[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

# Rate Constants for Combination of Iodine Atoms in Inert Solvents

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The effect of intermittent light on the rate of a chain reaction involving iodine atoms has been used to measure the average life-times of photochemically produced iodine atoms between about 15 and 35° in hexane, carbon tetrachloride and hexachlorobutadiene-1,3. Since quantum yields for iodine dissociation previously had been measured by a scavenger technique in the same solvents at the same temperatures, the data can be used to calculate rate constants for the combination of "old" iodine atoms that have escaped their original partners. The rate constants are all about $5 \times 10^9$ liter/mole sec. or greater and are in good agreement with the magnitudes to be expected if the rate of the combination reaction is determined by the rate of diffusion of atoms together. However, the data fail to support the proportionality between viscosity and diffusion coefficient predicted by hydrodynamic theories. Measurements in several laboratories of photostationary atom concentration, life-time, quantum yield and rate constant are all remarkably consistent with each other. Both life-time measurements with intermittent light and rate constant measurements with flash photolysis offer advantages under certain conditions.

## Introduction

If a solution of iodine in an inert solvent is illuminated, these two processes take place

$$I_2 + h\nu \longrightarrow 2I \qquad (1)$$

$$2I \longrightarrow I_2 \qquad (2)$$

If the rate of thermal dissociation is negligible compared to that of photochemical dissociation, a stationary state is reached in which the rates of processes 1 and 2 are equal and

$$\phi q = kI^2 \qquad (3)$$

where

$q$ = rate of absorption of light in einstein/l. sec.
$\phi$ = quantum yield for producing a pair of atoms that escape from each other and ultimately combine with atoms from other dissociations
$k$ = rate constant in l./mole sec. for process 2 *as written* but applied to "old" iodine atoms whose reactivity has ceased to decrease with time
$I$ = stationary concn. in mole/l. of iodine atoms destined to combine with atoms that were not their original partners

For the same steady state

$$\tau = \frac{I}{2\phi q} = \frac{1}{2kI} \qquad (4)$$

where

$\tau$ = av. age, at combination, of atoms that escape their original partners and combine with atoms from other dissociations

The various parameters have been defined with some care to permit comparison with the results of experimental measurements and theoretical treatments. Other less satisfactory definitions are possible. Thus both $\phi$ and $\tau$ could be defined in terms of all atoms that exist free enough for potential spectrophotometric detection regardless of their ultimate fate, but the empirical rate constant satisfying the above equations could not then be related simply to any model based on kinetic theory. The complications associated with these definitions are discussed in previous publications.[2-4]

The stationary atom concentration, $I$, has been defined to satisfy equations 3 and 4 rigorously rather than to correspond to a measurable quantity. However, since atoms that recombine with their original partners almost certainly do so in $10^{-9}$ sec. or less, and since the average life-time for combination with other atoms is in the range of $10^{-1}$ sec., atoms destined to subsequent recombination with their original partners make a negligible contribution to measured values of $I$ even if a considerable fraction of absorbed quanta produce atoms that do recombine with their original partners.

The rate of absorption of photons, $q$, is measurable by standard photochemical techniques. Therefore, all of the other four parameters in equations 3 and 4 are calculable if two of them are independently measurable. Of the four, $I$ and $\tau$ depend on light intensity and are not as important as the intensity independent parameters $k$ and $\phi$. As Marshall and Davidson[5] commented, equations 3 and 4 can be rearranged to

$$k/\phi = q/I^2 \qquad (5)$$

$$k\phi = 1/4q\tau^2 \qquad (6)$$

Values of $k$ and $\phi$ provide insight into the nature of molecular motions in liquids and also permit the calculation of absolute rate constants for individual steps of atomic reactions that have been studied kinetically. Various experimental techniques have been applied to the problem, and all four of the parameters have now been measured by independent means for some solvents at room temperature.

Rabinowitch and Wood[6] measured $I$ and hence $k/\phi$ for hexane and carbon tetrachloride at room temperature. The method determined the decrease in light absorption by molecular iodine as a result of an intense beam of non-monochromatic light perpendicular to the monitoring beam. Changes of only a few hundredths of a per cent. were observed, but the data were internally consistent with the effects anticipated.

