

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

**Absolute Quantum Yields for Dissociation of Iodine in Inert Solvents**BY FREDERICK W. LAMPE<sup>1</sup> AND RICHARD M. NOYES

RECEIVED DECEMBER 15, 1953

When iodine atoms are produced in air-saturated solutions containing enough allyl iodide, they react quantitatively with the production of a molecule of iodine from each atom. We have used this observation to measure the efficiency with which light of 4358 Å. causes dissociation of molecular iodine and allyl iodide into fragments that escape their original partners. Data in hexane, carbon tetrachloride and hexachlorobutadiene-1,3 suggest that the quantum yield for escaping fragments is greatly diminished as the molecular weight of the solvent increases. We regard these observations as the best present support for the idea that the fragments from a photochemical dissociation are produced in a "cage" of surrounding solvent molecules from which they must escape in the initial act if they are to avoid recombination.

**Introduction**

If a molecule in solution absorbs a quantum containing sufficient energy to cause dissociation, the potential fragments may not become permanently separated because of deactivation of the excited molecule, failure to escape the "cage" of solvent molecules in which they are formed, or diffusive recombination after a very temporary escape. If these various effects can be distinguished, then studies of quantum efficiencies for photochemical dissociation in solution may furnish useful information on the nature of liquids and on rate processes controlled by diffusion together of reactants.

Two types of procedure are available for obtaining these quantum efficiencies. One involves measurement of two of these three quantities: photostationary concentration of fragments, average lifetime of fragments and rate constant for recombination. This approach has been used for solutions of iodine at room temperature in hexane or heptane and to less extent in carbon tetrachloride. The photostationary concentration was measured by Rabinowitch and Wood<sup>2</sup> from the decrease in optical density of a solution under strong illumination. It was also calculated<sup>3</sup> by comparing the rate of a photochemical reaction involving iodine atoms with the extrapolated rate of the thermal reaction at higher temperatures and assuming that the equilibrium constant for the thermal dissociation of iodine is the same in solution as the known gas phase value. The results were in fortuitously good agreement. The average lifetime of iodine atoms in an illuminated solution has been measured<sup>3</sup> by applying rotating sector techniques to an exchange reaction of iodine atoms. Marshall and Davidson<sup>4</sup> have recently followed the recombination of iodine atoms from the change in absorbency of the solution immediately after a flash photolysis. Their rate constant in heptane agrees within a factor of two with the constant calculated in hexane from the photostationary and lifetime measurements, and their constant in carbon tetrachloride is in excellent agreement with the value calculated from the photostationary data of Rabinowitch and Wood and the results of the present work.

(1) Based on a dissertation submitted by Frederick W. Lampe to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry. Persons wishing to consult the more complete report or to obtain a microfilm thereof may address the Library, Columbia University, New York 27, New York.

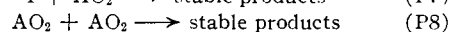
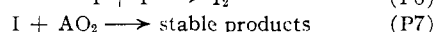
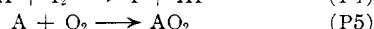
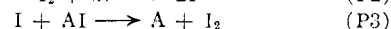
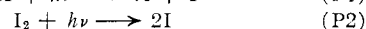
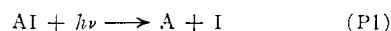
(2) E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 547 (1936).

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

(4) R. Marshall and N. Davidson, *ibid.*, **21**, 2086 (1953).

Although these independent studies are gratifyingly self-consistent and reasonable, these techniques do not lend themselves easily to measurements of quantum yield. Two types of experiment are necessary, and the procedure of Rabinowitch and Wood involves measuring a change of a few hundredths of a per cent. in light absorption and pushes techniques to the limit.

