

THE EFFECT OF THE WAVE LENGTH ON
THE PHOTOCHEMICAL DECOMPOSITION OF ETHYLENE
IODIDE IN CARBON TETRACHLORIDE SOLUTION

Thesis by

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The iodine-sensitized photochemical decomposition of ethylene iodide in carbon tetrachloride solution was found by Schumacher and Wiig¹ to be expressed by the equation

$$\frac{\Delta (I_2)}{\Delta t} = k (C_2H_4I_2) I_0^{\frac{1}{2}} \quad (1)$$

when the transmission of the solution is small. They advanced a mechanism leading to the equation

$$\frac{d(I_2)}{dt} = k_2(C_2H_4I_2) \sqrt{\frac{k_1}{k_5}} (I_{abs})$$

The primary process of this mechanism is the absorption of a quantum by an iodine molecule, with subsequent dissociation of this excited molecule into atoms. The decomposition is then a chain reaction catalyzed by these atoms, the mechanism being identical with that of the thermal decomposition.

Schumacher and Stieger² studied the effect of the wave length on the reaction, and found that the constant of equation (1), divided by the wave length, was one sixth as great at 5461 Å as it was at 4358 Å. Since the convergence limit of the band spectrum of iodine vapor is at 4995 Å, they interpreted this result as being due to a lack of dissociation of the excited iodine molecules in the band region. However, they overlooked the fact that the absorption coefficient of 5461 Å is much larger than that of 4358 Å, and it will be shown in this paper that the rate does not fall off greatly when the absorption coefficient and the transmission are considered. Schumacher and Wiig subtracted the measured thermal reaction from the total reaction to obtain the photochemical reaction. This will also be shown to be incorrect, because of the close connection between the mechanisms. Their reaction mixtures were not stirred during the decomposition, and their calculations of the constant depended on the assumption that the reactions were small. In the present paper are presented (1) results of measurements of the absorption coefficients, (2) a consideration of the correction for thermal reaction, (3) a derivation of the dependence of the rate on the absorption coefficient and on the transmission of the solution, and (4) results of experiments on the photochemical decomposition.

Experimental

The carbon tetrachloride was purified according to the method of Polissar³. The ethylene iodide was prepared according to the method of Mooney and Ludlum⁴, and contained a small amount of iodine. A weighed amount was dissolved in a weighed amount of the purified carbon tetrachloride. The solution was titrated for free iodine, ^{with thiosulfate} and the concentration of the iodide calculated. In most of the experiments the iodine concentration was increased by adding iodine which had been resublimed from potassium iodide.

The cylindrical pyrex reaction cell was 4.0 cm. in diameter, 2.1 cm. between the plane ends, contained 28 cc. of solution at room temperature, and had an air space of 25 cc. above the solution. It was always sealed during an experiment, precautions being taken to avoid any decomposition of the carbon tetrachloride during the seal-off. It was furnished with a vertical magnetically operated plunger to act as a stirrer.

The thermostat was so constructed that the reaction cell could be placed in a small air space surrounded by the vapor of a boiling liquid except for the path of the light beam. Since considerable time was required for the cell to come to the thermostat temperature, the cell was heated just to

the right temperature before being placed in the thermostat. It was then left twenty minutes before being illuminated. In the preliminary experiments, with boiling water in the thermostat, the temperature of the cell may have been a degree low; in the later experiments, using carbon tetrachloride, it was probably within $.2^{\circ}$ of 76.6° . The experiments at 99° were corrected for the thermal reaction occurring before illumination. At the end of an experiment 5 cc. of the reaction mixture at room temperature were pipetted into slightly acidified potassium iodide solution and titrated with thiosulfate.

The light source was a quartz mercury arc, usually taking 5 to 5.5 amperes at 45 to 55 volts. The light was passed through a filter box and two lenses and a beam was defined by a diaphragm. After passing through the thermostat it was focused by another lens on a Moll micro-thermopile immersed in water. The intensity was measured hourly during a run by removing the thermostat from the path of the beam. The linearity of the galvanometer deflection with the current through it was tested and corrections were applied where necessary. Suitable Corning glass filters were used to isolate the lines 4358 and 5461 \AA° . That the filters used absorbed all other ^{visible} lines was seen