Zimmerman and Noyes[7] measured $\tau$ and hence $k\phi$ for hexane at 25°. The method involved the effect of a rotating sector on the rate of the exchange reaction between isotopically labelled iodine and *trans*-diiodoethylene. Most measurements were at 4358 Å., but a few additional measurements of relative quantum yield at 5780 Å. per-

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[1] Based on the Ph.D. Dissertation of Howard Rosman. The original dissertation and microfilms thereof are available from the Library of Columbia University.

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[2] R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954).

[3] R. M. Noyes, THIS JOURNAL, **77**, 2042 (1955).

[4] R. M. Noyes, *ibid.*, **78**, 5486 (1956).

[5] R. Marshall and N. Davidson, *J. Chem. Phys.*, **21**, 2086 (1953).

[6] E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 547 (1936).

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

mitted comparison with the data of Rabinowitch and Wood and in principle defined all the parameters.

The method of flash photolysis and spectrophotometric observation of the rapid recombination was used by Marshall and Davidson[5] and later by Strong and Willard[8] and by Aditya and Willard[9] to measure $k$ directly at room temperature in carbon tetrachloride and in hexane and heptane.

Finally, Lampe and Noyes[10] used a scavenger technique with allyl iodide and oxygen to measure $\phi$ directly in three solvents at two or three temperatures each. These data were the first providing any information on the temperature dependence of any of these parameters.

The present study was undertaken to use the method of Zimmerman and Noyes[7] to measure life-times of iodine atoms under the exact experimental conditions for which Lampe and Noyes[10] had already measured quantum yields. Although some of the rate constants so obtained duplicated those from other studies, and although related work on direct measurement of rate constants by flash photolysis was known to be continuing in other laboratories, it was felt that the comparison by independent methods was justified in order to assess the best techniques for further measurements on problems of this sort.

## Experimental

**Materials.**—Three solvents were used. Hexane was prepared from commercial grade 60–70° petroleum ether by repeated stirring with 30% fuming sulfuric acid, then treatment with acid permanganate and sodium carbonate solution. It was distilled and stored over sodium.[7] Fisher Chemical Co. "Spectrograde" carbon tetrachloride was used without further treatment. Commercial hexachlorobutadiene-1,3 was vacuum distilled before use. Tests indicated that all three solvents absorbed no more than 2 × $10^{-6}$ mole/liter of iodine under the conditions of our subsequent experiments; this is no more than 2% of the iodine present and was corrected for.

The *trans*-diiodoethylene was prepared by passing acetylene into an alcoholic solution of iodine.[11] It was purified by recrystallization from alcohol.

Resublimed C.P. grade iodine was used without further purification. Solutions in the various solvents were activated by shaking with aqueous solutions of carrier-free iodine-131 from the U. S. Atomic Energy Commission. Concentrations were determined spectrophotometrically.

**Apparatus.**—The apparatus was essentially that described previously[7] except that the reaction cells were smaller. The diameter of 1.70 cm. permitted a more homogeneous beam of light throughout the cell. Quantities of solution used were chosen so that the cell was just filled at the temperature of the experiment.

The 4358 Å. line was isolated from an AH4 mercury arc with Corning glass filters, and the beam was collimated before it reached the cell. A photocell–amplifier system was used to monitor the beam, and the absolute intensity was determined with a thermopile–galvanometer system calibrated against a lamp from the Bureau of Standards. The beam used in all experiments contained 1.86 × $10^{14}$ quanta/cm.$^2$ sec. = 3.09 × $10^{-10}$ einsteins/cm.$^2$ sec.

Intermittent light was produced with rotating sectors, the ratio of light to dark periods always being 1:3. Sectors with different numbers of openings, and a gear arrangement of the drive, permitted a wide range of flashing rates with the same driving motor.

**Procedure.**—Solutions of *trans*-diiodoethylene and radioactive iodine in a particular solvent were mixed and degassed by repeated freezing and evacuation. The mixture was then illuminated for a known time with continuous or with intermittent light. After the run, the iodine was extracted with aqueous sulfite, and the radioactivities in aqueous and organic layers were measured with a liquid counter. The observed counting rates were corrected for different efficiencies of counting in different liquids. Then the average rate of the photochemical exchange reaction was calculated by standard equations. Blank experiments established that the effect of thermal exchange was entirely negligible but that a small correction should be applied because of exchange induced in the separation procedure.