A simpler procedure for measuring quantum yields is to use a scavenger to react with fragments produced photochemically. The scavenger should react negligibly slowly in the dark, and the quantum yield for photochemical reaction should be independent of the intensity of absorbed radiation and of concentration of scavenger. This technique was cleverly developed by Rutenberg and Taube<sup>5</sup> to use cerous and manganous ions for studying the photodissociation of halogens in water. Studies of the photochemical exchange between iodine and allyl iodide<sup>6</sup> (AI) suggested that a similar technique could be used for solutions of iodine in inert solvents. The following steps of the proposed mechanism are of interest in a solution in which exchange processes are neglected



If one makes the usual steady state assumption that  $d[\text{I}]/dt = 0$ , this mechanism predicts<sup>1</sup>

$$\frac{d[\text{I}_2]}{dt} = \phi_{\text{I}_2}q_{\text{I}_2} + \phi_{\text{AI}}q_{\text{AI}} - k_6[\text{I}]^2 - k_7[\text{I}][\text{AO}_2] \quad (1)$$

where  $\phi$  is the quantum yield for dissociation of a species and  $q$  is the rate of absorption of light by the species in quanta/ml. sec. This equation can be written from inspection if one notes that a molecule of iodine is produced from every free atom that does not react by (P6) or (P7). If the light intensity is low and the allyl iodide concentration is high so that the sequence of (P3) and (P5) is much more frequent than the radical-radical steps (P6) and (P7), the allyl iodide is an effective scavenger and the last two terms in equation 1 can be neglected.

If iodine and allyl iodide are the only species that absorb light, we can write

(5) (a) A. C. Rutenberg and H. Taube, *THIS JOURNAL*, **72**, 5561 (1950); (b) **73**, 4426 (1951).

(6) D. J. Sibbett and R. M. Noyes, *ibid.*, **75**, 763 (1953).

$$q_{I_2} = \frac{1}{L} \int_0^L \alpha_{I_2}[I_2] I_0 e^{-x(\alpha_{I_2}[I_2] + \alpha_{AI}[AI])} dx = \frac{(1 - e^{-2.3D})}{2.3D} I_0 \alpha_{I_2}[I_2] \quad (2)$$

where  $I_0$  is the incident intensity on the cell in quanta/cm.<sup>2</sup> sec.,  $L$  is the length of light path in cm.,  $\alpha$  is the absorption coefficient of a species, and the optical density  $D = \log I_0/I$ . If steps (P6) and (P7) can be neglected, equation 1 can be rewritten

$$R = \frac{2.3D}{1 - e^{-2.3D}} \frac{d[I_2]}{dt} = \phi_{I_2} \alpha_{I_2} I_0 [I_2] + \phi_{AI} \alpha_{AI} I_0 [AI] \quad (3)$$

If the rate of photochemical production of iodine is measured in a number of solutions containing the same concentration of allyl iodide,  $R$  should be a linear function of the concentration of iodine and the data should permit evaluation of  $\phi_{I_2}$  and  $\phi_{AI}$ , the only unknown quantities in equation 3. We have made such measurements in three different solvents over a range of temperatures and have obtained data completely consistent with these equations and in numerical agreement with the predictions of independent experiments.

### Experimental

**Materials.**—The hexane was commercial petroleum ether purified with fuming sulfuric acid and acidic permanganate as described previously.<sup>3</sup>

Best grade carbon tetrachloride was used without further purification. Irradiation of solutions of iodine that had been prepared in the dark indicated no measurable reaction.

Hexachlorobutadiene-1,3 from the Hooker Electrochemical Company was used without further purification. Spectrophotometric and radiochemical tests indicated that it contained an impurity that reacted rapidly with  $2 \times 10^{-6}$  mole/liter of iodine. After this reaction (which was corrected for), the solvent appeared to be completely inert.

Allyl iodide was washed with sulfite, vacuum distilled under nitrogen and stored as described by Sibbett and Noyes.<sup>7</sup>

Resublimed C.P. iodine was used without further purification.

