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Fast Reactions of Polar Molecules in Processes with No Activation Energy

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The rate constants of ion–molecule and radical recombination reactions involving polar species have been calculated using an intermolecular potential averaged over the molecular orientations. A transition state is proposed in which the two species are confined in a square potential well. The energy of the system within the well is then quantized. Calculations using the square potential well model show that electrostatic effects cannot be ignored for these polar species, and they give good agreement with experimental rate determinations.

Introduction

Two main classes of reactions occur with virtually zero activation energy: the ion–molecule reactions[1] and radical combination reactions.[2]

$$A^+ + B \longrightarrow C^+ + D \qquad (1)$$

$$A\cdot + B\cdot \longrightarrow AB \qquad (2)$$

Both types of reaction have very large rate constants, of the same order of magnitude as the collision frequency, from which we conclude that the activated complex is loosely held together, allowing "free rotation" of the participating molecules.

Eyring, Hirschfelder, and Taylor[1] calculated the rate constant of a reaction of type 1 by transition-state theory, assuming a model for the activated complex such that the two reactant molecules form a rotational state in which the total energy from the centrifugal force of rotation plus the attractive polarization force is a maximum. A similar complex was proposed by Gorin[2] for the recombination of free radicals. In this case, the centrifugal force is opposed by the attractive induced dipole–induced dipole dispersion force between the radicals. Field, Franklin, and Lampe[3] showed that the rate constants of ion–molecule reactions could be calculated by balancing the attractive polarization force against the combined kinetic energy of the ion and molecule at the moment of collision. This theory was later extended by Gioumousis and Stevenson.[4] A similar procedure was carried out by Mahan for radical combination reactions.[5]

When the reacting species are polar, the theory suffers from the disadvantage that the additional attractive forces due to the permanent multipole moments

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[1] H. Eyring, J. O. Hirschfelder, and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936).

[2] E. Gorin, *Acta Physicochim. URSS*, **6**, 691 (1938).

[3] F. H. Field, J. L. Franklin, and F. W. Lampe, *J. Am. Chem. Soc.*, **79**, 2419 (1957).

[4] G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

[5] B. H. Mahan, *ibid.*, **32**, 362 (1960).

in the reactants are not taken into account. The present communication extends the theory to include these forces, and a new model for the transition state is proposed.

The Intermolecular Potential

The long range intermolecular potential between two molecules can be expressed as a sum of three terms, if no electronic overlap takes place.[6]

$$V = V_{\mathrm{ES}} + V_{\mathrm{IND}} + V_{\mathrm{DIS}}$$

V_{ES} represents the electrostatic contribution from the permanent charges and multipole moments on the molecules. V_{IND} is the inductive contribution due to the interaction of the permanent charges and multipole moments on one molecule with the induced multipole moments on the other molecule. V_{DIS} is the dispersion contribution from the interaction of the induced multipole moments on the two molecules. Consider two molecules A and B, one of which has charge e, permanent dipole moment μ_a, permanent quadrupole moment Q_a, etc., and the other has no charge, but permanent dipole moment μ_b, permanent quadrupole moment Q_b, etc. The electrostatic potential contains terms from the charge–dipole, charge–quadrupole, and dipole–dipole interactions, all of which are orientation dependent. If the molecules are in thermal equilibrium, the potential can be averaged over all orientations, and V_{ES} is given in terms of the intermolecular separation by[6]

$$V_{\mathrm{ES}} = -\frac{1}{3kT}\frac{e^2\mu_b^2}{r^4} - \frac{1}{20kT}\frac{e^2Q_b^2}{r^6} - \frac{2}{3kT}\frac{\mu_a^2\mu_b^2}{r^6} - \ldots$$

