

PHOTOCHEMICAL REACTIONS IN NON-AQUEOUS SOLUTIONS

I. The Photochemical Formation of Chlorine Dioxide from  
Chlorine Monoxide in Carbon Tetrachloride Solution

II. The Photochemical Reaction of Iodine with Cyclohexene  
in Benzene Solution

Thesis by

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**THE PHOTOCHEMICAL FORMATION OF CHLORINE DIOXIDE  
FROM CHLORINE MONOXIDE IN CARBON TETRACHLORIDE  
SOLUTION**

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That chlorine monoxide,  $\text{Cl}_2\text{O}$ , is sensitive toward light has long been recognized. In recent years several quantitative investigations of the photochemistry of this compound have been undertaken. Bowen<sup>1</sup> studied the effect of light in the region 4100–4700 Å. on carbon tetrachloride solutions of chlorine monoxide; apparently on the assumption that the products of the reaction were simply chlorine and oxygen, he found from 0.81 to 1.02 molecules of the monoxide decomposed per quantum absorbed. He later measured<sup>2</sup> the effect of light on gaseous chlorine monoxide and concluded that in the gaseous state apparently two molecules of monoxide were decomposed for each quantum of blue and violet light absorbed.

<sup>1</sup> E. J. Bowen, *J. Chem. Soc.*, 123, 1199 (1923).

<sup>2</sup> Bowen, *ibid.*, 123, 2330 (1923).

The gaseous reaction was studied more extensively by Bodenstein and Kistiakowsky.<sup>3</sup> They concluded that two molecules of monoxide were decomposed per quantum absorbed irrespective of whether the light absorber was chlorine monoxide or added chlorine. They found further that the decomposition was accompanied by the formation of chlorine dioxide; this was shown by the fact that gaseous monoxide developed, on illumination, the absorption bands of the dioxide in the blue and violet. They believed, however, that the quantity of dioxide formed was very small, and they apparently did not regard its formation and presence as any important complicating circumstance in the measurement of the quantum yields.

The mechanism of the decomposition of chlorine monoxide (without reference to ClO<sub>2</sub> formation) has been discussed by Schumacher and Wagner.<sup>4</sup> They have shown that for 4350 Å. the absorption process may be either  $\text{Cl}_2\text{O} + h\nu \rightarrow \text{Cl}_2 + \text{O}$  or  $\text{Cl}_2\text{O} + h\nu \rightarrow \text{ClO} + \text{Cl}$ , and regard the latter as more probable. The character of the absorption spectrum of gaseous Cl<sub>2</sub>O<sup>5</sup> indicates that this wave length is energetically capable of producing either of at least two different dissociations.

In the present paper is described an examination of the reaction in carbon tetrachloride solution. It is found that chlorine dioxide is formed on illumination of the solution and that the amount formed is by no means negligible compared with the amount of monoxide decomposed. Moreover, the comparatively high light absorption coefficients of the dioxide make the presence of even small amounts of this compound a disturbing factor in the measurement of the quantum yield of the monoxide decomposition.

### The Materials

**Carbon Tetrachloride.**—Some difficulty was experienced in preparing sufficiently good carbon tetrachloride. The starting point was commercial c. p. material; since this showed some photochemical reaction with chlorine, it was subjected to the following treatment.<sup>6</sup> The liquid was boiled for nine hours in an all-glass reflux apparatus, chlorine being bubbled through continuously. The chlorine was boiled off and the liquid treated with anhydrous sodium carbonate, and distilled twice from an all-glass still with a fractionating column. A middle fraction was used. This product was still found to develop acidity when chlorine was dissolved in it and the solution illuminated for four hours with the blue light source described below. (The acidity was detected by pouring the illuminated chlorine solution into an excess of potassium iodide, titrating to an end-point with thiosulfate and then adding iodate.) Finally some of this carbon tetrachloride which had been refluxed with chlorine was saturated with chlorine dioxide; after standing for several days it was again washed and fractionated. This product developed no acidity on four hours' illumination with chlorine and was used in the experiments described below.

<sup>3</sup> M. Bodenstein and G. Kistiakowsky, *Z. physik. Chem.*, **116**, 371 (1925).

<sup>4</sup> H. J. Schumacher and C. Wagner, *ibid.*, **5B**, 199 (1929).

<sup>5</sup> C. F. Goodeve and J. I. Wallace, *Trans. Faraday Soc.*, **26**, 254 (1930).

<sup>6</sup> H. Grüss, *Z. Elektrochem.*, **29**, 144 (1923).

**Chlorine Monoxide.**—The chlorine monoxide was prepared in carbon tetrachloride solution by adding an excess of mercuric oxide to carbon tetrachloride about half saturated with chlorine at room temperature. The oxide reacted quickly to give the brownish chlorine monoxide solution. The solid material was filtered off using asbestos in a Gooch crucible. Occasionally the preparations showed a small amount of free chlorine on analysis.

