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Abstract

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QUANTUM YIELDS OF THE PHOTODISSOCIATION OF IODINE IN SOLUTIONS

As was stated earlier (^{1}), in chemical reactions in solutions repeated collisions of molecules may play a significant role. Rabinovich and Wood showed (^{2}) that, owing to recombination of atoms and radicals in the "cage," the quantum yields in the photodissociation of molecules in solutions may be less than unity. Noyes considered the mechanism of the photodecomposition of iodine (^{3}) in carbon tetrachloride and in a medium of saturated hydrocarbons. In solvents that form strong complex compounds with atomic iodine, the dissociation reaction of iodine has not been studied. There is an opinion (^{4}) that stabilization of iodine through the formation of complexes leads to a decrease in the probability of recombination and that the quantum yields here may be close to unity. In this connection, it is of interest to study the photodissociation of iodine in various solvents. The quantum yields were determined by the method of fixing iodine atoms with tetraethyltin (TES) in solutions containing oxygen. The use of tetraalkyl tin compounds instead of allyl iodide (^{4}) has the advantage that they do not appreciably absorb light in the visible and near-ultraviolet regions of the spectrum.

The light source was a PRK-2 mercury lamp powered by alternating current from a ferroresonance voltage stabilizer. To isolate lines near 436 mμ, Hg 436 and CC4 light filters were used (transmission at 436 mμ 24.6%, at 405 mμ 0.2%, at 490 mμ 0.3%; in the remaining regions the transmission was insignificant). The reaction vessel was a glass thermostated cuvette with an internal diameter of 1.9 cm and a capacity of 4.5 cm^3. According to actinometric measurements (^{6}), the useful luminous flux was $1.95 \cdot 10^{15}$ quanta/sec. When attenuation of the light flux was necessary, neutral light filters were used. The iodine concentration was determined spectrophotometrically on an SF-4 instrument at the absorption maximum of iodine in the visible region. The reaction rate was found from the decrease in iodine concentration with time, the degree of conversion of the starting substances not exceeding 5%. The absorption of light at 436 mμ was also determined. The quantum yield was calculated as the ratio of the number of iodine molecules that had entered into reaction to the number of absorbed light quanta. The work was carried out with carefully purified substances.

The kinetics of the photochemical reaction of iodine with TES was studied beforehand in order to determine the possibility of using TES as a substance capable of fixing iodine atoms. It was observed that solutions containing iodine and a tetraalkyl tin compound, stable in the dark, rapidly become decolorized under the action of visible light. Apparently, the primary photoreaction is the dissociation of the iodine molecule:

$$J_2 + h\nu \rightarrow 2J. \tag{1}$$

In the absence of oxygen, the observed quantum yields are, as a rule, greater than unity, i.e., the reaction proceeds by a chain mechanism, for example according to the scheme:

$$J + R_4Sn \rightarrow RJ + R_3Sn, \tag{2}$$

$$R_3Sn + J_2 \rightarrow R_3SnJ + J. \tag{3}$$

The chain reaction may also proceed through the stage of formation of a free radical R. In solutions saturated with oxygen, the quantum yields are less than unity. Oxygen apparently reacts with the active radica-

which leads to chain termination:

$$\begin{aligned} R_3Sn + O_2 &\rightarrow R_3SnO_2, \\ R_3SnO_2 &\rightarrow \text{stable products.} \end{aligned} \tag{4}$$

In the absence of oxygen, the rate of the photoreaction decreases sharply after iodine has been consumed in an amount of 1 mole per 1 mole of TEO. If, however, the reaction is carried out in air, the consumption of iodine is reduced to approximately 1/2 mole per 1 mole of TEO. In this connection it may be assumed that the main direction of the reaction in the presence of oxygen is determined by stages (1), (2), and (4). The dependence of the quantum yield on the TEO concentration was studied (Fig. 1). At a sufficiently high TEO concentration the quantum yield tends to a limiting value that does not depend on the light intensity. Under these conditions the limiting stage is probably stage (1). At low TEO concentrations, recombination of iodine atoms apparently has an effect:

$$2J \rightarrow J_2. \tag{5}$$

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

By the value of the TEO concentration at which the quantum yield is equal to half its limiting value, one can estimate $K_2/\sqrt{K_5}$. For carbon tetrachloride this quantity is of the order of unity if the concentration is expressed in moles per liter and the time in seconds. If for K_5 one takes the known (7) value $0.7 \cdot 10^{10}$, then for K_2 a value of the order of 10^5 l/mole • sec is obtained.

Fig. 1. Dependence of the quantum yield on TEO concentration in solutions saturated with air, at 25°. 1 –CCl_4, 2 –cyclohexane; absorption of light, respectively, 5.8 and $8.7 \cdot 10^{11}$ quanta/ml • sec; iodine concentration $8.5 \cdot 10^{-5}$ mole/l.

