thermal junctions in the circuit, one in the metal and one in the solution, the result has relatively little meaning except as it establishes the order of magnitude of the effects to be expected in other cases. For comparison it may be mentioned that the potential of the e.c. max. in 1.0 N KCl varies from −0.574 v. at 0° to −0.522 v. at 85°. All of these figures are stated relative to a normal calomel electrode at 25°.

Anyone who wishes to perform experiments like those discussed in this paper will have use for data on the absolute value of the minimum capacity at the various temperatures employed. Table I gives such data at five temperatures. It should be mentioned that absolute values of capacity are always a little uncertain and may require revision by several tenths of a per cent. as better methods are worked out.

TABLE I

MINIMUM VALUES OF THE DIFFERENTIAL CAPACITY[a]

Temp., °C.	1 N KCl	0.8 N NaF	0.1 N NaF	0.01 N NaF
	Microfarads per square centimeter			
0	16.58	16.00	15.76	15.65
25	16.50	15.97	15.74[b]	15.62[b]
45	16.43	15.90	15.66	15.52
65	16.27	15.77	15.52	15.37
85	16.08	15.56	15.31	15.13

[a] In those cases where there are two minima, the table refers to the one on the cathodic branch of the curve. [b] This is a redetermination of a value published previously in the author's Technical Report No. 14 to the Office of Naval Research, dated February 18, 1954.

It is a great convenience in this work to have values of the surface charge density, q, at some sufficiently cathodic potential that the effect of the anion is virtually eliminated. For this purpose Table II gives values of q at a potential of −1.205 v. This potential is sufficiently cathodic for all but the most strongly adsorbed anions (I^-, SCN^-, $S^=$) and is convenient for the integration of capacity data by the trapezoidal rule using potential intervals of 0.01 v. These data, like those in Table I, are a little uncertain in absolute value but give correct results for the potential of the e.c. max. when used together.

TABLE II

SURFACE CHARGE DENSITY, q, AT POTENTIAL AT −1.205 VOLTS[a]

Temp., °C.	1 N KCl	0.8 N NaF	0.1 N NaF	0.01 N NaF
	Microcoulombs per square centimeter			
0	14.60	14.20	13.58	12.73
25	14.22	13.73	13.03	12.14
45	13.86	13.49	12.79	11.83
65	13.51	13.14	12.40	11.47
85	13.28	12.86	12.10	11.14

[a] All potentials measured relative to a normal calomel electrode at 25°.

Conclusion

The investigation of the capacity of the electrical double layer in aqueous solutions of sodium fluoride in contact with mercury at several temperatures has provided a clue to the behavior and structure of the double layer. This has permitted the formulation of a theory which is at least qualitatively understandable and for which the next step will be to provide a quantitative expression. The author wishes to make it clear that he is merely *proposing* a theory and is not yet prepared to underwrite it.

Acknowledgments.—The author is grateful to Professor Earle S. Scott for stimulating discussions leading to the formulation of the theory proposed in this paper. He is indebted to Miss Vera Brewus for making many of the measurements and to the Office of Naval Research for the support of the project of which this work forms a part.

AMHERST, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Primary Quantum Yield for the Dissociation of Iodine Molecules in Carbon Tetrachloride Solution and the Rate Constant for the Recombination Reaction[1]

BY R. L. STRONG AND J. E. WILLARD

RECEIVED NOVEMBER 24, 1956

The quantum yield for the dissociation of iodine molecules in carbon tetrachloride solution at room temperature by a continuous spectrum of visible light has been found to be 0.13 ± 0.04. The determination has been made by the flash photolysis technique with a d.c. analog computer used to aid in correcting for the fact that the duration of the flash is appreciable relative to the time of recombination of I atoms. The recombination rate constant obtained is $k = 5.7 \pm 0.5 \times 10^9$ liters mole^{-1} sec.$^{-1}$ where $d[I_2]/dt = k[I]^2$. The relative extinction coefficients of iodine in the gas phase and in carbon tetrachloride solution and the visible spectrum of the xenon flash lamp have been determined.

Introduction

When a gaseous iodine molecule in the presence of a foreign gas absorbs a quantum of visible light, it always dissociates.[2] If, however, it is surrounded by a "cage" of solvent molecules, the atoms may lose their energy to the cage walls and immediately recombine[3] or they may recombine by diffusion after having escaped only a molecular diameter or so from each other.[4]

Knowledge of the quantum yield for the escape of such atoms from each other is relevant in interpretations of the over-all quantum yields of photochemical reactions, in reasoning about caging ef-

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(1) R. L. Strong and J. E. Willard, Abstracts of the New York Meeting of the American Chemical Society, Sept., 1954, p. 26-R.