The inductive potential, averaged over all orientations is

$$V_{\mathrm{IND}} = -\frac{1}{2}\left[\frac{\alpha_b e^2}{r^4} + \frac{2\alpha_b\mu_a^2}{r^6} + \frac{3\alpha_b Q_a^2}{r^8} + \ldots\right] - \frac{1}{2}\left[\frac{2\alpha_a\mu_b^2}{r^6} + \frac{3\alpha_a Q_b^2}{r^8}\right]$$

for cylindrically symetrical molecules, α_a and α_b are the polarizabilities of molecules A and B. The dispersion contribution, again for symetrical molecules is given by

$$V_{\mathrm{DIS}} = -c/r^6 - (\text{terms in } 1/r^8 \text{ and } 1/r^{10})$$

Various values of the constant c have been given;[7] probably the most successful is that due originally to Slater and Kirkwood, but recently reinterpreted.[8,9] The factors n_a and n_b refer to the total numbers of electrons in molecules A and B, and a_0 is the radius of the first Bohr orbit

$$c = {}^3/_2 e^2 a_0^{1/2}\alpha_a\alpha_b/[(\alpha_a/n_a)^{1/2} + (\alpha_b/n_b)^{1/2}]$$

When an ion approaches a polar molecule, only two terms in the intermolecular potential depend on r^{-4}, all others can be neglected, and hence the long range attractive potential is

$$V = -\left(\frac{e^2\mu_b^2}{3kT} + \frac{\alpha_b e^2}{2}\right)1/r^4 = -\lambda_1/r^4$$

When two radicals approach each other, the first term in the potential depends on r^{-6}, and all terms in other powers of r can be neglected. V is therefore given by

$$V = -\left(\frac{2\mu_a^2\mu_b^2}{3kT} + \alpha_b\mu_a^2 + \alpha_a\mu_b^2 + c\right)1/r^6 = -\lambda_2/r^6$$

The Rate of Reaction

The total kinetic energy of the two reactants before collision is ${}^1/_2 m^*u^2$ (m^* is the reduced mass, and u is the relative velocity), assuming thermal equilibrium. If reaction is to occur, the attractive potential must outweigh this kinetic energy, and there will exist a critical separation r_c such that all encounters closer than this lead to activated complex formation. The expressions for r_c in the two types of reactions are therefore

$$r_c^4\ (1) = 2\lambda_1/m^*u^2; \quad r_c^6\ (2) = 2\lambda_2/m^*u^2$$

The microscopic collision cross section σ is given by $2\pi r_c^2$ and the reaction rate constant by $k = 2\pi r_c^2 u$. Hence the two types of reactions have rate constants given by

$$k_1 = 2^{3/2}\pi\lambda_1^{1/2}(m^*)^{-1/2}; \quad k_2 = 2^{4/3}\pi\lambda_2^{1/3}(m^*)^{-1/3}u^{1/3}$$

Radical recombinations have a small temperature dependence due to the remaining term $u^{1/3}$ in the rate expression. The relative thermal velocity in the direction of the line of centers of the radicals is $(8kT/\pi m^*)^{1/2}$, giving

$$k_2 = 2^{11/6}\pi^{5/6}\lambda_2^{1/3}(m^*)^{-1/2}(kT)^{1/6}$$

Alternatively, the molecules in the transition state can be treated as a single entity confined in a square potential well. The energy of the system within the well is quantized, and the various levels are given by $En = n^2h^2/8m^*r^2$. For each state defined by the quantum number n, there exists a value of r such that the total energy E equal to the sum of the attraction

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(6) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, pp 950, 986.

(7) H. Pauly and J. P. Toennies, *Advan. At. Mol. Phys.*, **1**, 195 (1965).

(8) L. Salem, *Mol. Phys.*, **3**, 441 (1960).

(9) C. Mavroyannis and M. J. Stephen, *ibid.*, **5**, 629 (1962)

due to polarization and the quantized energy En is a maximum. For larger values of r the complex breaks up, and for smaller values of r the molecules proceed to reaction. At this critical separation r_c, the total energy E is a maximum so that r_c can be found for each value of n by differentiating E with respect to r and equating to zero.

$$r_c^2\ (1) = \frac{2^4\lambda_1 m^*}{n^2h^2};\quad r_c^4\ (2) = \frac{2^3 \times 3 \times \lambda_2 m^*}{n^2h^2}$$

Substitution of this value of r into the expression for the total energy E gives the value of the critical energy E_c corresponding to each value of n.