In principle, any ratio of rates with intermittent and continuous illumination is sufficient to calculate the average life-time of an iodine atom chain under continuous illumination.[7,12] However, for a constant error in rates, the calculation is most accurate if the period of a light flash is between one and ten times the average life-time. In our experiments, for each temperature and solvent, seven to ten runs were made with intermittent illumination at different frequencies, and the best average life-time was computed after weighting the results according to an estimated value of the life-time. If the calculated value differed significantly from the first estimate, the weights could be reassigned and the averaging repeated. Mean life-times obtained in these experiments ranged between 0.088 and 0.59 second. The averaging procedure was chosen to give the minimum weighted sum of squares of deviations, and probable errors were estimated from these weighted deviations.

## Results and Discussion

**Summary of Results.**—For each temperature and solvent, the measured average life-time was substituted into equation 6 to obtain $k\phi$, and $k$ itself was calculated with the value of $\phi$ measured previously[10] for the same conditions. The values of $k\phi$ and of $k$ are presented in Table I.

TABLE I

RATE DATA FROM CURRENT LIFE-TIME AND PREVIOUS[10] QUANTUM YIELD MEASUREMENTS

| Solvent | Temp., °C. | $10^{-9}k\phi$, l./mole sec. | $10^{-9}k$, l./mole sec. | $10^{-3}k_e$, l./mole sec. |
|---|---|---|---|---|
| $C_6H_{14}$ | 15.0 | 5.6 ± 0.8 | 11.4 ± 1.8 | 3.8 ± 0.5 |
| | 25.0 | 8.6 ± .9 | 13.1 ± 1.6 | 5.7 ± .8 |
| $CCl_4$ | 17.5 | 0.75 ± .08 | 6.8 ± 1.0 | 3.7 ± .5 |
| | 25.0 | 1.2 ± .3 | 8.2 ± 2.1 | 5.2 ± 1.0 |
| | 38.0 | 2.8 ± .5 | 13.2 ± 2.6 | 8.2 ± 1.3 |
| $C_4Cl_6$ | 15.0 | 0.19 ± .02 | 4.6 ± 0.8 | 6.5 ± 1.1 |
| | 25.0 | 0.46 ± .07 | 6.1 ± 1.2 | 6.5 ± 1.1 |
| | 35.0 | 1.00 ± .11 | 6.7 ± 1.2 | 7.5 ± 1.2 |

The exchange is assumed to take place entirely through the elementary process

$$I^* + C_2H_2I_2 \longrightarrow C_2H_2II^* + I \qquad (7)$$

The atom so produced then exchanges rapidly with molecular iodine.

If $R$ is the rate of exchange calculated for continuous illumination by standard equations, then the rate constant, $k_e$, for this exchange step is given by

$$k_e = R/[C_2H_2I_2][I] = R/2[C_2H_2I_2]\phi q\tau \qquad (8)$$

Values of $k_e$ calculated from our data and the previous quantum yields are also presented in Table I.

The values of $k$ and $k_e$ at different temperatures in each solvent were fitted to the standard Arrhenius equation, $k = Ae^{-E/RT}$, and the results are presented in Table II. The quoted uncertainties of the parameters are based on the probable errors quoted in Table I.

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(8) R. L. Strong and J. E. Willard, THIS JOURNAL, **79**, 2098 (1957).

(9) S. Aditya and J. E. Willard, *ibid.*, **79**, 2680 (1957).

(10) F. W. Lampe and R. M. Noyes, *ibid.*, **76**, 2140 (1954).

(11) H. P. Kaufmann, *Ber.*, **55B**, 249 (1922).

(12) R. G. Dickinson in W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 202.

The temperatures to be employed in this study were predetermined by the quantum yield measurements of Lampe and Noyes,[10] and the range is much too narrow to determine the activation energies with any precision. Although the estimated probable errors are at least comparable to the trends observed, the consistencies in the temperature dependence of $k$ and $k_e$ make it appear that *relative* rate constants are probably known with considerably better precision than the absolute values. Thus, all four sets of measurements at three temperatures fit the Arrhenius equation several times better than would be expected from the quoted uncertainties in the individual points.