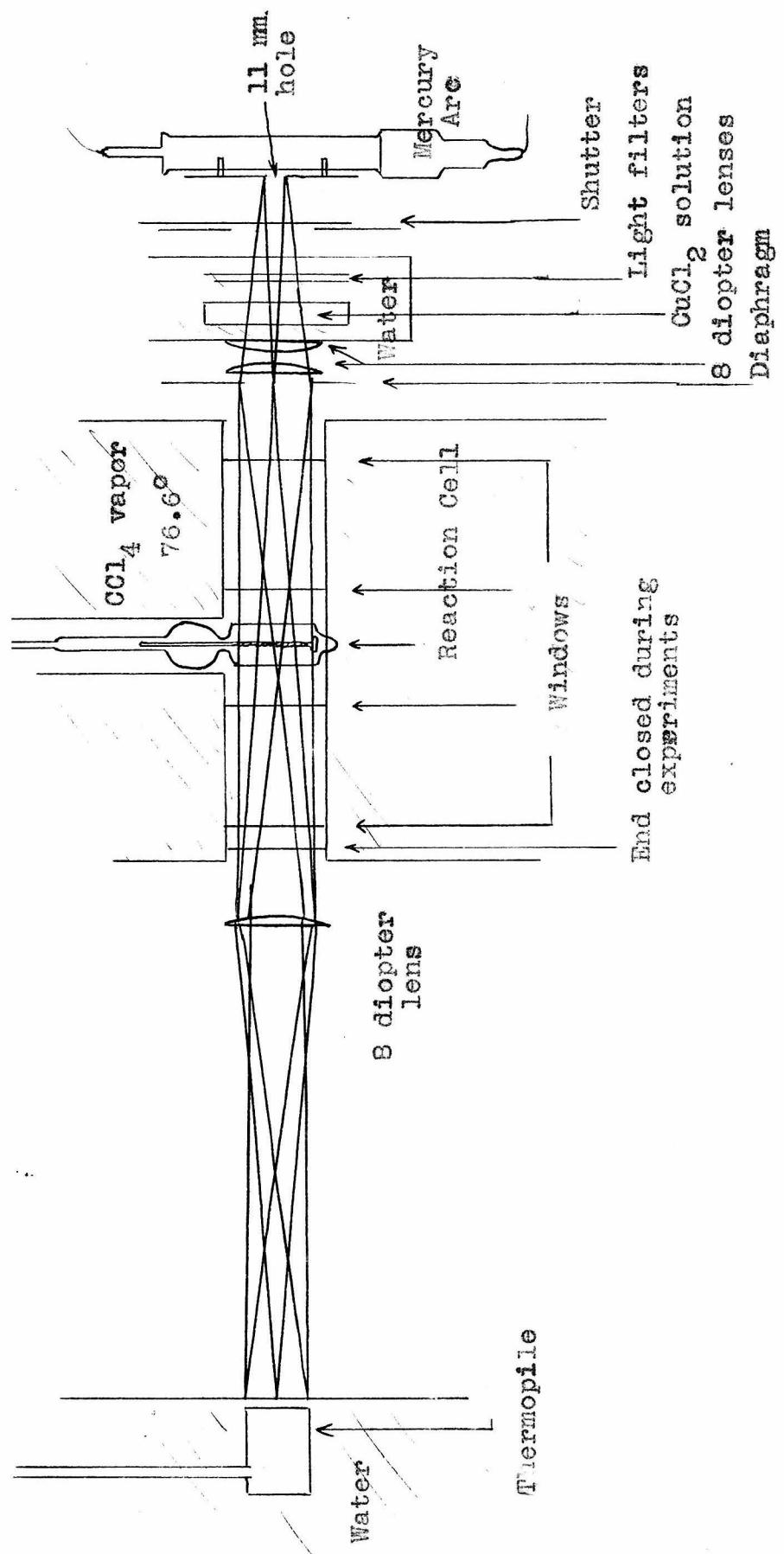


Diagram of the Optical System

Scale 1/8 inch = 1 cm.

in a spectroscope. A 1 cm. layer of a 10% solution of cupric chloride dihydrate served to absorb infra-red and short ultra-violet.