$$E_c\ (1) = \frac{n^4h^4}{2^8\lambda_1(m^*)^2};\quad E_c\ (2) = \frac{n^3h^3}{2^{7/2}3^{3/2}\lambda_2^{1/2}(m^*)^{3/2}}$$

The partition function is then found by summing for the complexes in all the possible states n.

$$f_n = \int_{n=0}^{\infty} g_n e^{-Ec(n)/kT}\,\mathrm{d}n$$

The total partition functions of the two types of reaction for the square potential well are

$$f_n\ (1) = 2^3\Gamma(^1/_2)\lambda_1^{1/2}m^*(kT)^{1/2}/h^2$$
$$f_n\ (2) = 2^{10/3}\Gamma(^2/_3)\lambda_2^{1/3}(m^*)(kT)^{2/3}/h^2$$

The rate constant is then found by combining this partition function, which represents the activation energy, with the ratios of the remaining electronic and translational partition functions. The ratio of the vibrational partition functions can be taken as 1 since the vibrational interaction in the transition state is very weak. The rate constants are therefore

$$k_1 = K \times 2^{3/2}\pi^{-3/2}\Gamma(^1/_2)\lambda_1^{1/2}(m^*)^{-1/2} \qquad \text{(A)}$$

$$k_2 = K \times 2^{11/6}\pi^{-3/2}\Gamma(^2/_3)\lambda_2^{1/3}(m^*)^{-1/2}(kT)^{1/6} \qquad \text{(B)}$$

These expressions are of the same form as the ones derived from conventional theory, but differ by powers of π owing to the different description of the transition state. The complete rate expressions, inserting the appropriate values of λ_1 and λ_2, and assuming $K = 1$ are

$$k_1 = \frac{2^{3/2}e}{\pi(m^*)^{1/2}}\left(\frac{\mu_b^2}{3kT} + \frac{\alpha_b}{2}\right)^{1/2} \qquad \text{(C)}$$

$$k_2 = \frac{2^{11/6}\pi^{-5/6}(kT)^{1/6}}{(m^*)^{1/2}}\left(\frac{2\mu_a^2\mu_b^2}{3kT} + \alpha_b\mu_a^2 + \alpha_a\mu_b^2 + \frac{^3/_2 e^2 a_0^{1/2}\alpha_a\alpha_b}{(\alpha_a/n_a)^{1/2} + (\alpha_b/n_b)^{1/2}}\right)^{1/3} \qquad \text{(D)}$$

Comparison with Experiment. Ion–Molecule Reactions

The measurement of the rates of ion–molecule reactions has usually been carried out for nonthermal conditions.[10] The ion under study is accelerated by the applied voltage, and often the original thermal energy of the ion represents only a small fraction of the total energy. The rate expressions given above were derived assuming thermal equilibrium, so that they cannot be applied directly to the reactions occurring in a mass spectrometer. However, an increasing number of ion–molecule reactions are being studied in spectrometers modified to allow thermal equilibrium of the reactant ions,[11] and the results of these studies are suitable for comparison with the theory. Table I shows the calculated and observed rate constants for a series of ion–molecule reactions involving polar molecules. Since the determinations of the rates under thermal equilibrium show that the rate constants are not very different from determinations with accelerated ions,[11–13] a few examples of the latter have been included (shown with an asterisk). Dipole moments were taken from the experimental tables of McClellan,[14] and polarizabilities from Hirschfelder, Curtiss, and Bird.[6]

For molecules with dipole moments greater than 1.0 D., the electrostatic contribution (proportional to $\mu_b^2/3kT$) dominates the attractive intermolecular potential, but molecules with small dipole moments and large polarizabilities have comparable electrostatic and inductive contributions. The rate constants calculated using the square potential well model are less by a factor of about 5 than those calculated using the original rotational model, and as Table I shows, the agreement between the calculated and observed rates is good.

Radical Recombination Reactions

The rate constants of several radical recombinations in the gas phase are known, and these can be compared directly with the theory since the free radicals do not usually possess undue excess energy. However, the radicals themselves are not observed, and the rate constants are measured indirectly, so that the accuracy of the experimental measurements is not high.

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[10] F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. Reaction Kinetics*, **1**, 69 (1961).