Some previous studies[13,14] of photochemical reactions of iodine in solution have used the assumption that the photostationary concentration of iodine atoms (and hence $k/\phi$) was independent of temperature if the illumination remained constant. The measurements now show both $k$ and $\phi$ increase with temperature, while $k/\phi$ decreases slightly with temperature but changes by a smaller percentage than either the rate constant or the quantum yield individually. Thus the original assumption of Dickinson and Lotzkar[13] appears to have been reasonably satisfactory, but it should be applied with caution to other systems.

TABLE II

ARRHENIUS PARAMETERS FOR COMBINATION AND EXCHANGE IN DIFFERENT SOLVENTS

| Solvent | $C_6H_{14}$ | $CCl_4$ | $C_4Cl_6$ |
|---|---|---|---|
| log $A$ (l./mole sec.) | 11.9 ± 2.7 | 14.1 ± 1.7 | 12.2 ± 1.8 |
| $E$, cal./mole | 2400 ± 3700 | 5600 ± 2300 | 3300 ± 2400 |
| log $A_e$ (l./mole sec.) | 9.0 ± 2.6 | 8.7 ± 1.4 | 4.7 ± 1.6 |
| $E_e$, cal./mole | 7100 ± 3400 | 6800 ± 1900 | 1200 ± 2200 |

**The Exchange Reaction.**—The rate constants, $k_e$, for the exchange step 7 show very little dependence on solvent. Although the value in hexachlorobutadiene at 15° seems anomalously high, the activation energies in the other two solvents are consistent with previous observations[14] of the photochemical exchange over a wider range of temperatures. This lack of sensitivity to solvent is what would be anticipated for a radical reaction provided there is very little separation of charge in the transition state, and provided there are not specific interactions with solvent molecules.

We are less able to account for the fact that the absolute value of $k_e$ in hexane at 25° is about three times that observed by Zimmerman and Noyes[7] even though the life-times and rate constants for atom recombination are in good agreement. The previous work[7] also found that absolute rates of exchange would differ considerably from one solution of diiodoethylene to another even though lifetimes for the same rate of absorption of quanta would be unaffected. The discrepancies could be explained hypothetically if some impurity, X, tends to form complexes reversibly with iodine atoms.

$$I + X \rightleftarrows IX \qquad (9)$$

If the diffusion coefficient of IX is not greatly different from $I$, and if IX complexes always react with iodine atoms or other complexes when they encounter them, the rate of recombination would not be affected much. On the other hand, the exchange reaction 7 does not go at every encounter and may not go as easily with IX as with I.

**Atomic Combination as a Diffusion Controlled Reaction.**—As a general rule, for reactions in different solvents or for different positions of attack of a molecule by a reagent, ratios of rates are more nearly unity the faster the reactions considered. In other words, highly reactive species are less selective in the reactions they undergo and are less influenced by external conditions. However, as Table I shows, the rate constants for combination of iodine atoms vary much more with changing solvent than do the million-fold smaller rate constants for the exchange reaction between iodine atoms and diiodoethylene.

This dependence on solvent of the rate of a very fast non-polar reaction is merely an additional piece of evidence that the combination of iodine atoms in solution is a type of reaction that is not amenable to treatment by conventional absolute reaction rate theory.[15] For most chemical reactions, it does not introduce serious difficulty to assume that a transition state is in quasi-equilibrium with reactants in the ground state and that all modes of motion except one in the transition state are excited to the extent expected from the temperature of the system. However, if iodine atoms can react with each other on virtually every encounter, the distribution of atoms in space ceases to be random. In particular, if an atom has lived a significant time since its formation, the probability of finding any other atom except its original partner near it is less than the probability of finding an iodine atom near a position chosen at random in the solution.[2] Because the distribution of iodine atoms is not random, it is impossible to write a partition function from which to calculate the entropy of translation of iodine atoms in the solution, and any theory based on conventional statistical thermodynamics is inapplicable. Although Table II contains Arrhenius parameters calculated from the temperature dependence of $k$, they must be regarded as empirical quantities of no direct use for calculating enthalpy and entropy changes during formation of a transition state.