The limiting value of the quantum yield increases with increasing iodine concentration (Fig. 2). This can be explained by assuming that reaction (3) competes with reaction (4). Then the dependence of the quantum yield on iodine concentration has the form:

$$\Phi = \Phi_1 \left(1 + \frac{2K_3[\mathrm{J}_2]}{K_4[\mathrm{O}_2]}\right),$$

where Φ is the quantum yield of the overall reaction and Φ_1 is the quantum yield of iodine photodissociation. Experimental study of this dependence makes it possible to find the values of Φ_1 and $2K_3/K_4[\mathrm{O}_2]$ for various solvents (see Table 1). The error in determining Φ_1 by this method may be estimated as 20%. The value obtained for carbon tetrachloride, $\Phi_1 = 0.14$, agrees with that known from the literature (5), and in the case of *n*-hexane the discrepancy between the value found (0.54) and the previously known values (5) (0.59 and 0.66) is insignificant.

Fig. 2. Dependence of the quantum yield on iodine concentration at 25°. 1 –CCl_4, 2 –*n*-xylene, 3 –*n*-hexane; a –without a neutral light filter, b, c – with neutral light filters transmitting respectively 54.0 and 21.7% of the light at 436 m .

Fractional quantum yields (see Table 1) are due to recombination of atoms. In this connection attention should be paid to the difference between collisions in gases and in solutions. In a gas under normal conditions one molecule undergoes $\sim 10^9$ collisions per second. The number of molecules in 1 cm^3 is -

is about 10^{19}. Consequently, the probability of a repeated collision with one and the same molecule is very small ($\sim 10^{-10}$). In solution the picture is different.

Fig. 3

Figure 3: Fig. 3

After the first collision, molecules of the dissolved substance, surrounded by a tight ring of solvent molecules, continue to collide repeatedly until the solvent molecules wedge in and separate the colliding pair ([1]). Therefore, in solution one should distinguish two types of collisions: 1) the total number of collisions, including repeated ones in the "cage," and 2) primary collisions (not counting repeated ones). The total number of all collisions of dissolved molecules in 1 cm^3 per 1 sec is $\sim n^2c^2/6ND$, where n is the number of dissolved molecules in 1 cm^3, c is the mean velocity of the molecules, N is the total number of all molecules of both solvent and solute in 1 cm^3, and D is the diffusion coefficient. The number of primary collisions is $\sim 2n^2D/Nr^2$, where r is the amount of displacement at which the repetition of collisions is disrupted owing to the wedging-in of solvent molecules. Thus the number of repeated collisions of one pair in the cage is equal to c^2r^2/aD^2, where a is a numerical coefficient of about 10.

Table 1

Data for the photoreaction of tetraethyltin with iodine at 436 mμ in solutions saturated with air under normal conditions

Solvent	Φ_1	$2K_3/K_4[\text{O}_2]$, l/mole
CCl_4	0.14	1070
n-Hexane	0.54	1200
Cyclohexane	0.26	1050
Benzene	0.32	600
n-Xylene	0.28	1050
n-Dioxane	0.13	800
Diethyl ether	0.78	3000

When the viscosity is high, the number of repeated collisions increases, and more favorable conditions are created for recombination of atoms. As a result, the quantum yields decrease as the viscosity of the medium increases (Fig. 3). Despite the fact that benzene, *n*-xylene, dioxane, and diethyl ether form complex compounds with atomic iodine, the values of the quantum yield in these cases fit well on the general curve (Fig. 3). Apparently, recombination of atoms is not hindered here. This can be understood by taking into account that complexes of iodine atoms with diamagnetic molecules have unpaired electrons and react with a low activation energy, like ordinary free radicals.

Fig. 3. Dependence of the quantum yield of iodine photodissociation on the viscosity of the medium. 1 —diethyl ether, 2 —*n*-hexane, 3 —benzene, 4 —*n*-xylene, 5 —cyclohexane, 6 —CCl_4, 7 —*n*-dioxane, 8 —polyvinyl alcohol with molecular weight 333 ([8]), 9 —hexachlorobutadiene ([8]).

Thus, the ability of the solvent to form complexes does not noticeably affect the magnitude of the quantum yield. Probably, the viscosity of the solvent and other kinetic factors play a role here. If, as in our case, the atoms have excess energy (in the form of kinetic energy), then the probability of escape from the cage increases somewhat. As a result, the number of repeated collisions decreases, which may be reflected in an increase of the quantum yield with increasing frequency of the incident light.

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REFERENCES

1. Ya. K. Syrkin, ZhFKh, **4**, 652 (1933).
2. E. Rabinovitch, W. C. Wood, Trans. Farad. Soc., **32**, 1381 (1936).
3. R. M. Noyes, Zs. Elektrochem., **64**, 153 (1960).
4. S. J. Rand, R. L. Strong, J. Am. Chem. Soc., **82**, 9 (1960).
5. F. W. Lampe, R. M. Noyes, J. Am. Chem. Soc., **76**, 2140 (1954).
6. C. G. Hatchard, C. A. Parker, Proc. Roy. Soc., **235A**, 518 (1956).
7. S. Aditya, J. E. Willard, J. Am. Chem. Soc., **79**, 2680 (1957).
8. D. Booth, R. M. Noyes, J. Am. Chem. Soc., **82**, 1868 (1960).

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