

In order to find out whether decarboxylation was taking place in our systems, a solution consisting of 1.3 *M* $\text{Cl}_3\text{CCO}_2\text{H}$ and 0.2 *M* $(\text{CH}_3)_3\text{NH}\cdot\text{O}_2\text{CCl}_3$ in acetic acid was placed in a n.m.r. sample tube. The tube was then degassed, sealed, and heated at 100° for 1 hr. At the end of this treatment, the n.m.r. spectrum was compared with that of an unheated sample of the same solution at room temperature. The heat treatment resulted in the formation of a new n.m.r. line at 5.50 p.p.m. downfield from that of the CH_3 protons of acetic acid. This line could be assigned to chloroform. There was no trace of a chloroform n.m.r. line in the unheated sample.

If decarboxylation were taking place at a significant rate during the measurements of the relative acid strength of trichloroacetic acid, the result would be an increase in the ratio $[\text{HOAc}]/[\text{Cl}_3\text{CCO}_2\text{H}]$ with time, and hence, according to eq. 14, an increase of *R* with time. In order to test for this eventuality, we measured *R* immediately after the preparation of each solution, and then again after the lapse of a fixed interval of time. The changes in *R* were small enough so that extrapolation to zero time presented no problem. In the case of added ammonia, the values of *R*, measured immediately after the preparation of each solution, required no correction; in the case of added trimethylamine, the corrections amounted to less than 7%.

Special Techniques for Supersaturated Solutions of Ammonium Picrate.—When pure picric acid is added to a solution of

ammonium acetate in glacial acetic acid, a precipitate of ammonium picrate is formed immediately and the concentration, c_B , of ammonium salts remaining in solution is reduced to a small and undetermined value. On the other hand, when a solution of ammonium acetate in acetic acid is added to a solution of picric acid in acetic acid, a metastable liquid solution results. The lifetime of the metastable solution, before precipitation begins, seems to depend on c_B . At room temperature, when $c_B \approx 0.04$ *M*, the lifetime is too short to permit completion of the n.m.r. measurement of *R*, which takes about 20 min.; but when $c_B \approx 0.02$ *M*, the lifetime is greater than 12 hr. at the picric acid concentrations used in our experiments. Once precipitation has started, it proceeds rapidly, but prior to the onset of precipitation, there is no evidence for turbidity when the solution is examined under light with a magnifying glass. During their lifetime, the metastable solutions were handled just as if they were stable, and the measured values of *R* remained constant.⁴⁷

Acknowledgment—It is a pleasure to thank Drs. B. Linder, E. G. McRae, and S. Meiboom for helpful discussions.

(47) We are grateful to Dr. Z. Luz for doing the n.m.r. measurements immediately after the preparation of each solution; thus, *R* was obtained at the earliest possible time.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON, EUGENE, OREGON]

Diffusion Coefficients of Iodine Atoms in Carbon Tetrachloride by Photochemical Space Intermittency

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The existence of the photochemical space intermittency effect has been confirmed, and the method has been used to measure the diffusion coefficients of iodine atoms in carbon tetrachloride at 25 and 38°. These results and less extensive previously reported studies by the same method constitute the first measurements of the diffusion coefficient of a reactive free radical in solution. Diffusion coefficients of iodine atoms are about five times larger than those of iodine molecules in the same solution; the difference is somewhat greater than had been expected.

Introduction

If photochemically produced radicals are destroyed in pairs, and if the medium is illuminated with a pattern of light and dark areas, the average steady-state concentration of radicals is dependent upon the size and shape of the illuminated regions as well as upon the total area illuminated. The theory of this photochemical space-intermittency effect was developed previously,¹ and the nonlinear differential equations were solved numerically for certain specific examples. Salmon and Noyes² subsequently demonstrated that the predicted effect did indeed exist for iodine atoms in hexane.

If quantum yields for radical production and rate constants for recombination are known independently, the effect can be used to determine diffusion coefficients of reactive free radicals; these quantities cannot be measured by any other known process. The present paper reports such a measurement for iodine atoms in carbon tetrachloride.

Experimental

Apparatus.—The apparatus was constructed by Dr. G. A. Salmon. It is shown schematically in Fig. 1. The light source, S, consisted of a medium pressure mercury arc (CH_5) surrounded by a jacket through which thermostated water was pumped. The light from the arc passed through a circular aperture, A, and the 4358-Å. line was isolated with an interference filter, F.