Under the conditions of our experiments, iodine atoms live of the order of $10^{-1}$ second before combining with other atoms. If two atoms undergoing an encounter are sure to combine with each other, each of the "old" atoms in the solution can be regarded as a sink for other iodine atoms. The concentration of iodine atoms (expressed as the probability of finding one in a microscopic unit of volume) will be vanishingly small at the surface of a particular atom and will rise with increasing separation until it reaches the bulk *a priori* value for the solution as a whole. It is interesting that the concentration gradient is the same about each

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(13) R. G. Dickinson and H. Lotzkar, THIS JOURNAL, **59**, 472 (1937).

(14) R. M. Noyes, R. G. Dickinson and V. Schomaker, *ibid.*, **67**, 1319 (1945).

(15) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

"old" atom, which can only undergo combination once, as it would be about a sink of the same size that could consume atoms indefinitely.

The calculation of the rate of combination as the rate of diffusion into a sink involves a simple application of Fick's first law in a manner apparently first carried out by Smoluchowski.[16] For our case, the solution is

$$k = \frac{2\pi\rho DN}{1000} = \frac{4\pi\rho D_1 N}{1000} \qquad (10)$$

where

$\rho$ = encounter diameter in cm.
$N$ = Avogadro's number
$D$ = diffusion coefficient (in cm.$^2$/sec.) for relative motion of 2 iodine atoms
$D_I = D/2$ = diffusion coefficient for iodine atoms

Equation 10 is strictly valid only if the solvent medium can be regarded as a continuum even at molecular dimensions, and if diffusive displacements are small compared to molecular dimensions. The equation can be modified by assuming a pseudo-lattice structure for molecules near an iodine atom or by assuming a finite size for diffusive displacements. These modifications do not alter the form of the equation but effectively introduce an encounter diameter, $\rho$, that differs slightly from the sum of the radii of the two atoms. No plausible microscopic model can change by as much as a factor of 2 the value of $k$ calculated from equation 10 for species of known size and diffusion coefficient.

In order to test the applicability of equation 10, we have assumed $\rho = 4.3 \times 10^{-8}$ cm. or twice the van der Waals radius of iodine. Then the equation has been used with our measurements of $k$ to calculate $D_I$, the diffusion coefficient of iodine atoms under the specified conditions. The results are presented in Table III, the indicated uncertainties being the same percentages as were claimed for $k$ in Table I. For the sake of comparison, Table III also contains reported diffusion coefficients for molecular iodine whenever they have been measured under our conditions.

TABLE III

COMPARISON OF RATE CONSTANTS WITH PREDICTIONS OF DIFFUSION THEORY

| Solvent | Temp., °C. | $10^5 D_I$, cm.$^2$/sec. (from eq. 10) | $10^5 D_{I_2}$, cm.$^2$/sec. (exptl.) | Ref. | $10^{-8} k\eta/T$, $\frac{\text{l. poise}}{\text{mole sec. deg.}}$ |
|---|---|---|---|---|---|
| $C_6H_{14}$ | 15.0 | 3.5 ± 0.6 | | | 1.48 |
| | 25.0 | 4.0 ± .5 | 4.05 | 17 | 1.29 |
| $CCl_4$ | 17.5 | 2.1 ± .3 | 1.30 | 18 | 2.34 |
| | 25.0 | 2.5 ± .6 | 1.50, 1.45 | 17, 18 | 2.22 |
| | 38.0 | 4.1 ± .8 | 1.84 | 18 | 3.22 |
| $C_4Cl_6$ | 15.0 | 1.4 ± .2 | | | |
| | 25.0 | 1.9 ± .4 | | | 6.15 |
| | 35.0 | 2.1 ± .4 | | | 5.55 |