(2) W. A. Noyes and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941.

(3) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(4) R. M. Noyes, *J. Chem. Phys.*, **18**, 999 (1950).

fects which may occur in the tracks of ionizing radiations[5a] and atoms activated by nuclear processes,[5] and in considerations of diffusion controlled kinetics[6] in general.

In principle this quantum yield can be determined by flash photolysis experiments in which the rate of recombination of iodine atoms in a solution is measured by the change in transmittance of an analyzing beam immediately after the iodine has absorbed a known number of quanta from an intense short-duration flash. Extrapolation of the recombination curve (on the straight line plot of 1/[I] *vs.* time) to zero time would give the concentration of iodine atoms initially produced (and escaping parent recombination) if the flash were instantaneous. In practice the rates of recombination in solution are so fast, and minimum flash times so long, that appreciable recombination occurs before the flash is over, thus invalidating a simple extrapolation and making it necessary to solve for the quantum yield ϕ in the equation

$$-\mathrm{d}[\mathrm{I}_2]/\mathrm{d}t = (1/2)(\mathrm{d}[\mathrm{I}]/\mathrm{d}t) = \phi(I_a) - k[\mathrm{I}]^2 \quad (1)$$

where I_a is the rate of light absorption, which varies with time. We have done this with the aid of an analog computer.

The method employed here is more quantitative than that employed for similar determinations by Marshall and Davidson[7] and differs radically in approach from that used by Lampe and Noyes.[8]

Methods and Results

Equipment and Materials.—The flash photolysis equipment used in the present work has been described elsewhere.[9]

The carbon tetrachloride solvent was Mallinckrodt AR low sulfur grade further purified by degassing and distilling through a phosphorus pentoxide train on the vacuum system used for filling the reaction cell. Mallinckrodt AR grade iodine was further purified by grinding with reagent grade potassium iodide followed by sublimation from the mixture through phosphorus pentoxide on the vacuum system.

Solution of the Differential Equation.—The value of ϕ in eq. 1 can be determined with the aid of a d. c. analog computer if I_a (the rate of light absorption in quanta cc.$^{-1}$ sec.$^{-1}$) is known as a function of time, if k has been determined, and if the iodine atom concentration is known at time t (these determinations will be described below).

In a d. c. analog computer, voltages are made to behave in a manner analogous to that prescribed by the variables and coefficients in the given differential equation.[10] To accomplish this, several computing elements, each consisting of a very high gain d. c. amplifier modified by input and feed back components in such a way that its output voltage is some mathematical function of the input voltage, are connected so that the various parts of the differential equation are represented by operations in the computing elements. With time as the independent variable the computer is operated, and the solutions of the problem are recorded as the voltage variations with time. Recording is usually done by means of a direct-writing recording potentiometer, although some computers[11] work on a time scale so fast that the complete solution to the problem can be repeated automatically many times a second, thus making visual observation on a cathode-ray oscilloscope possible.

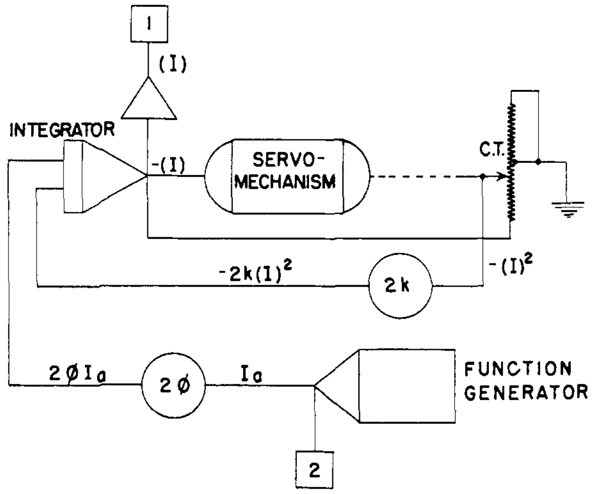

Fig. 1.—Computer block diagram.