The Absorption Coefficients

The absorption coefficients have been measured by several investigators, but the results are not very accurate. Measurements were, therefore, made with the same apparatus used for the decomposition. Since the values obtained agreed well among themselves, they were used in preference to those found in the literature. They were calculated from the equation

$$\alpha = \frac{1}{(I_2)l} \log_e \frac{T_0}{T}$$

where (I_2) is the concentration of iodine in equivalents per kilogram of solution, l the inside thickness of the cell = 2.1 cm., T_0 the transmission of the cell containing carbon tetrachloride only, and T the transmission of the cell containing the iodine solution. The values obtained are given in Table I. Since they all involve the thickness of the cell, their absolute values may not be as accurate as their relative values. The average values at room temperature calculated using concentrations in mols per liter and decadic logarithms

TABLE 1
 ABSORPTION COEFFICIENTS OF SOLUTIONS OF IODINE
 IN CARBON TETRACHLORIDE

t	4352 Å		5461 Å	
	(I ₂)	α	(I ₂)	α
20°	.001787	121.0	.000140	1310
	.00240	119.4	.000300	1258
	.00309	124.0	.000511	1287
	.00329	120.0	.000599	1255
	Mean	121.1 ± 1.5	Mean	1278 ± 23
76.6°	.00238	124.9	.000215	1223
	.00340	124.0	.000307	1214
	.00475	123.7	.000430	1191
		Mean	124.2 ± .5	Mean
99°	.001544	123.5	.000140	1210
	.001937	125.2	.0001790	1231
	.00309	122.3	.000280	1206
	.00397	123.8	.000360	1210
	Mean	123.7 ± .8	Mean	1214 ± 8

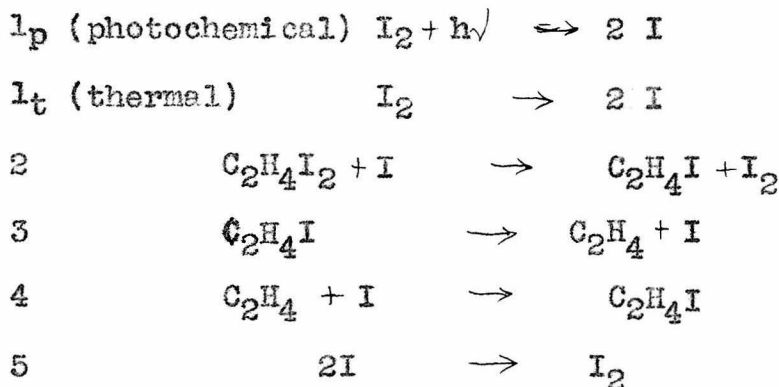
The mean values, calculated with the concentrations in equivalents per liter and natural logarithms, are:

20°	76	800
76.6°	84	820
99°	85	840

respectively
 are 700 and 66 compared to the values of Gillam
 and Morton⁵, 800 and 60; and Getman⁶, 800 and 100.
 Ghosh and Murthi⁷ give 417 for 5461 Å.

The Correction for Thermal Reaction

For any catalytic chain reaction in which the thermal and photochemical mechanisms are identical and the photochemical rate is proportional to the square root of the intensity, the square of the photochemical rate is equal to the square of the observed rate minus the square of the independently observed thermal rate⁸. This can easily be seen for the present case. The combined mechanism



leads to the expression

$$\frac{d(I_2)}{dt} = k_2(C_2H_4I_2) \sqrt{\frac{k_{1p}}{k_5} (I_{abs}) + \frac{k_{1t}}{k_5} (I_2)}$$

If the true photochemical rate is considered to be

$$P = k_2(C_2H_4I_2) \sqrt{\frac{k_{1p}}{k_5} (I_{abs})}$$

and

$$T = k_2(C_2H_4I_2) \sqrt{\frac{k_{1t}}{k_5} (I_2)} = \text{thermal rate}^1$$

$$\text{Then } \frac{d(I_2)}{dt} = \sqrt{P^2 + T^2}$$

Therefore, if the intensity of light is uniform throughout the solution, a correction of only 2% should be subtracted if the independently observed thermal rate amounts to 20% of the total rate. On the other hand, if the light is very strongly absorbed so that the light reaction takes place in a very thin layer, the whole thermal reaction should be subtracted. In intermediate situations the correction is uncertain. To avoid this uncertainty, the temperature of the final experiments was reduced from 99° to 76.6°, for there the independently observed thermal reaction is only .5 to 3% of the total, instead of 3 to 10%. No correction for it was made.