The comparison of diffusion coefficients in Table III is complicated by the fact that the rate of combination should depend on the diffusion coefficient of iodine *atoms*, while all diffusion data in the literature measure coefficients for *molecules*. In principle, the diffusion coefficient for atoms could be obtained by studying the effect of size of alternating dark and light areas on the rate of the same reaction we used for the sector studies, but the experiments would be difficult to conduct. Even though the diffusion coefficient of iodine atoms has not been measured, it should be the same as or slightly greater than that of molecules in the same solvent, and the difference could scarcely be more than about a factor of two. The agreement in Table III seems to be entirely satisfactory. The rate constants in carbon tetrachloride are a little larger than can be accounted for easily unless the structure of the solvent somewhat increases the apparent encounter diameter, and the rate constant in hexane is slightly smaller than might be anticipated from the large diffusion coefficient for molecules in this solvent. However, the data are certainly consistent with the hypothesis that the rate of reaction is determined by the diffusion of atoms together, and it would be clearly impossible to account for these large rate constants if there were a considerable probability that two iodine atoms undergoing an encounter would escape ultimate combination with each other.

If the combination reaction is diffusion controlled, the data permit a test of the applicability of hydrodynamic theory to molecular diffusion. All such theories for the thermal motion of a sphere through a continuous medium agree that the diffusion coefficient should be proportional to $T/\eta$ where $\eta$ is the viscosity of the medium. If the encounter diameter $\rho$ is unaffected by changing solvent and temperature, application of hydrodynamic theory to equation 10 predicts that $k\eta/T$ should have the same value for all of our measurements even though the absolute diffusion coefficients for iodine atoms are unknown. We have taken viscosity values from handbooks or made measurements with calibrated viscometers, and the values of $k\eta/T$ are presented in the last column of Table III. The values are far from constant and suggest that change of solvent affects the viscosity more than it affects the diffusion coefficient of iodine atoms. Hammond and Stokes[19] recently reached similar conclusions about the relative behaviors of viscosity and diffusion coefficients. Viscosities are determined by the size and forces between solvent molecules, while diffusion coefficients are determined by interactions between solvent and solute molecules; it is not surprising that the effects of changing solvent fail to show the parallelism predicted by simple hydrodynamic theory.

**Critique of Method.**—The rotating sector technique measures the average life-time of a kinetic chain until it is terminated by the combination of the chain carrying atoms. We have assumed that this life-time in a solution containing about 0.1 mole/liter of diiodoethylene is the same as the life-time of an iodine atom would be if no diiodoethylene were present. This assumption will be valid if reaction 7 goes directly in a single step without forming an intermediate and if there is no significant interaction between iodine atoms and diiodoethylene molecules. Even if reaction 7 involves an inter-

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(16) M. v. Smoluchowski, *Z. physik. Chem.*, **92**, 129 (1917).

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

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

(19) B. R. Hammond and R. H. Stokes, *Trans. Faraday Soc.*, **51**, 1641 (1955).

mediate $C_2H_2I_3$, the assumption we have made will be valid if the life of an intermediate is short compared to the time an iodine atom exists free between exchanges or if intermediates undergo termination reactions with iodine atoms and with each other with the same relative reactivity as two iodine atoms.

Although the retarding effect of air[7] in systems like this suggests that intermediates may live long enough to react with oxygen if it is present, we have not previously found any dependence of measured life-time on diiodoethylene concentration.[7] Also, the small variation of apparent exchange rate constant with diiodoethylene concentration can be explained in terms of the exchange reaction between iodine atoms and molecules.[20] Because of these tests, and because of the consistency of these results with those from different measurements as discussed below, we believe that these experiments do indeed measure the life-times of iodine atoms for these rates of light absorption in the pure solvents.

**Comparison with Other Data.**—As was indicated in the Introduction, a complete description of the system is possible from measurements of any two of the four quantities $I$, $\tau$, $\phi$ and $k$. Workers in various laboratories have now measured all four of these quantities for hexane and carbon tetrachloride at 25°. In Table IV, we present the values of the rate constant, $k$, calculated in these solvents from direct measurement and from all possible pairs of measurements. Indicated uncertainties are estimated probable errors.