The computer setup represented by the schematic block diagram in Fig. 1 was assembled on a Reeves Electronic Analog Computer (REAC).[12] The voltage corresponding to d[I]/dt was treated as if it were known and was fed into the integrator computing element. Its output, − [I] (each electronic integration results in a change of sign), was applied to a squaring unit that consisted of a servodriven potentiometer. The voltage corresponding to $-[\mathrm{I}]^2$ was finally multiplied by the constant $2k$ by means of a potentiometer and amplifier, giving $-2k[\mathrm{I}]^2$. This was fed into the integrator input along with the light intensity function (I_a) multiplied by 2ϕ. As defined by the differential equation, the sum of these two quantities ($2\phi I_a - 2k[\mathrm{I}]^2$) is equal to d[I]/d$t$, which has been assumed to be the input to the integrator. Thus the voltage corresponding to [I] must vary as prescribed by the differential equation. The value for ϕ was obtained by recording the voltage representing [I] as a function of time (output 1) and adjusting the potentiometer (2 ϕ) until

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(5) Discussion of reactions of this type and references are given by J. E. Willard in (a) *Ann. Rev. Phys. Chem.*, **6**, 141 (1955); (b) *Ann. Rev. Nucl. Sci.*, **3**, 193 (1953).

(6) See, for example: R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954); J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **76**, 3274 (1954).

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

(8) F. W. Lampe and R. M. Noyes, THIS JOURNAL, **76**, 2140 (1954).

(9) R. L. Strong, J. C. W. Chien, P. Graf and J. E. Willard, *J. Chem. Phys.*, in press.

(10) A thorough discussion of the construction and operation of analog computers is given by G. A. Korn and T. M. Korn, "Electronic Analog Computers," McGraw-Hill Book Co., Inc., New York, N. Y., 1952.

(11) For example, the Philbrick Repetitive Analog Computer, developed by the George A. Philbrick Researches, Inc., Boston, Massachusetts.

(12) Reeves Instrument Corporation, New York, N. Y. We are indebted to Mr. W. G. McClintock and the staff of the Computer Laboratory, Rensselaer Polytechnic Institute, Troy, N. Y., for their valuable aid in setting up and operating the REAC Computer. We are also grateful to Prof. H. A. Peterson, Chairman of the Department of Electrical Engineering, the University of Wisconsin, and to Mr. M. G. Spooner for their aid in making preliminary measurements on a Philbrick Repetitive Computer.

the voltage corresponded to the experimentally determined value of the iodine atom concentration at 150 microseconds.

The change in the relative light intensity of the flash as a function of time is shown in Fig. 2. This curve was adequately generated by a cathode-ray function generator, or photoformer,[13] in which an opaque mask shaped like the function is placed over the lower portion of a cathode-ray screen. As the electron beam sweeps across the tube face, an applied bias voltage on the vertical plates of the CRT tends to force the spot upward away from the mask. As soon as it emerges from behind the mask, however, a photocell mounted in front of the screen applies a voltage on the vertical plates phased so the beam is forced downward toward the mask. The net effect of the two voltages is that the beam will tend to travel just below the edge of the mask. Assuming that the voltages on the CRT plates are proportional to the deflections, the voltage on the vertical plates is forced to vary as a function of the voltage on the horizontal plates, the function being determined by the shape of the mask boundary. This voltage was fed into the computer as representative of I_a, and observed at output 2 (Fig. 1).

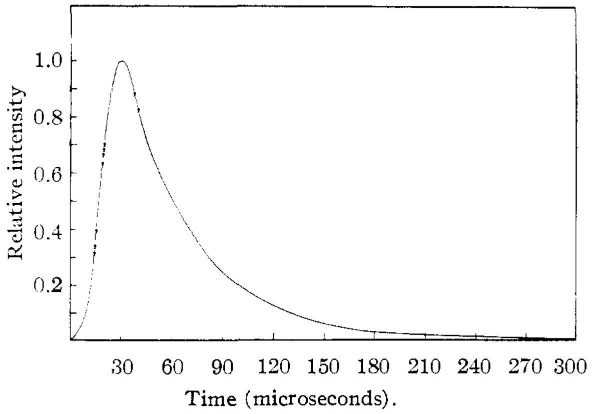

Fig. 2.—Relative light intensity from the flash lamp as a function of time.