Effect of the Absorption Coefficient

The rate of this reaction depends strongly on the absorption coefficient of the light used. An equation derivable from the following assumptions has been given by Allmand⁹ and expresses this dependence for the general case where the rate is proportional to $(I_{\text{abs}})^{\frac{1}{2}}$.

Consider a thin layer at a distance x from the illuminated side of a solution of thickness l , which is entirely in the path of a uniform beam. Let $(\frac{dc}{dt})_x$ be the local rate of photochemical reaction in this layer, I_{abs} the rate of absorption of radiation (Einsteins per unit volume per unit time) in this layer, I_x the intensity of the radiation (Einsteins per unit area per unit time) in this layer, f some function of the concentrations, A the concentration of the light-absorbing constituent, α the molar absorption coefficient of A (Definition $I_x = I_0 e^{-\alpha Ax}$), I_0 the intensity of radiation incident on the solution (Einsteins per unit area per unit time), and $\frac{dc}{dt}$ the average rate of reaction in the solution. Assume (1) A and concentrations of reactants are uniform throughout the solution. (2) Beer's law ($I_x = I_0 e^{-\alpha Ax}$) applies. (3) Rate at one layer is unaffected by neighboring layers of solution (diffusion rate for intermediate products is small). Then:

$$I_{abs} = I_0 \alpha A e^{-\alpha Ax}$$

$$(\frac{dc}{dt})_x = (I_{abs})^{\frac{1}{2}} f = I_0^{\frac{1}{2}} \alpha^{\frac{1}{2}} A^{\frac{1}{2}} e^{-\frac{\alpha}{2} Ax}$$

$$\frac{dc}{dt} = \frac{1}{l} I_0^{\frac{1}{2}} A^{\frac{1}{2}} f \int_0^l e^{-\frac{\alpha}{2} Ax} dx = \frac{2f I_0^{\frac{1}{2}}}{l \alpha^{\frac{1}{2}} A^{\frac{1}{2}}} (1 - e^{-\frac{\alpha}{2} Al})$$

In general the solution will not be entirely illuminated. If the beam has an area \underline{a} and the solution a volume \underline{V} , the average rate in the vessel will be

$$\frac{dc}{dt} = \frac{2afI_0^{\frac{1}{2}}}{V\alpha^{\frac{1}{2}}A^{\frac{1}{2}}} \left(1 - e^{-\frac{\alpha Al}{2}}\right)$$

Applying this equation to the present reaction, let $A = \underline{x}$ = concentration of free iodine, \underline{S} = concentration of total iodine, free and combined, $\underline{f} = k_2(S-x)\sqrt{\frac{k_1}{k_5}}$, and $\underline{K} = \frac{2ak_2}{V}\sqrt{\frac{k_1}{k_5}}$. Then

$$\frac{dx}{dt} = \frac{\underline{K}}{\alpha^{\frac{1}{2}}x^{\frac{1}{2}}} \frac{I_0^{\frac{1}{2}}}{x^{\frac{1}{2}}} \left(1 - e^{-\frac{\alpha xl}{2}}\right) (S-x)$$

$$\underline{K} = \frac{\alpha^{\frac{1}{2}}}{I_0^{\frac{1}{2}}(t-t_0)} \int_a^b \frac{x^{\frac{1}{2}} dx}{(1 - e^{-\frac{\alpha xl}{2}})(S-x)}$$

where \underline{a} and \underline{b} are the iodine concentrations before and after illumination. Since this expression cannot be integrated, the values of \underline{K} were calculated from \underline{a} and \underline{b} by the use of Simpson's Rule with four sections, or by the prismoidal formula in some experiments. This approximation introduces an error of less than .5%. The galvanometer deflections were made proportional to \underline{I}_0 by multiplying by the wave length.

The results of the measurements are given in Table 2, in which Exp. is the number of the experiment, G. the galvanometer deflection in centimeters, Δt the time of illumination in minutes, $S_2O_3^-$ the iodine before and after illumination expressed in cc. of .005438 N thiosulfate required to titrate 5 cc. of the solution at room temperature, T₀ and T respectively the calculated transmissions of the solution at the beginning and at the end of illumination, $(C_2H_4I_2)$ the initial concentration of ethylene iodide in equivalents $(\frac{C_2H_4I_2}{2})$ per kilogram of solution.