The beam was rendered parallel with the lens, L, and the mirror, M, was used to direct the beam vertically through a window in the bottom of the conventional water thermostat, T. This design was chosen so that the light path through the reaction cell would be vertical and the main component of convection would be parallel to the beam.

The beam was broken into light and dark areas by the pattern, P, mounted against the bottom face of the reaction cell, C. The beam was monitored by a conventional photometer detector, D, mounted in a tube with a window to eliminate distortion at the air-water interface of the thermostat.

The patterns, P, were mounted on glass plates 1 in. square. Each was a "leopard" pattern of circular spots arranged so that each spot had six nearest neighbors and so that the distance between centers of adjacent spots was exactly three times the spot diameter. The pattern was created as a photograph with a high-contrast, small-grain emulsion. The developed emulsion was then protected with a microscope cover glass, and the edges were sealed to keep out moisture. The first master design was prepared by drafting the approximately 10,000 spots by hand, and the individual patterns were then prepared by the Eastman Kodak Company by photographing this master. Because of the difficulty of getting sufficient uniformity with hand drafting, a new master having spot diameters of 0.179 cm. was prepared by Metal Marking Industries, Englewood, Colo., by a photographic process that involved repeated adjacent reproductions of the same small drafted design. The company then prepared individual patterns by photographing this master. Spot diameters in these patterns were measured with a microcomparator and ranged from 0.00796 to 0.1002 cm. The background of each pattern could be regarded as completely opaque, but the spots did not transmit the entire incident intensity. Lamp intensities were adjusted so that the same total amount of light was transmitted by the pattern used in every run.

(1) R. M. Noyes, *J. Am. Chem. Soc.*, **81**, 566 (1959).

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

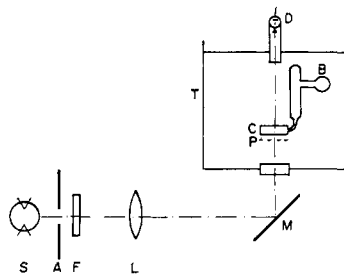


Fig. 1.—Schematic representation of apparatus.

The circular reaction cell, C, was 1.8 cm. in diameter. The light path was 0.5 cm. This quantity was kept short to minimize loss of sharpness in the light pattern but was long enough that a negligible fraction of photochemically produced atoms diffused to a wall. Because the cell itself could not stand the thermal shock associated with the degassing procedure, the proper amount of reactant solution was degassed in bulb, B, and then transferred to the cell after the system had been disconnected from the vacuum line.

Optical Properties.—The parallel beam was tested for homogeneity by making traverses with a pinhole detector across an area a little above where the cell would be. Some variations were as much as 5% from the mean intensity, but most of the cell was illuminated more uniformly than this.

Absolute beam intensities were determined at selected readings of the monitoring photometer. The ferrioxalate actinometer reaction of Parker and Hatchard³ was used for this purpose, and the photometer response was shown to be linear over the range of interest.

It was only after the runs were completed that the sharpness of the light pattern was tested by exposing a film placed on the top of the cell. The sharpness left something to be desired. Most optical systems are designed either to create a homogeneous parallel beam or to cast a pattern onto a surface. Little attention has been given to casting a sharp pattern in a parallel beam. The exposed film indicated a series of elliptical spots, each somewhat larger than the circular opening in the pattern employed. The major and minor axes of these exposed spots were 0.0170 and 0.0032 cm., respectively, greater than the diameters of the circular openings regardless of the sizes of those openings. Since the film was separated from the pattern by about 0.80 cm., the edge of each small beam deviated from parallel by about 36' in the direction of a major axis and by about 7' in the direction of a minor axis. The same deviations were presumably present in the main beam when it was tested for homogeneity, but they were not considered significant for a light path of only 5 mm.

Further tests demonstrated that the sizes of spots reaching the top face of the cell were affected only slightly by gross changes in the position of the focusing lens, but that they were strongly dependent upon the size of the aperture A. The elliptical pattern was obviously caused by the linear nature of the arc source and the finite size of the aperture. The quality of the pattern cast in these experiments is much more dependent upon a point source of light than it is upon the quality and design of lenses and other optical accessories. Improved apparatus requires a very intense light source and a small aperture that accepts very little of the available energy.

For the purposes of treating the present data, spot size was calculated by averaging major and minor axis lengths and assuming that deviations in the center of the cell were half those on the top. This treatment indicated that the individual beams traversing the cell had radii 0.0025 cm. greater than the radii of the pattern used. The theory for treating this effect is developed below.