TABLE IV

COMPARISON OF RATE CONSTANTS (REPORTED AS $10^{-9}k$) FOR ATOM COMBINATION MEASURED IN DIFFERENT WAYS AT 25°

| Quantities measured | $C_6H_{14}$ | $CCl_4$ | Ref. |
|---|---|---|---|
| $I^a + \phi$ | 12.5 ± 2.7 | 6.7 ± 1.0 | 6, 10 |
| $I^a + \tau$ | 11.4 ± 2.8 | | 6, 7 |
| | 12.8 ± 3.0 | 7.4 ± 2.0 | 6, This work |
| $\phi + \tau$ | 10.3 ± 1.4 | | 10, 7 |
| | 13.0 ± 1.6 | 8.2 ± 2.1 | 10, This work |
| $k$ | $22^b$ ± 4 | 7.2 ± 1.1 | 5 |
| | | 5.7 ± 0.5 | 8 |
| | 18 ± 6 | 6.9 ± 0.6 | 9 |

[a] Since Rabinowitch and Wood used non-monochromatic light about 5000 Å. while other measurements were made at 4358 Å., the values of $k/\phi$ from their data have been decreased 20% as a rough correction based on our previous data[7] in hexane. [b] These measurements were in heptane instead of in hexane.

The consistency of the data provides gratifying vindication that all experimental methods are measuring what was hoped to the expected accuracy. The only suggestion of a discrepancy involves a tendency for flash photolysis measurements in saturated hydrocarbons to give slightly higher values for $k$, but the data in carbon tetrachloride all seem to be in excellent agreement.

**Selection of "Best" Methods of Measurement.**—One purpose of this study was to assess the relative utilities of different experimental techniques applied to photostationary systems. If the two most promising techniques can be chosen, future work can be concentrated on them.

The Rabinowitch and Wood[6] technique for measuring photostationary radical concentrations was a brilliant conception that permitted a clear posing of the problems finally solved by the additional techniques. The measurements were based on spectrophotometric changes due to *molecular* iodine. While the results were obviously correct, the effects observed were barely outside the probable errors to be expected even from measuring techniques available today, and we do not think that the method deserves inclusion as one of the two most reliable. If the measurement of photostationary concentration were modified to be based on spectrophotometric or paramagnetic absorption measurement of effects due to the *atomic* dissociation products, the technique might well become a method of choice.

The direct measurement of quantum yield depends upon some scavenger to react with the products of photochemical dissociation. If a suitable clean reaction is available, the technique is so simple that this measurement should almost certainly be one of the two methods of choice in photostationary systems. Rutenberg and Taube[21] have shown that manganous ion in the presence of pyrophosphate is an excellent scavenger for halogen atoms in aqueous solution. The allyl iodide scavenging technique of Lampe and Noyes[10] is not as clean because the allyl iodide is also dissociated by light, but we still think that this method is one of the two that should be chosen for studies involving photochemical dissociation of iodine in organic solvents.

Circumstances probably will dictate whether flash photolysis or rotating sector techniques will be combined with quantum yield measurements. The direct measurement of $k$ by flash photolysis is probably capable of more accuracy than the measurement of $k\phi$ by sector methods, especially since $k\phi$ depends on the square of the mean lifetime. Also, the measurement of one rate constant with a functioning flash photolysis apparatus probably involves distinctly less work than the measurement of a life-time by the method employed in this work.

On the other hand, the initial construction of apparatus for sector work is much simpler than it is for flash photolysis, and the thermostating is also much easier for sector work.

In summary, flash photolysis will almost certainly be the method of choice for a laboratory that has a going research program employing this equipment. However, sector measurements of the type described here probably will be more economical of effort if it is desired to measure a few lifetimes in order to establish absolute rate constants for individual steps in some chain reaction. Also, sector techniques almost certainly will be selected if temperature coefficients are to be studied in detail.

It should also be noted that in principle flash photolysis can be used to measure both quantum yields and rate constants at the same time. The first quantum yields so obtained[5] agreed well with

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(20) R. M. Noyes and J. Zimmerman, *J. Chem. Phys.*, **18**, 656 (1950).

(21) A. C. Rutenberg and H. Taube, THIS JOURNAL, **72**, 5561 (1950), and **73**, 4426 (1951).

those by the scavenger technique[10] but were much less precise. Strong and Willard[8] have improved on the accuracy by using an analog computer, and the advantages of getting both quantities from a single type of measurement are obvious. However, from its very nature flash photolysis can scarcely employ really monochromatic light, and scavenger techniques will continue to be preferred for measuring accurate quantum yields especially as a function of wave length.

