

the probable reliability of the results should be examined critically.

As is obvious from eq. 5, the computed value of D can be no more accurate than the estimate for $\sqrt{\phi q_0 k}$. The actinometric and spectrophotometric methods used to determine q_0 are almost certainly reliable to a very few per cent. Although values of ϕ and k at 38° are based on single investigations, the values at 25° have been discussed previously⁵ and shown to be consistent with a considerable body of quantitative data collected in several different laboratories. It hardly seems that D can be uncertain by more than 20% because of uncertainties in these other quantities.

The uncertainty in D is also proportional to that in (r_0/ρ') .² Accuracy of this quantity depends upon the sensitivity of the fit in Fig. 3 and 4 to horizontal displacements of the theoretical curve. These figures clearly do not allow variations of more than 0.10 in $\log(r_0/\rho')$; such variations would change calculated values of D by a factor of 1.6.

The above analysis indicates that the reported value of D for 25° can hardly be uncertain by more than a factor of 2.

It is somewhat surprising to find that our values of diffusion coefficients of iodine atoms are about a factor of 5 larger than those of iodine molecules under the

same conditions. Most persons would probably have predicted more nearly comparable diffusion coefficients for the two species.

The discrepancy between prediction and observation is in the direction to be anticipated if iodine atoms were being transported from illuminated to dark areas by other mechanisms than diffusion. The discussion under Corrections indicates that such transport would require currents with components in excess of 10^{-3} cm./sec. perpendicular to the light beams. All of our attempts to analyze the system fail by orders of magnitude to suggest the presence of such currents.

The significance of these results to the theory of diffusion-controlled reactions is discussed in a separate paper.¹⁰

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Validity of Equations Derived for Diffusion-Controlled Reactions

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The diffusion coefficient of iodine atoms in carbon tetrachloride is between two and three times larger than that calculated from the rate constant for combination with the use of customary equations for diffusion-controlled reactions. The discrepancy could be removed by assuming that only one collision in three or four leads to reaction, but several arguments oppose this explanation. A small error may be introduced into the derivation by the assumption that a reactive atom can be treated as a stationary sink, but this effect probably acts in a direction to magnify the observed discrepancy. The data indicate the existence of specific potential barriers that exert nonisotropic influences on the direction of relative displacements when atoms are separated by a molecular diameter or less.

Introduction

If a chemical reaction takes place in a system not at thermodynamic equilibrium, there is a net flux of potentially reactive molecules toward each other. This flux is associated with a concentration gradient. The effect is important only for very reactive species.

Smoluchowski¹ treated this problem as a diffusion into an absorbing sink. For a recombination reaction of indistinguishable species, X, the Smoluchowski equation indicates that for particles a sufficiently long time after their formation the observed rate constant, k' , is given by

$$k' = 4\pi\rho DN/1000 \quad (1)$$

In this equation, ρ is the encounter diameter of reactants in cm., D is the diffusion coefficient of reactants in cm.²/sec., and N is Avogadro's number. The factor $N/1000$ is included so that k' will be in l./mole sec. The rate constant is defined kinetically by the equation

$$k'[X]^2 = -\frac{1}{2} \frac{d[X]}{dt} = \frac{d[X_2]}{dt} \quad (2)$$

The derivation uses the boundary condition that the concentration of potential reactants goes to zero at a distance ρ from the center of another reactant. Although eq. 1 is usually presented as applicable to diffusion-controlled reactions, Collins² has pointed out that this boundary condition cannot be correct even for species that always react instantaneously upon encounter. Noyes³ has derived the more general equation

$$k' = [4\pi\rho DN/1000]/[1 + 4\pi\rho DN/1000k_c] \quad (3)$$

where k_c is the rate constant that would describe the reaction if the distribution of X molecules were that given by equilibrium statistical mechanics and had not been perturbed by reaction.

If the reactive species, X and Y, are distinguishable, the D in eq. 1 and 3 should be replaced by D' , the coefficient for relative diffusion, where $D' = D_X + D_Y$. The apparent discrepancy of a factor of two between the equations involves a symmetry correction like that in any discussion of interactions between like and unlike species.

(2) F. C. Collins, *J. Colloid Sci.*, **5**, 499 (1950).

(3) R. M. Noyes, *Progr. Reaction Kinetics*, **1**, 129 (1961).

(1) M. von Smoluchowski, *Z. physik. Chem.*, **92**, 129 (1917).

Equation 3 is unusual in that it is susceptible to direct experimental test without disposable parameters. The three quantities k' , ρ , and D have all been measured independently for iodine atoms in carbon tetrachloride, and k_c can be estimated with sufficient accuracy for the small correction introduced by the denominator.