Materials.—Average steady-state iodine atom concentration during a run was determined by the rate of isotopic exchange of elementary iodine with *trans*-diiodoethylene, CHI=CHI. This material was prepared from acetylene and iodine as described by Zimmerman and Noyes.⁴ It melted at 72.5–73.0° and was stored in a darkened bottle.

Reagent grade iodine was sublimed and used without further purification. A solution in carbon tetrachloride was activated

with an aqueous solution of iodine-131 from the Oak Ridge National Laboratories. The activated solution was dried with either sodium carbonate or magnesium sulfate.

Reagent grade carbon tetrachloride was purified by treatments both with ethanolic potassium hydroxide and with concentrated sulfuric acid. It was then dried with calcium chloride and distilled. Surprisingly rigorous purification and care in storage were required before satisfactory results were obtained. As the necessary purity was approached, the rate of the photochemical exchange reaction increased to a maximum and the dependence on incident homogeneous light intensity dropped from first order to square root. For the solvent finally employed, a tenfold change in light intensity, I , at 25° led to exchange rates in the ratio $10^{0.56} \pm 0.04$. Less extensive measurements at 38° indicated an exponent of 0.54.

Procedure.—Dried solutions of diiodoethylene and of activated iodine were mixed by the light of a ruby darkroom lamp. The resulting solution was $1.41 \times 10^{-4} M$ in iodine and 0.107 M in diiodoethylene. By means of a calibrated pipet, exactly enough solution was transferred to bulb B so that the cell C would be filled when the solution was tipped into it. The solution was chilled with liquid nitrogen, evacuated, separated from the pump, and rewarmed to room temperature. This procedure was repeated until the gas produced in such a cycle increased the pressure of the system less than 1μ . An identical portion of solution was subjected to the same treatment but subsequently kept in the dark.

The solution in the bulb was then tipped into the cell and illuminated under controlled conditions. At the end of the run, both the illuminated and dark solutions were extracted with freshly prepared aqueous sulfite and the radioactivity was measured by standard procedures. The difference was used to calculate the photochemically produced exchange. The separation procedure apparently induced a little exchange when the iodine solution had been freshly activated, but this apparent dark exchange became negligible with solutions that were a few days old.

With homogeneous illumination, rates of exchange at 25 and 38° were .19 and 25%, respectively, greater than predicted from the data of Rosman and Noyes.⁵ Throughout the work with diiodoethylene exchange, absolute rates of exchange have varied from one experimenter to another even though each experimenter obtained reproducible and self-consistent results and even though derived rates for iodine atom combination showed very good consistency⁵ for different experimenters and agreed with calculations from measurements of other types in other laboratories. We are unable to account for this behavior, although it may involve interaction of some impurity with the $C_2H_2I_2$ intermediate in the exchange.

Calculations.—The data were used to compute ϵ/ϵ_∞ , the ratio of the observed rate to the rate computed for indefinitely large spots on the basis of the rate with homogeneous illumination. This quantity was plotted against $\log r$, where r is the spot radius in cm. The resulting curve was then fitted to that calculated¹ for the reduced radius, ρ , where

$$\rho = (4\phi qk/D^2)^{1/2} r \quad (1)$$

In this equation, ϕ is the quantum yield for the production of a pair of free iodine atoms, q is the rate of absorption of light, k is the rate constant for the combination of atoms, and D is the diffusion coefficient of a free iodine atom.

The best fit of the observations to the theoretical curve was used to evaluate the factor relating r to ρ . The diffusion coefficient, D , was then calculated with the use of known values for all the other quantities in eq. 1.

Corrections for Data

Since photochemical space intermittency has never been employed before as a quantitative technique, it seems desirable to discuss in detail some of the potential corrections for treating experimental data. These corrections suggest points of concern for the design of future applications.

Divergence in Optical Pattern.—As is discussed under Optical Properties, the size of an individual beam did not remain constant as it traversed the cell. The situa-

(3) C. A. Parker and C. G. Hatchard, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956).

(4) J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 658 (1950).

(5) H. Rosman and R. M. Noyes, *J. Am. Chem. Soc.*, **80**, 2410 (1958).

tion in our apparatus could be approximated by assuming that the radius of the beam averaged 0.0025 cm. greater than that of the opening creating the beam. This deviation was independent of the size of the beam.