The independently variable quantity in a machine such as the REAC is time (τ). The dependently variable quantities are voltages and potentiometer settings, designated below as capital letters. By convention, 100 volts = 1 computer unit. The following transformation equations were used to transform the variables in eq. 1 to machine variables: $\tau = \alpha t$; $Y = a_y[\mathrm{I}]$; and $Z = a_z I_a$, where α, a_y and a_z are scale factors. Equation 1 thus becomes

$$\mathrm{d}Y/\mathrm{d}\tau = 2\phi Z(a_y/\alpha a_z) - 2kY^2/\alpha a_y \qquad (2)$$

in terms of machine variables. The time scale factor (α) is numerically equal to the number of seconds representing the unit of the independent variable under consideration. In this case it was desirable to let the machine operate for 15 seconds corresponding to 150 microseconds problem time, so that $\alpha = 10^5$. A maximum rate of light absorption by the iodine in carbon tetrachloride was found to be 1.2×10^{20} quanta cc.$^{-1}$ sec.$^{-1}$ (as discussed below); the function generator was adjusted so that its output at the maximum of the curve was 0.75 computer unit (75 v.), giving $a_z = 6.25 \times 10^{-21}$ (computer units) (quanta cc.$^{-1}$ sec.$^{-1}$)$^{-1}$. Assuming a maximum iodine atom concentration of less than 10^{15} atoms cc.$^{-1}$, a value for a_y of 10^{-15} (computer units) (atoms cc.$^{-1}$)$^{-1}$ was chosen so that $Y = 1$ computer unit when $[\mathrm{I}] = 10^{15}$ atoms cc.$^{-1}$.

Experimentally, it had been found (see Table II) that $k = 5.7 \times 10^9$ liters mole^{-1} sec.$^{-1}$ = 9.5×10^{-12} cc. molecule^{-1} sec.$^{-1}$, and $[\mathrm{I}] = 9.2 \times 10^{-7}$ moles liter^{-1} = 5.54×10^{14} atoms cc.$^{-1}$ at 150 microseconds. Equation 2 then becomes $\mathrm{d}Y/\mathrm{d}\tau = 3.2\phi Z - 0.19Y^2$ and $Y = 0.554$ computer unit (55.4 v.) at 150 microseconds. The scale factor potentiometer corresponding to $3.2\,\phi$ was varied until this voltage was obtained, resulting in a value for ϕ of 0.13. A maximum error of ±0.04 was determined by feeding into the computer, maximum and minimum experimental values for k and the iodine atom concentration at 150 microseconds, and estimated maximum and minimum values for the light intensity function.

As shown by the recording for Y *vs.* τ, the iodine atom concentration reached a maximum value of *ca.* 1.4×10^{-6} mole per liter at 65 microseconds, although the light intensity from the flash lamp was at a maximum at only 30 microseconds.

Rate of Light Absorption.—The number of quanta absorbed from a flash of the flash lamp by the iodine in a Pyrex cell 10 cm. long and 25 mm. i.d. containing gaseous iodine at 1.07×10^{-5} mole per liter was 3.49×10^{15} per cc. This was determined by assuming a yield of two iodine atoms per photon absorbed and extrapolating a plot of $1/[\mathrm{I}]$ back to the time of initiation of the flash,[14] a valid procedure since the time required for atom recombination in the *gas* is long compared to the duration of the flash. On the basis of the fact that this value is the area enclosed by a curve identical in shape to that shown in Fig. 2, it can be shown by graphical methods that the peak rate of light absorption in the gas phase cell was 5.74×10^{19} quanta cc.$^{-1}$ sec.$^{-1}$.

To find the light absorption by a carbon tetrachloride solution of iodine in a cell placed in the same position and flashed with the same intensity as the gas cell, comparison was made of the extinction coefficients of gaseous and dissolved iodine (Table I), and the spectral distribution of the light from the flash lamp (Fig. 3) was determined. The experimental comparison was necessary because there are large inconsistencies in the extinction coefficient

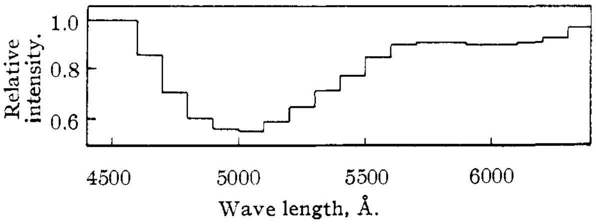

Fig. 3.—Spectral distribution of light from the flash lamp.

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(13) Reference 10, page 248.