Test of Equation

Table I illustrates a test of the validity of eq. 3 for the recombination of iodine atoms in carbon tetrachloride at 25 and 38°. The first column of figures contains the best measured or estimated values for the four quantities in the equation. The rate constant, k' , is based on measurements of quantum yield⁴ and average lifetime⁵; the value at 25° is supported by independent types of observation in other laboratories.⁵ The encounter diameter, ρ , is twice the van der Waals radius quoted by Pauling.⁶ The diffusion coefficient, D , is based on photochemical space intermittency measurements.⁷ The equilibrium distribution rate constant, k_c , is computed from the kinetic theory of gases with the equation

$$k_c = 2(\pi RT/M)^{1/2} \rho^2 N/1000 \quad (4)$$

The entries in the last column of Table I are values for each of these four quantities computed by eq. 3 with the use of the indicated values for the other three quantities. The validity of eq. 3 is measured by the extent to which the entries in the two columns agree within the anticipated errors of measurement.

TABLE I
TEST OF EQUATION FOR DIFFUSION-CONTROLLED REACTIONS

Quantity	Measured or assumed value	Calculated by eq. 3 from other three values
		25°
$10^{-9}k'$, l./mole sec.	8.2	17.7
$10^8\rho$, cm.	4.30	1.59
10^5D , cm. ² /sec.	8.0	2.96
$10^{-9}k_c$, l./mole sec.	55.2	12.0
	38°	
$10^{-9}k'$, l./mole sec.	13.2	22.8
$10^8\rho$, cm.	4.30	1.93
10^5D , cm. ² /sec.	11.8	5.30
$10^{-9}k_c$, l./mole sec.	56.4	19.9

Discussion

The entries in Table I clearly fail to satisfy eq. 3 exactly. The diffusion coefficient of iodine atoms is between two and three times larger than the equation would predict from the observed rate of combination. The same conclusion in less exaggerated form was indicated by less extensive studies in hexane.⁸

If the methods of measuring the quantities k' and D are as valid as is believed, the failure either involves the assumed values of ρ or k_c or else is inherent in the assumptions used to derive the equation. These possibilities are considered in turn.

Encounter Diameter.—The ρ values in the last column of Table I are even less than the internuclear separation in molecular iodine. It is clearly impossible

to obtain consistency by modifying the assumed size of the reactants.

Equilibrium Rate Constant.—Application of eq. 3 requires an estimate of k_c , the rate constant that would apply if an equilibrium distribution of iodine atoms could be maintained. Table I shows that consistency is possible if k_c is smaller by a factor of three or four than the value calculated for collisions in the gas phase. Such a number is equal to the observed k' for reaction in hexane⁸ and is certainly much less than the value of k_c in that solvent.

Since Rabinowitch⁹ has pointed out that for nonreactive species the number of collisions in liquid phase is, if anything, *greater* than the number for the same concentration in gas phase, the discrepancy cannot be explained in this way.

Since the iodine atoms are in doublet states, the data in Table I could be rationalized by assuming that interaction as a triplet was repulsive and thereby introducing a statistical factor of $1/4$ into the estimated value of k_c . However, probably most chemists believe that for atoms as heavy as iodine such factors would not be important in condensed phase. Thus, the quantum yield data of Meadows and Noyes¹⁰ indicate that when an iodine molecule in solution is excited to a metastable electronic state, it undergoes predissociation so rapidly that the excess energy of the quantum appears as kinetic energy of the $^3P_{1/2}$ atoms produced.

Russell and Simons¹¹ observed a third-order rate constant of 1.02×10^{11} l.²/mole² sec. for the recombination of iodine atoms in dilute carbon tetrachloride vapor at 20°. Since the computed rate constant for collisions of iodine atoms, k_c , is 5.47×10^{10} l./mole sec., these observations indicate that the rate of recombination is equal to the rate of such collisions multiplied by the probability that the center of a carbon tetrachloride molecule lies within a volume of 3000 \AA^3 around the colliding pair. Since gaseous carbon tetrachloride is so very efficient at promoting recombination, values of k_c in this solvent must be much greater than those given in the last column of Table I.

Stationary Sink Approximation.—The derivation of eq. 1 and 3 assumes diffusion into a stationary sink. Since the sink is a potentially reactive molecule, it is actually diffusing itself.

As long as the relative position of two specific indistinguishable molecules is all that is of interest, it is certainly permissible to regard one as stationary and to assume that the other undergoes random displacements at twice its actual frequency. The derivation of the equations extends the same idea by regarding the reference molecule as fixed and assuming that the other molecules diffuse with twice their actual diffusion coefficients.

The correct treatment with a fixed reference molecule would be to assume that the surrounding molecules made half of their displacements individually in random directions and that half of the displacements were correlated in time though still in random directions. Since the radial distribution function is concave to the r -axis, random displacements that are correlated in time will

(4) F. W. Lampe and R. M. Noyes, *J. Am. Chem. Soc.*, **76**, 2140 (1954).

(5) H. Rosman and R. M. Noyes, *ibid.*, **80**, 2410 (1958).

(6) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 260.