The following nomenclature is employed: r , radius of individual beam of light in cell; r_0 , radius of opening in pattern that creates beam; d , increase of beam radius over pattern radius; q , rate of absorption of light per unit volume in beam; q_0 , rate of absorption if beam were strictly parallel; f , ratio of separation of centers of adjacent spots to spot diameter in beam; f_0 , ratio of separation of centers to spot diameter in pattern. For our experiments, $f_0 = 3.000$.

These quantities are related by the following equations.

$$r = r_0 + d \quad (2)$$

$$q = q_0/(1 + d/r_0)^2 \quad (3)$$

$$f = f_0/(1 + d/r_0) \quad (4)$$

The reduced radius, ρ , is defined by eq. 1. Also, let

$$\rho' = (4\phi q_0 k/D^2)^{1/4} r_0 \quad (5)$$

Hence, ρ' is the value of ρ that would be computed by an observer unaware of divergence in the beam. Finally, let

$$\delta' = (4\phi q_0 k/D^2)^{1/4} d \quad (6)$$

Then

$$\rho = \rho' \sqrt{1 + d/r_0} = \rho' \sqrt{1 + \delta'/\rho'} \quad (7)$$

The previous paper¹ developed numerical solutions for $\bar{\gamma}/\bar{\gamma}_\infty$. This quantity is the ratio of the average concentration of radicals in all space to the average that would be observed for indefinitely large beams if the values of f and q were the same. However, beam divergence caused f and q to vary for different patterns. Let \bar{c}/\bar{c}_∞ be the ratio of the space-average radical concentration to the concentration that would be observed for indefinitely large beams described by f_0 and q_0 . It is this ratio that is measured experimentally in our system. As shown in ref. 1

$$\gamma = (k/\phi q)^{1/2} c \quad (8)$$

$$\bar{\gamma}_\infty = 0.9070/f^2 \quad (9)$$

Then it follows from the above equations that

$$\bar{c}/\bar{c}_\infty = (\bar{\gamma}/\bar{\gamma}_\infty)(1 + \delta'/\rho') \quad (10)$$

Since values of $\bar{\gamma}/\bar{\gamma}_\infty$ have been computed¹ as functions of ρ for f values of 2, 3, and 5, values of \bar{c}/\bar{c}_∞ for $f_0 = 3$ can be estimated fairly well for $\delta'/\rho' \leq 0.5$. The plots in Fig. 2 for different values of δ' show that the principal effect of beam divergence is to shift the curve to the right without affecting its shape very much. Since the subsequent discussion indicates that our results are consistent with a δ' of about 0.5, beam divergence can be handled by a relatively small correction.

Of course the above treatment assumes unrealistically that the diverging beam is uniform over its entire area, but the correction for divergence is small enough that an additional correction for inhomogeneity could hardly be significant.

Lack of Sharpness at Boundary.—The theoretical development¹ assumed an absolute discontinuity be-

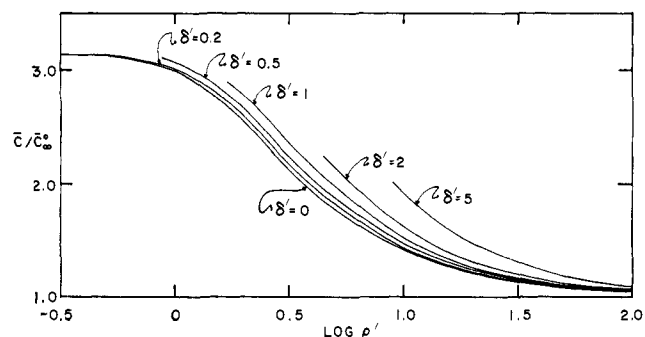


Fig. 2.—Effect of beam divergence on observed radical concentration.

tween dark and illuminated areas at the edge of a beam. Of course the transition really takes place over a finite distance. Examination of films placed on the top of the cell indicated that the distance was of the order of 0.001 cm. Since this distance is less than 20% of the root-mean-square distance an iodine atom diffused during its lifetime and since the definition of the beam was undoubtedly sharper in the cell than on its top face, it was not considered necessary to develop any corrections for the effect. Boundary sharpness may be a significant parameter in other applications of the method.

Macroscopic Transport Phenomena.—The method presupposes that diffusion is the only process by which iodine atoms are transported between dark and illuminated areas and between regions of different atom concentration within these areas. If thermal inhomogeneities or other macroscopic fluctuations cause currents within the cell, the method is inaccurate to the extent that iodine atoms are transported significant distances by such currents during their lifetimes.

