Short Communications

Application of Transition State Theory to Estimate Diffusion Controlled Bimolecular Reaction Rate Constants

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Diffusion controlled bimolecular rate constants can be calculated from eqn. (1) which is due to Smoluchowski[1] and Debye.[2] In (1) N_o is Avogadro's number, κ is a symmetry number equal to 1 for collisions between unlike molecules and f is related to the potential energy of interaction and is taken to be 1 for reactions between neutral molecules. In order to calculate k_{diff} it is necessary to estimate a, the sum of the effective radii of reactants, and $(D_A + D_B)$, the mutual diffusion coefficients. Approximations are involved in the estimation of these parameters and an independent means of arriving at k_{diff} is desirable.

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

The approach considered here is to apply transition state theory,[3,4] to the diffusion controlled reaction. In order to do this, a modification is necessary. The energy maximum on the reaction coordinate must be assumed to correspond to a *pre-collision site* ("transition state"), further progress along the coordinate results in a decrease in energy as the species begin to interact. According to this model the activation energy $(E_a)_{diff}$ corresponds to that necessary for the reactants to diffuse to the pre-collision site. Since there is no interaction between the reactants in the "transition state", the entropy change for the process is that of random diffusion, *i.e.* $\Delta S^{\ddagger}_{diff} = 0$. Under these conditions, transition state theory provides us with a direct relationship between $(E_a)_{diff}$ and k_{diff} (eqn. 2) where the term k/h is Boltzmann's constant divided by Planck's constant. Thus, in order to calculate k_{diff} it is only necessary to determine $(E_a)_{diff}$. The latter is readily determined by electrochemical techniques without

the necessity of having access to absolute values for any quantities.

$$\Delta S^{\ddagger}_{diff} = 0 = R(\ln k_{diff} - \ln ek/h - \ln T) + (E_a)_{diff}/T \qquad (2)$$

$$D = \tfrac{1}{2}l^2 kT/h \exp(-\Delta G^{\ddagger}_{diff}/RT) \qquad (3)$$

Diffusion can be treated as a kinetic process to obtain (3),[4,5] the right hand side of which is identical, with the exception of the jump distance (l), to the Eyring equation.[3,4] Thus, the diffusion coefficient (D) can be considered as a rate constant. The form of (3) suggests that the energy of activation for diffusion $(E_a)_{diff}$ can be obtained by correlation of $\ln D$ vs. $1/T$ as in the Arrhenius relationship.[4] In fact it has been suggested that $\Delta S^{\ddagger}_{diff}$ does not differ appreciably from zero.[4]

Activation energies of reactions following charge transfer at electrodes have recently been derived without the explicit knowledge of the rate constants.[6] Similarly, any relationship providing relative values of D can be used to determine $(E_a)_{diff}$. The peak current I^p during linear sweep voltammetry is related to D and T, among other quantities by eqn. (4).[7] The relationship required for determining $(E_a)_{diff}$ is given by (5) which suggests that the activation energy for diffusion can be derived from the slope of a correlation of $\ln(I^p)^2 T$ as a function of $1/T$. The principle advantage of such a procedure is that no absolute quantities are necessary and this greatly increases the precision in the derived values.

$$I^p = f(D^{\frac{1}{2}}/T^{\frac{1}{2}}) \qquad (4)$$

$$D \sim (I^p)^2 T \qquad (5)$$

The procedure outlined above was used to determine $(E_a)_{diff}$ for several processes in N,N-dimethylformamide (DMF) and acetonitrile (AN). Measurements were made over ~ 40 K and all correlation coefficients were > 0.999. The data are summarized in Table 1. The D values were estimated from the relative peak currents and adjusted to the value reported for nitrobenzene.[9]

The method being proposed for the estimation of k_{diff} for a reaction such as (6) is to obtain $(E_a)_{diff}$ for

Table 1. Activation energies for diffusion.

Compound	Solvent	$10^5 D^a/cm^2 s^{-1}$	$(E_a)_{diff}/(kcal/mol)^b$
Nitrobenzene	DMF	1.02	2.6(0.3)
Anthracene	DMF	0.89	2.7(0.2)
9-Phenylanthracene	DMF	0.48	3.0(0.3)
Nitrobenzene	AN	2.74	2.3(0.4)

[a] The value of D for introbenzene in DMF was taken from ref. 9 and the other values were calculated from the relative peak currents. [b] The numbers in parentheses are the standard deviations in three determinations.