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The authors are indebted to Professor George Porter of the University of Sheffield for pointing out that changes in viscosities of solvents are usually greater than changes in diffusion coefficients of a specific solute in these solvents.

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# Rate Studies on Complex Reaction Systems in a Stirred Flow Reactor: The Alkaline Hydrolysis of Diethyl Succinate[1]

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The applicability of the continuous flow stirred tank reactor to kinetic studies of complex reaction systems has been demonstrated for the two-step alkaline hydrolysis of diethyl succinate in 70% ethanol. The method is exact but loses some of its success, as do other kinetic procedures, when applied to reactions involving medium effects. The data obtained show that $k_1$, the specific rate for the first saponification step, is subject to a primary salt effect which is specific to the succinate ion formed during the reaction. The rate is depressed with increasing succinate ion concentration, the magnitude of the depression at the same time depending upon the sodium ion concentration in the reaction medium. The specific rate for the second saponification step, $k_2$, exhibits a positive salt effect with increasing sodium ion concentration. The salt effects are not determined by ionic strength. The differences in rate between the first and second steps appear to be wholly accounted for by differences in activation entropy, with the activation energy for the second step actually lower than that for the first. An improvement in experimental technique has been described whereby the reaction vessel is internally rather than externally thermostated. Actual reaction temperatures are, therefore, not influenced by differences in heats of reaction brought about by differences in concentrations of reactants. It has also been shown that pumping devices employing pulsating flows may be used without adverse effect upon approach to and attainment of steady-state conditions.

The theory of the continuously flowing stirred tank reactor has been discussed previously by Denbigh[2] and by Hammett.[3] When applied to the study of non-integrable complex reaction systems, this technique offers an exact method for evaluation of specific rates, since rate equations are immediately expressible in algebraic rather than differential form. We have applied the technique to the saponification of diethyl succinate, a symmetrical diester in a solvent medium of 70% ethanol. This system, an example of a pair of competitive, consecutive second-order reactions, may be represented by the equations

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{C} + \mathrm{E}$$

$$\mathrm{B} + \mathrm{C} \xrightarrow{k_2} \mathrm{D} + \mathrm{E}$$

A represents the diester, B the hydroxide ion and C the half-saponified or monoester.

Ingold,[4] Ritchie,[5] and Westheimer, Jones and Lad[6] were successful in determining values of $k_1$ in such reaction systems by independent measurement of $k_2$ on the monoester combined with approximate methods of integration in experiments involving the complete system. Frost and Schwemer[7] have presented a "time-ratio" method of numerical analysis which permits evaluation of both rate constants from the data of a single run. The method, however, suffers from the disadvantage that the initial concentrations must be stoichiometrically equivalent. Wideqvist[8] has extended the usefulness of this method to all ratios of initial concentrations but relies upon a graphical integration for evaluation of the new parameter introduced.

**Symbols.**—These symbols are used in this paper

| | |
|---|---|
| $a_0$, $b_0$ | concn. of reactants in the entering liquid |
| $a_s$, $b_s$, $c_s$ | concn. of reactants in the reactor at steady state |
| $a'$, $b'$, $c'$ | concn. of reactants at point of quenching |
| $u$ | total flow rate |
| $V$ | reactor volume |
| $V^1$ | volume of exit tube |
| $w$ | reduced flow rate = $u/V$ |
| $r_1$, $r_2$ | instantaneous rates of first and second reaction steps |
| $k_1$, $k_2$ | second-order specific rates of first and second reaction steps |

**Method of Evaluation of Specific Rates.**—The flow equations for each reactant in the steady state are

$$w(a_0 - a_s) - r_1 = 0 \qquad (1)$$

$$w(b_0 - b_s) - r_1 - r_2 = 0 \qquad (2)$$

$$-wc_s + r_1 - r_2 = 0 \qquad (3)$$

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(6) F. H. Westheimer, W. A. Jones and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942).

(7) A. A. Frost and W. C. Schwemer, THIS JOURNAL, **73**, 4541 (1951); **74**, 1268 (1952).

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