Although the results at 99° are not as reliable as those at 76.6°, a value of the temperature coefficient was calculated from the mean values of K. It is 1.7 per 10° at 4358 Å and 1.6 at 5461 Å, compared to the value found by Schumacher and Wig¹, 1.57%.

TABLE 2

RESULTS OF THE KINETIC MEASUREMENTS

Exp.	$G^{\frac{1}{2}}$	Δt	$S_2O_3^=$		T_0	T	$(C_2H_4I_2)$	$10^6 K$
			initial	final				
Wave length 5461 Å, temperature 99°:								
25	4.36	30.0	.20	3.67	.71	.0018	.1174	5.18
28	2.77	30.0	.20	5.22	.71	.00012	.1174	5.69
30	3.70	40.0	.20	4.38	.71	.00053	.1174	5.08
34	4.36	45.0	1.26	6.32	.115	.000019	.1174	5.54
35	3.88	45.0	1.26	5.85	.115	.000042	.1174	5.52
Mean								5.40 ± .22
Wave length 4358 Å, temperature 99°:								
26	2.77	30.0	.20	1.10	.97	.82	.1174	6.29
29	2.58	60.0	.20	2.60	.97	.67	.1174	6.95
31	3.09	60.0	5.05	10.47	.41	.16	.1174	6.28
32	2.70	60.0	5.05	9.79	.41	.18	.1174	6.28
Mean								6.45 ± .20
Wave length 5461 Å, temperature 76.6°:								
37	5.19	90.0	1.05	5.25	.16	.00012	.1174	1.798
38	5.29	60.0	1.05	4.05	.16	.00092	.1174	1.788
42	3.98	116.5	.76	5.07	.27	.00016	.1174	1.843
43	4.47	125.5	.76	5.70	.27	.000054	.1174	1.797
44	4.50	90.0	1.06	4.78	.16	.00026	.1174	1.803
51	3.95	154.0	3.01	8.30	.6056	.0000006	.1323	1.922
53	2.26	257.5	3.01	7.79	.0056	.0000015	.1323	1.777 ^a
61	3.42	252.0	2.39	6.16	.016	.00024	.06615	1.740
Mean								1.809 ± .039
Wave length 4358 Å, temperature 76.6°:								
39	3.19	61.0	7.31	9.11	.27	.20	.1174	1.910
40	3.11	128.0	7.35	11.25	.27	.14	.1174	1.980
48	2.51	116.3	3.18	5.80	.57	.36	.1323	1.923
49	2.66	241.0	3.18	6.45	.57	.32	.1323	1.080 ^b
50	2.75	138.5	3.23	6.71	.57	.30	.1323	1.907
52	1.31	270.5	3.01	6.33	.59	.33	.1323	1.962 ^a
54	2.54	245.5	3.01	9.58	.59	.18	.1323	1.821
62	2.28	225.5	2.39	4.68	.66	.44	.06615	2.080
Mean								1.945 ± .058

^bNot used in calculating the mean.

^aIntensity reduced by means of a fine screen.

Discussion of the Results

The values of the specific rate are not greatly different at the two wave lengths. This indicates that iodine molecules, under the conditions of these experiments, dissociate nearly as often when excited by 5461\AA as when excited by 4358\AA , and therefore that ^{in carbon tetrachloride solution} there exists no threshold frequency for the dissociation at the convergence limit of iodine vapor. It is proposed to explore the band region further by undertaking experiments with yellow light.

Acknowledgment

I am indebted to Professor R. G. Dickinson, who suggested this problem, for much help and many valuable suggestions during the progress of this work.

Summary

The absorption coefficients of solutions of iodine in carbon tetrachloride have been measured at 4358 and 5461 Å. At 20°, for 4358 and 5461 Å they are respectively 121 and 1280; at 76.6°, 124 and 1210; at 99°, 124 and 1210, when the concentrations are expressed in equivalents per kilogram of solution and natural logarithms are used.

The relative rates of the iodine-sensitized photochemical decomposition of ethylene iodide in carbon tetrachloride solution with wave lengths 4358 and 5461 Å have been determined. When the effect of the absorption coefficient is considered, the specific rates are not greatly different at the two wave lengths, indicating that under these experimental conditions, iodine molecules excited with light of band region frequency (as far as $\lambda = 5461$) dissociate nearly as often as those excited with light of the frequency of the region of continuous absorption.

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