(14) Additional details of this work are given in the Ph.D. Thesis of R. L. Strong filed with the University of Wisconsin library in 1954.

values in the literature. Measurements of optical density as a function of wave length on gaseous iodine (using a Beckman DU spectrophotometer) were compared with similar measurements on the same iodine dissolved in a weighed amount of carbon tetrachloride. By assuming a value of 905[8,15] for the extinction coefficient of iodine in carbon tetrachloride at 5200 Å., its wave length of maximum absorption, the concentration in the carbon tetrachloride solution and the extinction coefficients at the other wave lengths were calculated.[14]

At wave lengths greater than 4995 Å. the spectrum of iodine gas consists of bands rather than a continuum[2] even at an argon pressure of 710 mm. Therefore, relatively large fluctuations in the measured values of the extinction coefficients were obtained at the longer wave lengths because of the use of a narrow spectrophotometer effective band width.

The relative intensity of the flash lamps[9] (containing 70 mm. of Xe and flashed at 27 μf. and 9000 v.) for successive 100 Å. bands from 4400 to 6500 Å. shown in Fig. 2 was determined with the aid of an Applied Research Laboratories 150 cm. grating spectrograph and an ARL projector densitometer.[14,16,17]

The rate of radiant energy absorption may be expressed as $I_a' = I_0(1 - 10^{-\epsilon cd}) = I_0(1 - e^{-2.3\epsilon cd})$ in units of quanta traversing unit area per sec. Expanding the exponential term in a series gives $(1 - e^{-2.3\epsilon cd}) = 2.3\epsilon cd - (2.3\epsilon cd)^2/2! \dots$; for small absorption ($\epsilon cd << 1$) the higher power terms may be neglected, so that $I_a' = I_0(2.3\epsilon cd)$. The average number of quanta absorbed per unit volume per second, I_a, is given by $I_a = (A/V)I_0 (2.3\epsilon cd)$, where A is the area of the cross-section of the radiation beam and V is the volume of the vessel, (A and V will cancel out when the comparison is made between the light absorbed by the gas and solution cells under identical experimental conditions, assuming no differences in incident light at the interface surfaces.) It follows, then, that

$$(I_a)_{gas} \cong (A/V)\, 2.3[I_2]_{gas}\, d\Sigma(I_0)_\lambda\, (\epsilon_{\lambda,\, gas})(\lambda/hc)$$

$$(I_a)_{soln} \cong (A/V)\, 2.3[I_2]_{soln}\, d\Sigma(I_0)_\lambda\, (\epsilon_{\lambda,\, soln})(\lambda/hc)$$

where λ is the average wave length of a 100 Å. band, and λ/hc is the conversion factor from ergs to quanta at each wave length. Therefore

$$(I_a)_{soln} = (I_a)_{gas} \frac{[I_2]_{soln}\ \Sigma(I_0)_\lambda\, (\epsilon_{\lambda,\, soln})\lambda}{[I_2]_{gas}\ \Sigma(I_0)_\lambda\, (\epsilon_{\lambda,\, gas})\lambda}$$

Average values for the extinction coefficients for each 100 Å. band for iodine gas and iodine in carbon tetrachloride solution were calculated from the extinction coefficients measured in this work (Table I) and values of $(I_0)_\lambda$ were determined from Fig. 3. A value of 1.22 was calculated for the ratio: $(\Sigma (I_0) (\epsilon_{\lambda,\, soln})\lambda)/(\Sigma(I_0)_\lambda(\epsilon_{\lambda,\, gas})\lambda)$. The concentration of iodine in the carbon tetrachloride cell was 1.84 × 10^{-5} mole per liter, and the concentration of iodine in the gas phase cell (argon pressure = 532 mm.) was 1.07 × 10^{-5} mole per liter, so that the maximum rate of light absorption by the iodine in carbon tetrachloride was 1.2 × 10^{20} quanta cc.$^{-1}$ sec.$^{-1}$.

TABLE I

EXTINCTION COEFFICIENTS FOR IODINE AT ROOM TEMPERATURE

	Extinction coefficients[a]		
		In the gas phase	
Å.	In CCl_4 soln.	480 mm.[b]	710 mm.[b]
4400	82	74	60
4500	150	104	
4600	243	157	155
4700	369	224	216
4800	517	335	332
4900	663	447	445
5000	804	577	579
5100	882	676	683
5200	905	724	745
5300	863	709	708
5400	763	660	641
5500	633	606	656
5600	487	472	489
5700	361		
5800	263	335	318
5900	181		
6000	131	125	101
6200	74		

[a] ϵ from the expression $I = I_0\, 10^{-\epsilon cd}$ where c is the concentration of iodine in moles per liter and d the length of absorbing path in cm. [b] Pressure of argon in mm.