**Apparatus and Procedure.**—Experiments were carried out in a cylindrical Pyrex cell 5.00 cm. long and 2.0 cm. in diameter which could be mounted reproducibly either in a thermostat on an optical bench or in a Beckman spectrophotometer. Water of a known temperature was pumped through the thermostat, and the cell was illuminated with light of 4358 Å. isolated with filters from a thermostated AH-4 mercury arc. The absolute intensity of the lamp was measured with a thermopile-galvanometer circuit calibrated against a standard lamp, and a photo tube was used for monitoring.  $I_0$ , the intensity incident on the solution, was always  $1.46 \times 10^{14}$  quanta/cm.<sup>2</sup> sec. =  $2.42 \times 10^{-10}$  einstein/cm.<sup>2</sup> sec. The optical system is described in more detail elsewhere.<sup>1,3</sup>

After each period of illumination, the cell was thermostated to about 25° and the optical density was measured at the iodine maximum in the solvent used. The cell was then returned to the optical bench, thermostated to the temperature of the run, and illuminated again.

In order to convert the readings to change in iodine concentration and light absorbed by a species, it was necessary to know extinction coefficients (defined by  $\log I_0/I = L \sum_i \epsilon_i c_i$ ) for the species at the 436m $\mu$  used for illumination and at the absorption maximum for iodine used in the analysis. The results of spectrophotometric measurements in all three solvents are reported in Table I. Allyl iodide did not absorb detectably at the iodine absorption maximum. In addition, runs in hexachlorobutadiene-1,3 were corrected for an optical density of 0.041 due to absorption at 436 m $\mu$  by the solvent itself. The absorption spectrum of iodine in this solvent resembled that in the other inert solvents; apparently there was little if any interaction with the double bonds in the solvent molecules. The extinction co-

efficients did not vary detectably over the temperature range used in these studies.

TABLE I  
EXTINCTION COEFFICIENTS AT 25°

Solvent	C <sub>6</sub> H <sub>14</sub>	CCl <sub>4</sub>	C <sub>6</sub> Cl <sub>6</sub>
$E_{I_2}$ (436 m $\mu$ ) <sup>a</sup>	46 ± 1	67 ± 1	57 ± 7
$E_{AI}$ (436 m $\mu$ ) <sup>a</sup>	0.036 ± 0.002	0.038 ± 0.007	0.062 ± 0.011
$I_2$ absorption max., m $\mu$	525	518	519
$E_{I_2}$ (max) <sup>a</sup>	881 ± 4	920 ± 4	936 ± 10

<sup>a</sup> Extinction coefficients are in l./mole cm.

### Results and Discussion

**Treatment of Data.**—Equation 3 predicts that the rate of iodine production will vary during a run. However, our conditions were such that the average rate was not more than 2% greater than the initial rate. The procedure was to plot iodine concentration (optical density) against time of illumination and fit a least squares line through the points. The slope of this line was related to the rate of iodine production, taken to be at the initial concentration of iodine. Figure 1 is representative of the 73 individual runs of this sort, and the rates obtained are presented in Table II.

As is apparent from Table II, the runs were carried out in series at constant temperature and allyl iodide concentration. Values of  $R$  for the runs in a series were plotted against initial iodine concentration, and the points were fitted by least squares to

$$R = A + B[I_2] \quad (4)$$

From equation 3,  $A = \phi_{AI} \alpha_{AI} I_0 [AI]$  and  $B = \phi_{I_2} \alpha_{I_2} I_0$ . Figures 2 and 3 are plots for two series and are chosen to illustrate minimum and maximum scatter of individual runs. The quantum yields

TABLE II  
RATE OF IODINE PRODUCTION

Temp., °C.	[AI], mole/l.	Initial [I <sub>2</sub> ] × 10 <sup>5</sup> , mole/l.	R × 10 <sup>10</sup> , mole/l. sec.
Hexane			
15.0	0.0758	2.14	9.26
		3.35	10.7
		4.70	12.6
		5.89	15.1
		8.07	16.5
		10.10	19.6
25.0	.0758	0.07	9.18
		3.02	13.1
		4.55	15.9
		5.98	17.9
		7.06	20.4
		8.83	23.1
25.0	.101	1.59	13.0
		2.61	14.2
		3.86	17.6
		5.12	19.8
		7.77	22.9
		11.37	30.2
25.0	.00841	2.71	4.23
		5.79	8.03
		6.75	9.36
		8.52	12.0
		10.32	12.9
		12.42	14.9

(7) D. J. Sibbett and R. M. Noyes, *ibid.*, **75**, 761 (1953).