The time scale of importance is determined by these lifetimes. In an illuminated area, the average lifetime, τ , of an iodine atom is given by

$$\tau = c/2q\phi = \sqrt{qk\phi/4} \quad (11)$$

For our runs, $q = 3.52 \times 10^{-9}$ einstein/l. sec. Best values of the other quantities in carbon tetrachloride at 25° are $k = 7.4 \times 10^9$ l./mole sec. and $\phi = 0.14$. Then $\tau = 0.26$ sec. Since the data reported below indicate that the iodine atom diffuses about 7×10^{-3} cm. during this time, currents of 3×10^{-2} cm./sec. perpendicular to the boundary of an illuminated area would cause serious difficulty, and it would be desirable for any currents to be less than 10% of this amount.

The energy dissipated from the illuminating beam inevitably causes inhomogeneities of temperature and density. Since the heat capacity of carbon tetrachloride is 0.20 cal./g. deg., and the density is 1.6 g./ml., the energy of the beam would raise the temperature of an illuminated area about 7×10^{-7} deg./sec. if all of the energy remained in that area. Since none of our experiments lasted more than about 10^4 sec., the temperature rise in the illuminated areas was certainly much less than 0.01°.

The coefficient of thermal expansion is 1.24×10^{-3} deg.⁻¹; hence such a temperature rise in a 5-mm. cell would only create a pressure difference on the bottom of 10^{-5} g./cm.² between illuminated and dark areas. Since the viscosity is 9.0×10^{-3} poise, this pressure difference would cause a vertical velocity of 1.4×10^{-3} cm./sec. in

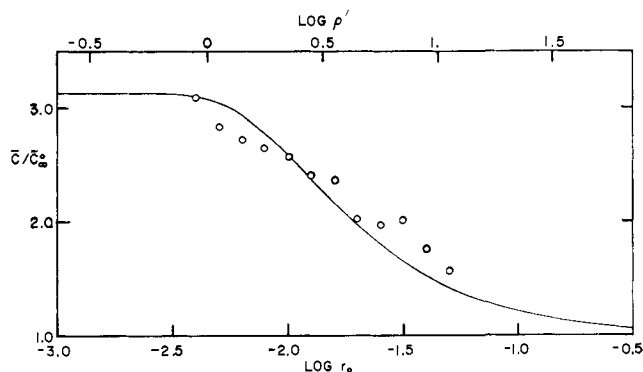


Fig. 3.—Photochemical space intermittency data at 25°

the center of the area illuminated with the coarsest pattern. Thus this combination of several extreme assumptions leads to a motion along the direction of illumination equal to the amount permitted perpendicular to that direction; our observations could not have been significantly disturbed by thermal effects from illumination.

It has subsequently been pointed out that convective effects would be reduced still further by introducing the light from the top rather than the bottom of the cell so that the maximum absorption would be in the upper part of the cell. Since only about 1% of the incident light was absorbed in our experiments, the direction of light passage was completely unimportant. We are redesigning the apparatus in case this factor is of significance in future applications.

It has also been pointed out that convection can be eliminated by designing a temperature gradient so that the top of the cell is warmer. We have not chosen to do so because vertical convective flow is obviously of very little importance in a cell with such short light path and because an attempt to accomplish this result might lead to lateral temperature gradients with much greater potential for obfuscating the results.

Diffusion of Iodine Molecules.—The analytical method relates a rate of isotopic exchange to an average concentration of iodine atoms. The mathematical treatment uses equations that assume all of the atoms of the element are equally available for exchange. If the isotopic composition differs in light and dark areas, the rate at which radioactivity ceases to become sulfite extractable is no longer related to the average atom concentration.

In the coarsest pattern used, the distance from the center of an illuminated area to the center of a dark area was 0.173 cm. The diffusion coefficient of iodine molecules in carbon tetrachloride at 25° is⁶ 1.5×10^{-5} cm.²/sec. Then the root-mean-square distance an iodine molecule would diffuse in 10^4 sec. is about 0.55 cm. It appears that diffusion of iodine molecules was sufficiently rapid to maintain virtually constant isotopic composition of the element. Any failure would have made the rates of exchange anomalously low for large spot sizes, and Fig. 3 and 4 show that rates were, if anything, large for these patterns.