[11] K. H. Ryan and J. H. Futtrell, *J. Chem. Phys.*, **42**, 824 (1965).

[12] J. C. J. Thynne and A. G. Harrison, *Trans. Faraday Soc.*, **62**, 2468, 2804 (1966).

[13] J. C. J. Thynne, F. K. Amenu-Kpodo, and A. G. Harrison, *Can. J. Chem.*, **44**, 1655 (1966).

[14] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., and London.

Table I: Calculated and Observed Rates of Ion–Molecule Reactions

Ion A	Molecule B	$\alpha_b \times 10^{24}$, cm^3	$\mu_b \times 10^{18}$, esu	$\mu_b^2/3kT \times 10^{24}$	k_1 (calcd), l. mole^{-1} sec^{-1}	k_1 (obsd), l. mole^{-1} sec^{-1}
H_2^+	H_2	0.8	...	...	2.3×10^{11}	4.0×10^{11} [a]
H_2O^+	H_2O	1.4	1.8	26	4.3×10^{11}	3.0×10^{11} [b]
D_2O^+	D_2O	1.4	1.8	26	4.1×10^{11}	2.2×10^{11} [b]
NH_3^+	NH_3	2.3	1.5	18	2.7×10^{11}	3.1×10^{11} [b]
$N_2H_4^+$	N_2H_4	3.4	1.9	29	2.8×10^{11}	0.8×10^{11} [b]
CH_3OH^+	CH_3OH	3.2	1.7	23	2.5×10^{11}	7.2×10^{11} [c]
HCl^+	HCl	2.6	1.2	12	2.3×10^{11}	*2.6×10^{11} [d]
HBr^+	HBr	3.6	0.8	5.0	1.1×10^{11}	*1.3×10^{11} [d]
H_2S^+	H_2S	3.8	0.9	6.5	2.0×10^{11}	*1.1×10^{12} [e]

[a] Reference 11. [b] Reference 12. [c] Reference 13. [d] Reference 4. [e] Reference 10. In the last three entries in the last column, the asterisks denote nonthermal conditions.

Table II: Radical Recombination Reactions; Properties of the Reactants

Radical A and B	$\mu \times 10^{18}$, esu	$\alpha \times 10^{24}$, cm^3	n	$2\mu^4/3kT \times 10^{59}$, erg cm^6	$2\alpha\mu^2 \times 10^{59}$, erg cm^6	$c \times 10^{59}$, erg cm^6
$CH_3\cdot$	...	2.2	9	...	...	12.2
$CCl_3\cdot$	1.0	7.8	57	1.2	1.6	205
$CF_3\cdot$	1.5	2.6	33	6.1	1.2	10.7
$C_2HCl_4\cdot$	1.2	11.4	81	2.5	3.3	443
$C_2H_2Cl_3\cdot$	1.2	9.4	65	2.5	2.7	290
$C_2H_3Cl_2\cdot$	2.0	7.6	49	19.3	6.1	182

Table III: Calculated and Observed Free Radical Combination Rate Constants

Radical A and B	$\lambda_2^{1/3} \times 10^{20}$	k_2(calcd), l. mole^{-1} sec^{-1}	k_2(obsd), l. mole^{-1} sec^{-1}
$CH_3\cdot$	5.0	8.9×10^{10}	2.3×10^{10} [a]
$CCl_3\cdot$	12.8	7.9×10^{10}	8.0×10^{10} [b]
$CF_3\cdot$	5.7	5.3×10^{10}	2.3×10^{10} [c]
$C_2HCl_4\cdot$	16.5	8.9×10^{10}	3.0×10^{9} [d]
$C_2H_2Cl_3\cdot$	14.3	8.3×10^{10}	3.0×10^{10} [d]
$C_2H_3Cl_2\cdot$	12.7	8.7×10^{10}	8.0×10^{9} [d]

[a] Reference 16. [b] Reference 17. [c] Reference 18. [d] Reference 19.