Determination of Recombination Rate Constants.—A typical oscillogram resulting from the recombination of iodine atoms in carbon tetrachloride at room temperature, compared with the scattered light trace (obtained by flashing the activating light with the filled reaction cell at the light axis and the analyzing beam off) is given in Fig. 4. The vertical difference between the

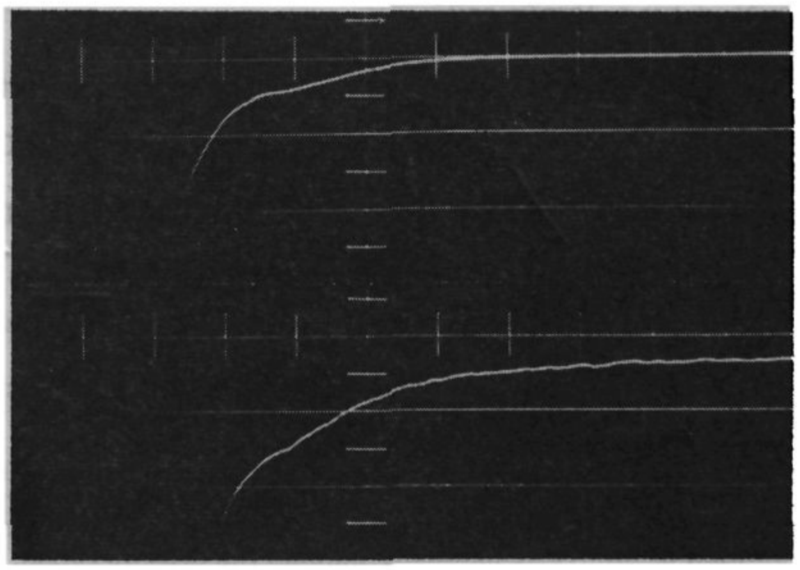

Fig. 4.—Oscillograms for recombination of iodine atoms in carbon tetrachloride solution. The top panel, taken without the analyzing beam on, shows the deflection due to scattered light; the bottom panel shows the sum of the deflections due to scattered light and to dissociation of the iodine. Sweep time, 50 μsec./1 cm. scale division; vertical sensitivity, 0.40 volt/cm., $[I_2]_0$, 1.84 × 10^{-5} mole/liter.

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(15) (a) G. Groh and S. Papp, *Z. physik. Chem.*, **A149**, 153 (1930); (b) W. R. Brode, THIS JOURNAL, **48**, 1877 (1926); (c) O. J. Walker, *Trans. Faraday Soc.*, **31**, 1432 (1935); (d) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, 2703 (1949); (e) A. I. Popov, K. C. Brinker, L. Campanaro and R. W. Rinehart, *ibid.*, **73**, 514 (1951).

(16) We are indebted to Dr. V. W. Meloche and Dr. Irving Shain of the Analytical Chemistry Division for making this equipment available and for assistance in its use.

(17) M. J. Christie and G. Porter, *Proc. Roy. Soc.* (*London*), **A212**, 398 (1952), have made extensive investigations of the spectral characteristics of the flash discharge in the region of 2600 to 4400 Å., which is below the wave lengths of interest in the present work.

scattered light trace and the recombination trace is proportional to the iodine atom concentration. The precision of these results was less than for those in the gas phase[9,14] because of the smaller per cent. initial dissociation, resulting from the caging effect, and the faster rate of recombination, resulting from the constant presence of solvent molecules to serve as the "third body." Nevertheless, the best curve through the $1/[I]$ *vs.* time plot clearly showed a second-order dependence of the rate on the iodine atom concentration. Values of k in the relation $d[I_2]/dt = k[I]^2$ were calculated as previously described[9,14] and are given in Table II for 20 determinations. Included in the table are the values obtained for the iodine atom concentration at 150 microseconds, which were used in the calculation of the primary quantum yield.