(7) S. A. Levison and R. M. Noyes, *J. Am. Chem. Soc.*, **86**, 4525 (1964).

(8) G. A. Salmon and R. M. Noyes, *ibid.*, **84**, 672 (1962).

(9) E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1225 (1937).

(10) L. F. Meadows and R. M. Noyes, *J. Am. Chem. Soc.*, **82**, 1872 (1960).

(11) K. E. Russell and J. Simons, *Proc. Roy. Soc. (London)*, **A217**, 271 (1953).

have a greater tendency to bring potential reactants together than will uncorrelated displacements.

The same qualitative conclusion is suggested by noting that for a very efficient stationary sink the radial distribution function is nearly the same whether the diffusion coefficient of species toward it is D or $2D$, although of course the flux is different for the two cases. Any diffusive motion of the reference molecule in a sink will permit it to sample regions of higher concentration of potential reactants and should increase reactivity.

Both of the above qualitative arguments suggest that the derivation of eq. 1 and 3 contains an approximation that deserves more quantitative treatment. However, such a treatment would apparently predict a larger rate constant than that calculated with the use of these equations. Since the discrepancy indicated in Table I is in the opposite direction, the moving sink effect merely reinforces the failure of the data to satisfy the predictions of theory.

Isotropic Medium Approximation.—The derivation of the equations assumes that the relative diffusion coefficient of two iodine atoms is independent of their separation. The experiments measured the bulk diffusion coefficient of isolated atoms in the solvent. When two atoms become separated by distances of the order of a molecular diameter or less, distributions of adjacent solvent molecules certainly exert nonrandom forces that influence the directions of relative displacements by the atoms. Although these nonrandom effects involve very small volumes of solution and are operative for an infinitesimal fraction of the lifetime of an atom, they can greatly influence observed rate constants.

These directional effects of solvent molecules apparently offer the best explanation for the discrepancies in Table I. As two iodine atoms diffuse toward each other, they are less apt to undergo a collision than they would be if the medium were a true continuum through which they moved with the same behavior as that of their bulk diffusion.

Although this effect causes the rate constant for recombination to be less than that predicted by a continuum model, the equilibrium constant for iodine dis-

sociation is almost the same in solution and in gas phase.¹² Hence the same effect must also operate to reduce the rate of thermal dissociation. This prediction is supported by the effect of wave length on the quantum yield for dissociation of iodine in solution.¹⁰ As the energy of the absorbed quantum increases, the quantum yield increases more rapidly than would be expected if the surrounding medium were a viscous continuum. The behavior has been explained¹³ by an argument similar to that employed here.

In carbon tetrachloride at 25°, the measured value of D is 2.7 times the value predicted by eq. 3.⁷ In hexane, the same ratio is 1.5.⁸ The difference is in the direction to be expected from the effect of solvent on quantum yield,^{13,14} but the data in hexane are not extensive enough to justify rigorous quantitative comparisons.

Since the "cage" effect was first proposed by Rabino- witz,⁹ it has not been clear whether it was necessary to invoke specific energy barriers in order to account for observations. Thus, models that assumed completely random displacements in an isotropic continuum¹⁵ appeared to offer a satisfactory description of most experiments. The measurements of quantum yield¹³ and of diffusion coefficient⁷ now make it necessary to postulate a small but significant potential barrier to the separation or bringing together of two reactive species. These experiments use pairs of very reactive atoms to probe small regions of space for very short times and to learn the degree of confidence to place in the mathematically tractable models that treat the medium as a continuum. Apparently it is unwise to assume that the absolute predictions of such models are valid to better than a factor of two, although the models may predict ratios of quantities more accurately than this.

Acknowledgment.—This work was supported in part by the U. S. Atomic Energy Commission under Contract AT(45-1)-1310.

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A Kinetic Analysis of Short-Chain, Radiation-Initiated Addition Reactions

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Kinetic expressions for product yields in short-chain, radiation-initiated free-radical addition reactions have been developed in a novel way, based upon radiation yields. It is shown by using model systems involving addition of isopropyl alcohol and isopropylamine to α -olefins that effects of reaction variables on yield of 1:1 adduct and ratios of 1:1 to 1:2 adduct are as predicted. A procedure is developed for using short-chain reactions to determine transfer constants. The true kinetic chain length of a chain reaction includes a contribution from the reaction $A \cdot + AB \rightarrow AB + A \cdot$, which, of course, is ordinarily unobserved. An isotopic experiment shows that in the systems under study it is unimportant. It is concluded that the conventional chain length for such reactions is close to the true chain length.

Ionizing radiation is generally useful for initiating free-radical addition reactions. Radiation initiation offers several advantages for kinetic studies. These include: (1) independence of initiation rate on temperature, and (2) uniform (or variable) rate of formation of

initiator radicals. A number of kinetic-type investigations using radiation initiation have been reported, including the addition of carbon tetrachloride to β -pinene¹

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