TABLE II (Continued)

Temp., °C.	[AI], mole/l.	Initial [I <sub>2</sub> ] × 10 <sup>6</sup> , mole/l.	R × 10 <sup>10</sup> , mole/l. sec.
Carbon Tetrachloride			
17.5	0.0929	2.77	3.25
		4.52	4.22
		6.78	5.64
		8.91	6.29
		10.71	6.31
		12.10	7.15
25.0	.0929	1.15	3.42
		2.48	4.18
		4.16	4.48
		5.24	5.63
		7.36	5.89
		10.58	8.68
25.0	.186	2.16	5.68
		4.22	8.13
		6.13	8.91
		7.85	10.2
		9.76	10.5
		14.77	12.8
38.0	.0929	1.08	4.35
		2.39	5.54
		4.91	6.74
		6.76	8.48
		8.44	10.8
		10.22	11.2
Hexachlorobutadiene-1,3			
15.0	0.0979	6.06	1.71
		7.65	2.09
		9.25	2.06
		11.38	2.46
		14.34	3.14
		16.18	2.92
25.0	.0979	3.94	2.44
		5.29	2.66
		7.65	4.08
		10.00	4.15
		12.68	4.68
		14.70	4.73
		17.10	6.18
25.0	.147	4.52	3.52
		7.16	4.22
		8.95	4.47
		11.21	5.25
		14.51	5.41
		15.81	6.31
35.0	.0979	3.90	3.82
		5.85	4.81
		7.97	5.25
		10.42	6.06
		14.12	8.05
		16.43	10.1

calculated from these plots are presented in Table III.

**Effect of Allyl Iodide Concentration.**—Series at different allyl iodide concentrations above 0.075 *M* but with the same temperature and solvent gave values of *A* proportional to concentration and of *B* independent of concentration, as would be predicted if the allyl iodide was acting as an effective scavenger. However, if the concentration is low

TABLE III

Solvent	QUANTUM YIELDS FOR PHOTODISSOCIATION			
	Temp., °C.	φ <sub>I<sub>2</sub></sub>		φ <sub>AI</sub>
Hexane	15.0	0.50 ± 0.04	0.44 ± 0.04	
	25.0	.66 ± .04	.54 ± .04	
Carbon tetrachloride	17.5	.11 ± .01	.13 ± .03	
	25.0	.14 ± .01	.14 ± .03	
	38.0	.21 ± .02	.18 ± .04	
Hexachlorobutadiene-1,3	15.0	.042 ± .006	.029 ± .006	
	25.0	.075 ± .009	.049 ± .008	
	35.0	.15 ± .02	.052 ± .012	

enough, steps (P6) and (P7) should be able to compete with the sequence (P3-P5). This competition should be more important at higher rates of absorption of radiation (higher iodine concentrations), and the plot for a series of runs at low allyl iodide should be curved. Such a plot is illustrated in Fig. 4; it was fitted by least squares to an equation of the form

$$R = A + B[I_2] + C[I_2]^2 \quad (5)$$

The values of the constants permit an additional test of the assumed mechanism. The data on photochemical exchange<sup>8</sup> were fitted on the assumption  $k_6 = 1/2k_7 = k_8$ . If a previously determined value<sup>3</sup> is taken for  $k_6$ , then the photochemical exchange data in hexane at 25° permit evaluation of  $k_8$  and  $k_4/k_5[O_2]$ . We have used these values and the quantum yield calculated from the data at higher allyl iodide concentration to estimate the constants in equation 5. The details of the calculations are presented elsewhere,<sup>1</sup> and the results are presented in Table IV. The agreement as to the magnitude of the curvature provides additional confirmation for a mechanism which seemed much more shaky when it was proposed on the basis of exchange data alone.