TABLE II

RECOMBINATION RATE CONSTANTS FOR IODINE IN CARBON TETRACHLORIDE AT ROOM TEMPERATURE

$[I_2]_0 = 1.84 \times 10^{-5}$ mole/liter

$k \times 10^{-9}$, l. mole^{-1} sec.$^{-1}$	$[I] \times 10^7$ at t = 150 μsec. mole/l.	$k \times 10^{-9}$, l. mole^{-1} sec.$^{-1}$	$[I] \times 10^7$ at t = 150 μsec. mole/l.
5.16	7.6	5.96	9.7
5.48	9.0	5.96	9.7
6.30	10.2	5.31	8.8
5.74	10.3	6.66	9.5
6.71	9.8	5.27	8.5
5.86	8.8	5.11	9.4
5.40	9.7	6.47	8.3
5.96	11.0	5.27	9.0
5.10	7.7	5.39	9.1
5.96	9.7	5.39	9.5

Av. of k values = $5.7 \pm 0.5 \times 10^9$ l. mole^{-1} sec^{-1}.

Discussion

The procedures outlined above gave a value of 0.13 for the fraction of the iodine molecules in carbon tetrachloride solution which, having absorbed a photon, produce iodine atoms which escape recombination to the parent partnership. The light used was the full light of the xenon flash lamp transmitted by a Pyrex cell.

Marshall and Davidson,[7] also using the flash technique, but making no attempt to correct quantitatively for the time dependence of the flash intensity or for the difference in the absorption spectra of iodine in the gas and in solution, and using only light of wave lengths greater than 5000 Å., obtained 0.19 molecule dissociated per quantum. From a determination of the quantum yield for disappearance of iodine in air-saturated solutions of allyl iodide in carbon tetrachloride solution, Lampe and Noyes[8] have obtained a value of 0.14 for the quantum yield of I atom escape from the parent partnership. This determination was made with 4368 Å. light. It is presumed that the allyl iodide reacts with all of the iodine atoms which escape recombination and that the radicals so formed are removed from further chemical activity by reaction with oxygen.

The fact that three laboratories using two widely different techniques obtain values as close together as those cited above is convincing evidence that the true value lies in the region indicated. It, together with the values which have been obtained for iodine in hexane[7,8] (0.41, 0.66) and in hexachlorobutadiene[9] (0.075), offers the most direct experimental evidence yet obtained for the "cage effect."[3] It will be desirable if it is possible for the direct measurements by the flash photolysis technique to be extended to determine the effect of wave length and of a variety of solvents. Use of the analog computer technique described in this paper makes quantitative determinations of this type possible even when the duration of the flash is necessarily appreciable relative to the time required for atom recombination.

Acknowledgment.—This work was supported in part by the United States Atomic Energy Commission, and by the University Research Committee with funds made available by the Wisconsin Alumni Research Foundation. It also was aided by fellowships supported by the United States Rubber Co. and the Minnesota Mining and Manufacturing Co.

MADISON 6, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Methyl *n*-Butyl Ketone[1,2]

BY WILLIAM T. BARRY, JR., AND W. D. WALTERS

RECEIVED DECEMBER 13, 1956

The gas-phase thermal decomposition of methyl *n*-butyl ketone has been studied in the neighborhood of 430–500°. The principal products of the reaction during the early stages are: (a) propylene and acetone, (b) ethane and methyl vinyl ketone and (c) methane, carbon monoxide and 1-butene. A small quantity of ethylene also has been found. Acid-forming constituents, *e.g.*, ketenes, are present in only small amounts. The order of the decomposition is about 1.3 and the variation of the rate with temperature gives an apparent activation energy of approximately 52 ± 3 kcal./mole for 200 mm. experiments. The reaction is predominantly homogeneous although it is inhibited to a slight extent by packing the reaction vessel. The addition of propylene markedly inhibits the decomposition. Small quantities of added biacetyl at 475° or ethylene oxide at 450° accelerate the decomposition.

The thermal decomposition of methyl *n*-butyl ketone over a copper–aluminum oxide catalyst has been reported by Mailhe.[3] The composition of the gaseous products was found to be carbon monoxide (18.9%), hydrogen (8.0%), methane (23.5%), saturated hydrocarbons (16.5%) and

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(1) This work was supported by the Office of Naval Research.

(2) Abstracted from the Ph.D. thesis submitted by William T. Barry, Jr.

(3) A. Mailhe, *Bull. soc. chem. France*, **31**, 863 (1922).