Results

The results of experiments at 25 and 38° are presented in Fig. 3 and 4. The plots show \bar{c}/\bar{c}_0 against $\log r_0$. The experimental conditions involved iodine

(6) R. H. Stokes, P. J. Dunlop, and J. R. Hall, *Trans. Faraday Soc.*, **49**, 886 (1953).

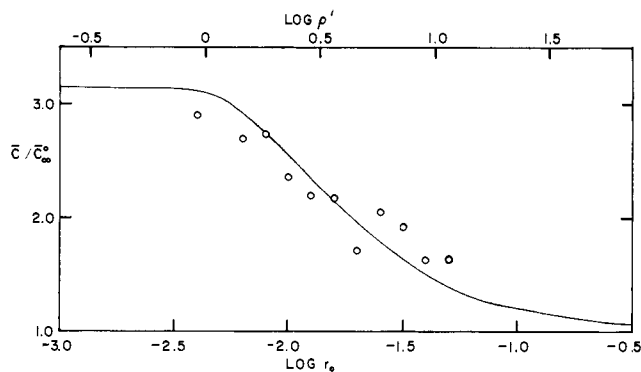


Fig. 4.—Photochemical space intermittency data at 38°.

and diiodoethylene concentrations of 1.41×10^{-4} and 0.107 mole/l., respectively. The patterns were such that $f_0 = 3.000$ and $q_0 = 3.52 \times 10^{-9}$ einstein/l. sec. Each point in Fig. 3 represents the average of two to six individual runs; many of the points in Fig. 4 represent values from single runs.

The experimental points were fitted to the theoretical curve assuming no divergence of the beam, and an approximate value of r_0/ρ' was determined at each temperature. Since this quantity is equal to d/δ' and since $d = 0.0025$ cm., values of δ' were computed and used to get better approximations for r_0/ρ' from the shifts at different δ' of the curves in Fig. 2. Successive approximations rapidly converged to give corrected values of r_0/ρ' . The curves in Fig. 3 and 4 and the scales for $\log \rho'$ use interpolations from Fig. 1 to get a fit consistent with the observed value of d .

Previously determined^{5,7} values of ϕ and k were combined with these corrected values of r_0/ρ' to compute diffusion coefficients, D , by means of eq. 5. The results of these calculations are summarized in Table I. For

TABLE I
DIFFUSION COEFFICIENTS OF IODINE ATOMS IN
CARBON TETRACHLORIDE

Temperature, °C.	25.0	38.0
r_0/ρ' , cm. (first approximation)	0.00524	0.00512
$r_0/\rho' = d/\delta'$, cm. (corrected value)	0.00447	0.00435
δ'	0.56	0.57
ϕ (ref. 7)	0.14	0.21
$10^{-9} k$, l./mole sec. (ref. 5)	8.2 ^a	13.2
$10^8 D$, cm. ² /sec.	8.0	11.8
$10^8 D_{I_2}$, cm. ² /sec. (ref. 6)	1.50	
(ref. 8)	1.45	1.84

^a A value of 7.4×10^9 would better describe the average of determinations by different methods. This value is used because the method is the same as that by which the only value available at 38° was obtained.

the sake of comparison, the last line of the table contains previously reported^{6,8} values of D_{I_2} , the diffusion coefficient of *molecular* iodine in the same solvent.

Discussion

The measurements presented in Fig. 3 and 4 demonstrate conclusively that the photochemical space-intermittency effect exists and that it should be a valid procedure for measuring diffusion coefficients. The present work and a less extensive previous study by the same method² constitute the first measurements of diffusion coefficients of reactive small radicals in solution⁹; hence

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

(8) E. W. Haycock, B. J. Alder, and J. H. Hildebrand, *J. Chem. Phys.*, **21**, 1601 (1953).

(9) P. B. Davies and A. M. North, *Proc. Chem. Soc.*, 141 (1964), have used the same technique to measure diffusion coefficients of polymer radicals.

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

Acknowledgment.—This work was supported in part by the U. S. Atomic Energy Commission under Contract AT(45-1)-1310. Most of the apparatus was constructed by Dr. G. A. Salmon. Dr. Richard D. Burkhart performed most of the work on the sharpness of the individual light beams. Dr. Arnold Weissberger and associates at the Eastman Kodak Company provided encouragement and helpful suggestions about the optical problems and prepared the first set of patterns used in this type of work.

(10) R. M. Noyes, *J. Am. Chem. Soc.*, **86**, 4529 (1964).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON, EUGENE, OREGON]

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).