In Table II, the relevant data are listed, as are the contributions to the intermolecular potential from the electrostatic, inductive, and dispersive effects. Planar trihalomethyl radicals have zero dipole moment, but even a small departure from planarity will produce an appreciable dipole moment. Large departures from planarity are to be expected in the transition state, so the radicals have been assigned dipole moments 10% less than the dipole moment of the corresponding hydrocarbon.[14] For instance, trifluoromethyl radicals have been given a dipole moment 10% less than fluoroform. Radical polarizabilities have been estimated from the known atom polarizabilities.[15]

By far the largest contribution to the long-range interradical attraction comes from the dispersion force. The induction contribution is small in all cases, but the electrostatic effect is not negligible when the radicals have large dipole moments and small polarizabilities, as have trifluoromethyl radicals. The calculated and observed rate constants are compared in Table III.[16–19] Considering the assumptions and approximations used in deriving (D) the agreement between the theoretical and experimental rates is good, particularly since the possible experimental errors are large. The rate constants calculated using the square potential well method are lower by a factor of

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(15) J. A. A. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., Amsterdam, 1953, p 90.

(16) A. Shepp, *J. Chem. Phys.*, **24**, 939 (1956).

(17) J. M. Tedder and J. C. Walton, *Chem. Comm.*, 140 (1966).

(18) P. B. Ayscough, *J. Chem. Phys.*, **24**, 944 (1956).

(19) P. B. Ayscough, F. S. Dainton, and B. E. Fleischfresser, *Trans. Faraday Soc.*, **62**, 1838 (1966).

about 6 from the constants derived from the original rotational model.

It has been pointed out by Johnston and Goldfinger[20] that serious perturbations must arise in the transition state from interactions between atoms attached to the bonding centers. This is particularly so for a radical recombination.

Conclusions

In the polar ion–molecule reactions, the major factor in the attraction of the two species is the electrostatic potential due to the permanent charge on the ion and the permanent dipole on the molecule, but the inductive contribution is not negligible. In combination reactions of polar radicals, the London dispersion force represents the major factor in the radical–radical attraction. The theory enables rate constants for this kind of process to be estimated, even when the reactants have permanent electrostatic multipoles, and good agreement with experiment is observed. It would be interesting to see the result of a reaction between an ion and a polar radical when the electrostatic and dispersion forces may be of comparable magnitude.

Acknowledgment. The author thanks Dr. C. R. Allen and Professor J. M. Tedder for helpful discussions.

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[20] H. S. Johnston and P. Goldfinger, *J. Chem. Phys.*, **37**, 700 (1962).

Kinetic Studies of Permanganate Oxidation Reactions. II. Reaction with Ferrocyanide Ion

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The kinetics of the reaction between permanganate and ferrocyanide have been studied in phosphate buffers in the pH range 1.6–6.30. Two pH-independent regions are observed and have been interpreted in terms of a reaction specifically between permanganate ion and the ion pair $[KFe(CN)_6]^{3-}$ in the pH 6 region, giving way to a reaction between permanganate and $[H_2Fe(CN)_6]^{2-}$ in the pH 2 region. The reaction is faster in the low pH region. The pertinent activation parameters have been evaluated for both pH regions. The rate constants obtained experimentally in these pH regions agree quite well with those calculated from Marcus' theory. No specific cation effects on the rate are observed when the reaction is studied in sodium ion buffers as opposed to potassium ion buffers.

Introduction

Redox reactions involving multiequivalent reductions have been of interest for some time.[2] The work of Sutin and co-workers on the kinetics of the oxidation of Fe(II) ions by permanganate and other oxidizing agents[3] and the results of Sheppard and Wahl[4] on the MnO_4^-–MnO_4^{2-} reaction concerning the cation bridge mechanism stimulated interest in the research here presented. This reaction must be of the outer-sphere variety, since both reactants are inert and stable and,

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[1] This paper is based on a dissertation submitted by M. A. Rawoof to the faculty of Howard University in partial fulfillment of the requirements for the Ph.D. degree.

[2] J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961).

[3] B. M. Gordon, L. L. Williams, and N. Sutin, *J. Am. Chem. Soc.*, **83**, 2061 (1961).

[4] J. C. Sheppard and A. C. Wahl, *ibid.*, **79**, 1020 (1957).