TABLE IV  
EVALUATION OF CONSTANTS IN EQUATION 5

Constant	Calcd. from other rate data	Obsd. from Fig. 4
<i>A</i>	$4.6 \times 10^{10}$	$4.55 \times 10^{10}$
<i>B</i>	$1.4 \times 10^{-5}$	$1.45 \times 10^{-5}$
<i>C</i>	$-6.9 \times 10^{-23}$	$-4.3 \times 10^{-23}$

**Effect of Oxygen.**—Figure 5 shows the data for a run in which at least most of the atmospheric oxygen was removed by sweeping the solution out with a stream of nitrogen for an hour before illumination. The behavior is obviously very different from the comparable run in air shown in Fig. 1. The rate of production of additional iodine was very low initially, and the subsequent increase may well have been due to leakage of air through the ungreased stopcock on the cell. This run confirms the proposal of the mechanism that oxygen is involved in the sequence of steps leading to production of new iodine. It is also in agreement with other observations that removal of oxygen greatly reduces quantum yields in the photolysis of allyl<sup>18</sup> and other<sup>9</sup> organic iodides.

Since previous studies<sup>6</sup> had shown that solutions saturated with oxygen and air showed the same

(8) W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

(9) S. Hacopian and T. Iredale, *Nature*, **166**, 156 (1950).

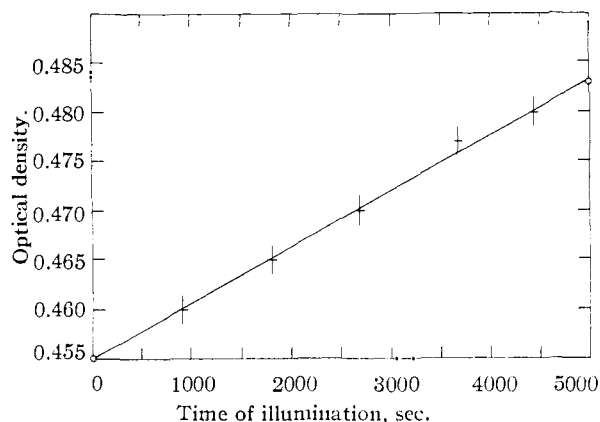


Fig. 1.—Rate of production of iodine during illumination, conditions: hexane at 25.0°,  $[AI] = 0.00841 M$ , initial  $[I_2] = 1.03 \times 10^{-4} M$ .

quantum yields for exchange at concentrations used in these experiments, we made no attempt to study the effect of increased oxygen concentrations. Actually, saturation of the solutions with air produced a greater concentration of oxygen than of molecular iodine.<sup>10</sup>

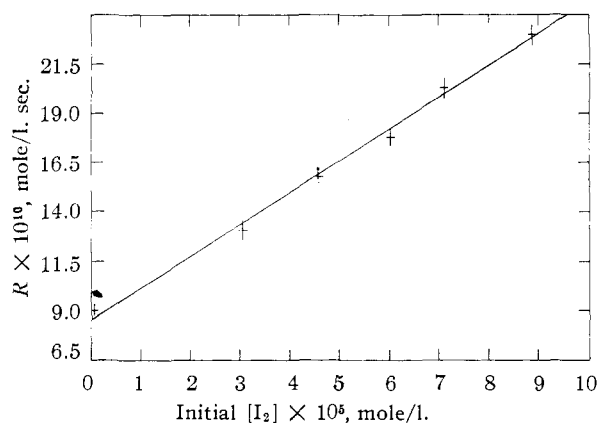


Fig. 2.—Effect of iodine concentration on rate of iodine production, conditions: hexane at 25.0°,  $[AI] = 0.0758 M$ .

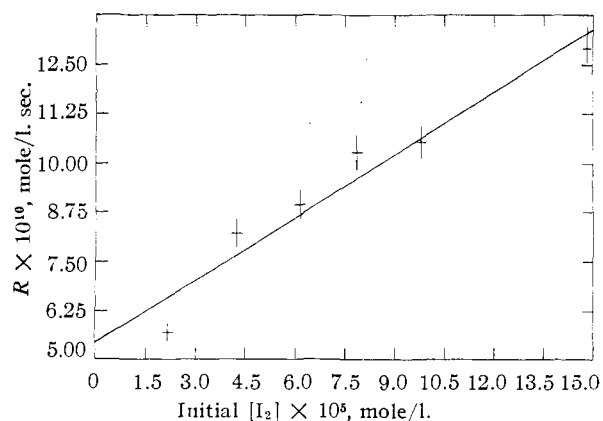


Fig. 3.—Effect of iodine concentration on rate of iodine production, conditions: carbon tetrachloride at 25.0°,  $[AI] = 0.186 M$ .

