecules in their separate viscous flows.[7] This served as the basis for proposing that if a diffusion controlled reaction has zero entropy of activation, eqn. (2) could be used to estimate k_{diff} by taking $(E_a)_{\mathrm{diff}}$ to be the average activation energy for the two species reacting in the bimolecular reaction.[1]

Benson[8] has treated the formation of collision pairs as an equilibrium (10) and from calculated mean life times and rates of formation, estimated equilibrium concentrations of AB. The conclusion was drawn that the entropy of the process is given by eqn. (11) and is equal to about −2.5 cal/K mol when r_{AB} is 4 Å and that this is an underestimation of the entropy of formation of chemically reacting pairs. Another approach to estimate ΔS for reaction (10) involves assuming that ΔH for the formation of the encounter pair is zero and that the cratic entropy change (ΔS_c) for bringing the pair together is given by eqn. (12) where [M] is the molarity of the solvent.[9] The values of ΔS_c for the solvents used in this study are −5.86, −5.08 and −5.26 cal/K mol for AN, DMF and DMSO, respectively.

$$\mathrm{A}+\mathrm{B}\rightleftarrows\mathrm{AB} \tag{10}$$

$$\Delta S=R\ln(8r_{AB}{}^3N/1000) \tag{11}$$

$$\Delta S_c=-R\ln[\mathrm{M}] \tag{12}$$

Some observed values of activation parameters for reactions believed to be diffusion controlled are

Table 5. Activation parameters for some diffusion controlled reactions.

Reaction	Solvent	E_a/kcal mol^{-1}	$\Delta S^{\dagger}$/cal K^{-1} mol^{-1}
$2\,I \rightarrow I_2$[a]	CCl_4	3.2	−5
β-Naphthylamine + CCl_4	cyclohexene	2.5	−7
(Fluoresence quenching)[b]	iso-octane	1.6	−8
tert-Butyl radical Self termination[c]	AN	2.03 ± 0.2	−7.24
Triplet energy transfer from indeno[2,1-*a*]indene[d]	AN	1.72 ± 0.3	−7.91

[a] Data from Ref. 10 cited in Ref. 8. [b] Data from Ref. 11 cited in Ref. 8. [c] Data from Ref. 12 based on kinetic data reported in Ref. 13. [d] Data from Ref. 12.

gathered in Table 5. In all cases, $\Delta S^{\dagger}$ was found to be more negative than −5 cal/K mol and also more negative than ΔS for reaction (10) calculated either by eqn. (11) or (12). The most pertinent data regarding diffusion controlled reactions in the solvents used in this study are those reported by Saltiel *et. al.*[12] and by Schuh and Fischer.[13] The self termination reaction of *tert*-butyl radical was observed to be diffusion controlled in a number of aprotic solvents.[13] Activation entropies were observed to vary in the range, −3.65 to −7.24 cal/K mol.[12] In general, for the aprotic solvents $\Delta S^{\dagger}$ was observed to be roughly equal to 4/3 ΔS_c. It was concluded that the activation entropy for an encounter of hydrocarbon solutes in nonhydroxylic solvents reflects more ordering in the solvent than is required for the fully formed encounter complex.[12]

It is interesting to compare $\Delta S^{\dagger}$ for the two reactions reported in acetonitrile (Table 5) with those calculated from eqn. (2) using the $(E_a)_{\text{diff}}$ data in Table 2 and k_{diff} calculated using eqn. (1). The k_{diff} and $\Delta S^{\dagger}$ calculated in this manner are summarized in columns 3 and 4 of Table 6. In AN, $\Delta S^{\dagger}$ varied from −7.28 to −8.80 cal/K mol a mean value of −7.86 ± 0.54 cal/K mol. The values of $\Delta S^{\dagger}$ determined for the self termination of *tert*-butyl

Table 6. Second order rate constants and entropies of activation for diffusion controlled reactions.

Compound	Solvent	$10^{-9}k_{\text{diff}}$/ M^{-1}s^{-1} [a]	$\Delta S^{\dagger}_{298}$/ cal K^{-1} mol^{-1} [b]	$10^{-9}k_{\text{diff}}$/ M^{-1}s^{-1} [c]
4-Cyanopyridine	DMF	8.64	−6.50	7.54
Nitrobenzene	DMF	8.19	−7.18	10.1
Anthracene	DMF	6.75	−7.29	8.78
Phenazine	DMF	5.75	−7.88	10.1
Nitromesitylene	DMF	5.51	−9.21	18.8
Fluoren-9-one	DMF	5.09	−6.88	5.38
9-Phenylanthracene	DMF	3.95	−8.22	8.21
Nitrobenzene	AN	15.0	−7.28	11.5
Nitromesitylene	AN	12.2	−7.53	10.6
Fluoren-9-one	AN	12.0	−7.86	12.3
Thianthrene	AN	10.7	−8.09	12.3
4,4′-Dimethoxybiphenyl	AN	10.5	−7.62	9.54
Tris-*p*-tolylamine	AN	7.09	−8.80	11.7
Nitrobenzene	DMSO	3.57	−6.68	3.02
Nitromesitylene	DMSO	2.78	−6.27	1.92
Phenazine	DMSO	2.39	−6.24	1.62
Fluoren-9-one	DMSO	2.11	−6.32	1.48

[a] Calculated from eqn. (1) assuming $a = 5$ Å and κ and f are unity. $D_A + D_B$ was taken to be twice D for the compound. [b] Calculated from eqn. (2) using k_{diff} from the previous column. [c] Calculated from eqn. (2) using $\Delta S^{\dagger} = 4/3\ \Delta S_c$.

and the triplet quenching of indeno[2,1-*a*]-indene in AN were −7.24 and −7.91 cal/K mol, respectively.

The discussion in the previous paragraph suggests that eqn. (2) will give reliable estimates of k_{diff} if proper account is taken of $\Delta S^\dagger$. The original suggestion[1] of assuming that $\Delta S^\dagger$ is zero obviously gives erroneous results. Available data[12] suggests that a best estimate of $\Delta S^\dagger$ for the diffusion controlled reaction is obtained from 4/3 ΔS_c. The k_{diff} in the last column of Table 6 were calculated from eqn. (2) using the pertinent $(E_a)_{\text{diff}}$ and ΔS_c assuming that $\Delta S^\dagger = 4/3\ \Delta S_c$. In AN this resulted in $k_{\text{diff}} = 1.13\ (\pm 0.11) \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$ at 298 K. The value reported for the self termination of *tert*-butyl was $6.7 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$ (at 293 K)[13] and for the triplet quenching of indeno[2,1-*a*]indene was $1.62 \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$ (at 303 K).[12]

In conclusion, we can compare the assumptions involved in the use of eqns. (1) and (2). For (1) κ and f are assumed to be unity and a must be estimated. The assumptions were made for the k_{diff} in column 3 of Table 6 and a was arbitrarily taken to be 5 Å. When using eqn. (2) the only assumption necessary is the value of $\Delta S^\dagger$ and good experimental data are available for this purpose.

EXPERIMENTAL

The solvents containing the supporting electrolyte, Bu_4NBF_4 (0.1 M) were passed through a column of neutral alumina before dissolving the substrate (2.0 mM). The chronoamperometric experiments were conducted using potential steps of 600 mV with the LSV peak potential for the compound centered in this interval. The apparatus for data acquisition was the same as that used in other recent work from this laboratory.[14]

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