Table 2. Diffusion controlled bimolecular rate constants.

Compound	Solvent	$10^9 k/M^{-1}s^{-1}$ calc. from eqn. (2)[a]		from eqn. (1)[b]	
		$(E_a)_{diff}$	$2(E_a)_{diff}$	$10^9 k/M^{-1}s^{-1}$	$E_a/(kcal/mol)$
Nitrobenzene	DMF	210	2.6	7.7	4.6
Anthracene	DMF	180	1.8	6.7	4.6
9-Phenylanthracene	DMF	110	0.67	3.6	5.0
Nitrobenzene	AN	350	7.1	21.0	4.0

[a] Calculated using eqn. (2), the first column corresponds to assuming E_a equal to $(E_a)_{diff}$ and the second to $2(E_a)_{diff}$. [b] The rate constants were calculated from (1) assuming a to be equal to 5 Å and $D_A + D_B$ to be twice the diffusion coefficient of the compound. E_a was calculated neglecting entropy.

both A and B, or suitable models, and to then apply the data in eqn. (2). A comparison of rate constants calculated using (2) and (1) are summarized in Table 2. The values calculated using (1) assumed a to be 5 Å in all cases and that $(D_A + D_B)$ was twice the value of D for the compound on which measurements were made. When experimental values of $(E_a)_{diff}$ are used directly in eqn. (2), the rate constants are considerably larger than those obtained from (1). This also shows up in the activation energies calculated from the latter rate constants assuming zero entropy, i.e. the E_a values are of the order of two times the values of $(E_a)_{diff}$.

$$A + B \rightarrow products \qquad (6)$$

A possible reason for the descrepancy noted above is that $(E_a)_{diff}$ relates to the diffusion of a single molecule when in fact it is the mutual diffusion of two molecule which must arrive to the pre-collision site that must be accounted for. This suggests that the activation energy for a diffusion controlled bimolecular reaction should be greater than $(E_a)_{diff}$ of the species reacting.* The rate constants calculated

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* The activation energy can be viewed as the energy necessary to provide a "hole" in the solvent which must be larger for the transition state than for a single diffusing species.

using (2) with $(E_a)_{diff}$ 2 times the experimental value are in much closer agreement with those obtained from the Smoluchowski-Debye equation. Further work is in progress to refine the $(E_a)_{diff}$ measurements and to evaluate k_{diff} estimated by (1) and (2).

In addition to the approximations already mentioned, there is a further drawback to the use of (1). It is a limiting case of the more general equation (7) where k is the rate constant which would be observed if the concentration of B molecules in the nearestneighbor shell of an A molecule was the same as the average over the whole system.[8] Thus, (1) is only applicable when $k \gg 4\pi a N_o/1000 \, D_{AB}$ where D_{AB} is $(D_A + D_B)$.

$$k_{diff} = 4\pi\kappa a N_o/1000 \, D_{AB}/(1 + 4\pi a N_o/1000 \, D_{AB} \, k^{-1}) \qquad (7)$$

Use of transition state theory cannot be justified on theoretical grounds in any case. The fact that has contributed to the wide use of it is that it works remarkably well in explaining rate phenomena. The extension to the use to diffusion controlled reactions, likewise has no theoretical justification. What is expected to be gained by the new approach is that it provides a consistent way of estimating diffusion controlled rate constants, the only

uncertainty involved being the applicability of the theory itself.

1. Smoluchowski, M. V. *Z. Phys. Chem. (Leipzig) 92* (1917) 129.
2. Debye, P. *Trans. Electrochem. Soc. 82* (1942) 265.
3. Hammes, G. G. *Principles of Chemical Kinetics*, Academic, New York 1978, Chapter 2.
4. Glasstone, S., Laidler, K. J. and Eyring, H. *The Theory of Rate Processes*, McGraw-Hill, New York 1941, pp. 522 – 525.
5. Bockris, J. O'M. and Reddy, A. K. N. *Modern Electrochemistry*, Plenum, New York, 1970, Vol. 1, p. 342.
6. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 51.
7. MacDonald, D. D. *Transient Techniques in Electrochemistry*, Plenum, New York 1977, Chapter 6.
8. North, A. M. *Q. Rev. Chem. Soc. 20* (1966) 421.
9. Kojima, H. and Bard, A. J. *J. Am. Chem. Soc. 97* (1975) 6317.

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