(10) St. Gniwosoz and Al. Walfisz. *Z. physik. Chem.*, **1**, 70 (1887).

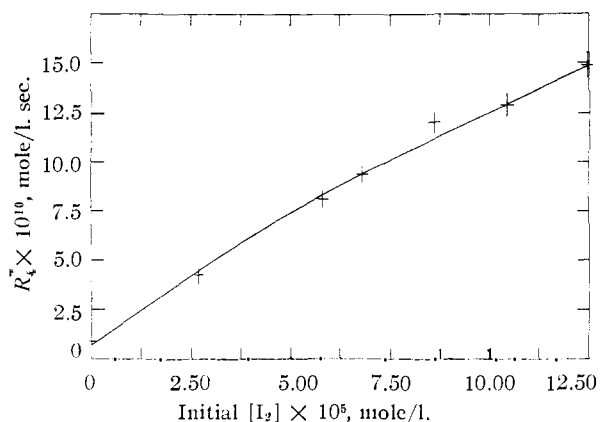


Fig. 4.—Change of rate with iodine concentration in low allyl iodide, conditions: hexane at 25.0°,  $[AI] = 0.00841 M$ .

**Validity of Interpretation.**—The experimental procedure assumes that during a run all change in optical density near 520  $m\mu$  is due to change in iodine concentration. This interpretation is supported by the observation that a solution of allyl iodide that had undergone some decomposition did not alter the shape of the absorption spectrum of a solution of iodine to which it was added.

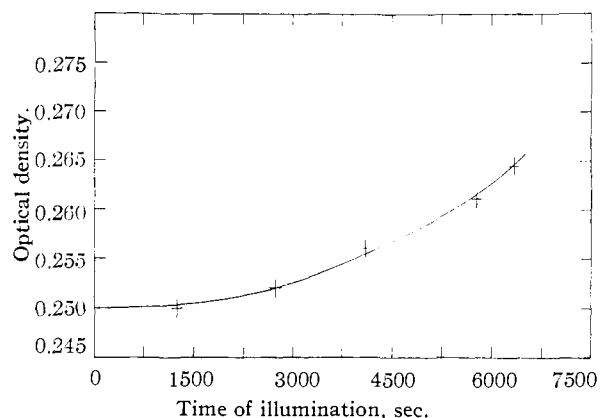


Fig. 5.—Effect of illumination under nitrogen, conditions: hexane at 25.0°,  $[AI] = 0.00841 M$ , initial  $[I_2] = 5.68 \times 10^{-5} M$ .

The assumption that allyl iodide is indeed acting as an effective scavenger is indicated by absence of change in apparent quantum yield when the allyl iodide concentration is changed by a factor as great as two. Moreover the data fit into a remarkable pattern of consistency among data by independent workers and methods. The magnitude of the deviation from linearity of Fig. 4 at low allyl iodide concentration already has been mentioned. The photostationary concentration data of Rabino-witch and Wood<sup>2</sup> and the rotating sector data on lifetimes by Zimmerman and Noyes<sup>3</sup> can be combined to indicate a quantum yield of  $0.59 \pm 0.09$  for light of 436  $m\mu$  in hexane at 25°. The present method indicates  $0.66 \pm 0.04$ . Finally, the rate constant of Zimmerman and Noyes for atom recombination is in agreement with the value from flash photolyses by Marshall and Davidson.<sup>4</sup> Although it is possible to question the validity of the measurements or interpretations in any of the individual

publications of this series, there can scarcely be any doubt of magnitudes of quantities attested by such consistency of different methods.

**Effect of Solvent.**—The data indicate that the quantum yield decreases markedly with increasing mass of solvent molecules. This result is consistent with the idea that the iodine atoms are produced in a "cage" of solvent molecules and must force their way out if they are to escape recombination with each other. Moreover, the escape from the "cage" probably must take place before the atoms have lost the excess kinetic energy with which they separate. The diffusion coefficient would constitute a rough measure of the ability of an atom to undergo a diffusive displacement after its energy is in thermal equilibrium with its surroundings, and the variation of quantum yield with solvent is greater than the probable variation in diffusion coefficient for iodine atoms.

The heavier the molecules in the "cage," the more critical is the orientation of iodine atoms that can escape and the lower is the quantum yield. One would anticipate that the greatest change in quantum yield with molecular weight would occur when the masses of iodine atoms and solvent molecules were about equal, and this prediction seems consistent with the large change between hexane and carbon tetrachloride. However, studies in only three solvents are not sufficient to demonstrate this effect.

The above argument is certainly an oversimplification. The quantum yields reported in Table III are affected because atom pairs that escape a cage may still undergo diffusive "secondary recombination."<sup>11</sup> The importance of this effect will depend upon the initial separation of the atoms and the mean displacement distance during diffusion. However, these differences do not seem adequate to account for the large differences in quantum yield, and we regard the present data as the best evidence currently available in support of the solvent "cage" around dissociating molecules.

**Effect of Temperature.**—The data indicate a distinct increase of quantum yield with temperature and the effect is greatest in the heavier solvents as would be expected if the separating atoms need more energy to escape in these solvents. Rutenberg and Taube<sup>5</sup> observed temperature effects of the same order of magnitude for dissociation of halogens in water. Arrhenius plots of  $\log \phi$

against  $1/T$  give slopes corresponding to activation energies of the order of those required for diffusion processes, but these naive plots extrapolate to quantum yields of unity at temperatures as low as  $70^\circ$ . Although these temperature effects are undoubtedly related to energy requirements for escape of original partners, we do not have any satisfactory procedure for quantitative interpretation.

**Rate Constants for Recombination.**—If no allyl iodide were present in an illuminated solution of iodine, the rate of production of atoms escaping original partners would equal the rate of combination of free atoms and

$$\phi_{12}q_{12} = k_6[I]^2 \quad (6)$$

Rabinowitch and Wood<sup>2</sup> measured photostationary concentrations and reported  $[I]/q_{12}^{1/2} = 1.6 \times 10^5$  (sec. atom/ml.)<sup>1/2</sup> in hexane and  $1.0 \times 10^5$  in carbon tetrachloride. These data were obtained at slightly longer wave lengths than  $436 \text{ m}\mu$ , but our previous studies<sup>3</sup> suggest that  $\phi_{12}$  should not vary more than about 20% in this wave length region. If our quantum yields at  $25^\circ$  are combined with the Rabinowitch and Wood data, we find  $k_6 = 2.6 \times 10^{-11}$  (atom/ml.)<sup>-1</sup> sec.<sup>-1</sup> in hexane and  $1.4 \times 10^{-11}$  in carbon tetrachloride. If our quantum yield in hexane is combined with the lifetime measurements of Zimmerman and Noyes,<sup>3</sup> we find  $k_6 = 1.7 \times 10^{-11}$ . Marshall and Davidson<sup>4</sup> have measured these rate constants directly by a flash photolysis technique and find  $3.6 \times 10^{-11}$  in heptane and  $1.2 \times 10^{-11}$  in carbon tetrachloride. The discrepancies seem to be somewhat outside of estimated errors but not badly so.

Diffusion coefficients for molecular iodine at  $25^\circ$  are<sup>12</sup>  $4.05 \times 10^{-5}$  cm.<sup>2</sup>/sec. in hexane,  $3.42 \times 10^{-5}$  in heptane and  $1.50 \times 10^{-5}$  in carbon tetrachloride. The rate constants certainly seem to vary similarly to the diffusion coefficients, and the rate data are not precise enough to warrant a quantitative comparison. We are planning to make lifetime measurements in the same solvents in which we have measured quantum efficiencies, and hope thus to obtain rate constants for recombination as functions of solvent and temperature.

**Acknowledgment.**—This research was supported in part by the United States Atomic Energy Commission under Contract AT(30-1)-1314.

NEW YORK 27, N. Y.

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

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