The mercuric oxide used in this preparation was obtained by adding a 50% solution of potassium hydroxide to a saturated solution of mercuric chloride at room temperature. The precipitated mercuric oxide was washed and then dried for two days or more at 120°.

**Chlorine.**—For the preparation of chlorine monoxide or for absorption measurements chlorine from hydrochloric acid and manganese dioxide, or from a tank, was purified by passing through a train of washing bottles with all-glass connections. The first two bottles contained potassium permanganate solution, the third concentrated sulfuric acid and a fourth glass wool to retain mist. Fresh materials were placed in the train before each experiment. The gas from the train was passed into carbon tetrachloride in a glass stoppered flask.

**Chlorine Dioxide.**—This was prepared according to the method of Bray.<sup>7</sup> Eight grams of potassium chlorate and 30 g. of oxalic acid were intimately mixed and moistened with 4 cc. of water in a flask with a side arm. The mouth of the flask was sealed and the mixture heated to 60°. The evolved gas was passed into carbon tetrachloride.

**The Apparatus.**—The arrangements for illuminating the solution and

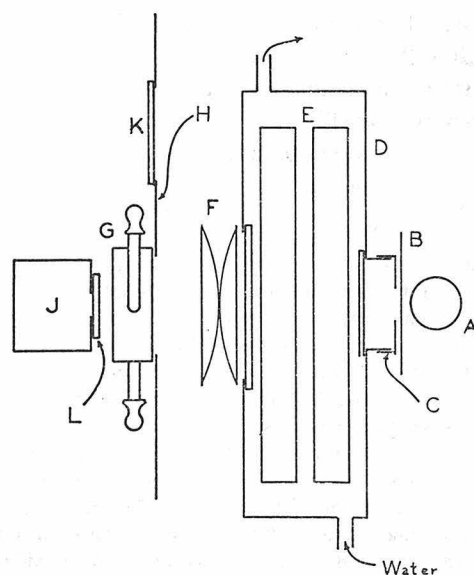


Fig. 1.—Plan view of photochemical apparatus.

measuring its transmission are shown in plan in Fig. 1. Light from the quartz mercury arc A operated from a d. c. generator with a voltage regulator, passed, when the shutter B was opened, through a hole 1 cm. in diameter in a removable cap, C. It then passed through the filter box D through which water was flowed. The light filters E were submerged in this box. The light was then collimated by the lenses F.

The pyrex glass reaction cell G was 1.06 cm. thick internally with flat faces 3 cm. in diameter. The volume of solution which it held was 6.9 cc. The cell was provided with two capillary

side arms for filling; these were fitted with ground glass caps.

**Filters.**—To remove infra-red, a 1-cm. layer of 6% copper sulfate solution was used.<sup>8</sup> To isolate  $\lambda$ 4358, a 4-mm. piece of Corning G 585

<sup>7</sup> W. C. Bray, *Z. physik. Chem.*, **54**, 592 (1906).

<sup>8</sup> W. W. Coblentz, *Bur. Standards Bull.*, **9**, 110 (1913).

was followed by a 2-mm. piece of Noviol A. On being photographed with a spectrograph, the radiation transmitted by these filters showed in addition to 4358 only the weak neighboring lines 4347 and 4339. To isolate 4047, a 1-cm. layer of 4% quinine hydrochloride was followed by a 5-mm. piece of Corning G 586 Å. Spectrographs of the radiation transmitted by this filter showed a trace of 4358 and various other lines down to 3900; most of the intensity, by far, was in 4047.

**Spectroscopic Experiments.**—Using a two-prism glass spectrograph we have photographed the absorption spectrum of chlorine monoxide in carbon tetrachloride solution. In agreement with Bowen the absorption was found to set in appreciably in the blue and to increase continuously toward the violet. After strong illumination of the solution with either white light or the line 4358 Å., a series of well-marked maxima of absorption situated at about 4350, 4240, 4130, 4020, ... Å. developed. Since these absorption maxima are not attributable to chlorine, their source was sought in chlorine dioxide. It was found that chlorine dioxide solutions gave maxima in the same positions as the illuminated chlorine monoxide solutions; a 0.0015 molal chlorine dioxide solution showed the maxima to about the same extent as a 0.034 molal chlorine monoxide solution which had been exposed for three hours to our source of 4358 Å.

These experiments show that chlorine dioxide is produced in carbon tetrachloride solution by the illumination of chlorine monoxide but give only a rough suggestion of the quantity. We have accordingly attempted to estimate the number of molecules of chlorine dioxide produced per quantum absorbed and, taking account of the presence of chlorine dioxide, to reexamine the quantum yield in the decomposition of chlorine monoxide.

**Absorption Coefficients.**—Absorption coefficients of carbon tetrachloride solutions of chlorine, chlorine monoxide and chlorine dioxide were determined for the radiations 4358 and 4047 Å. Light from the mercury arc was passed through one of the filters described above, collimated, passed through a cell containing the solution, and then allowed to fall on a Moll thermopile connected with a galvanometer. The cell was removed and immediately replaced by a sheet of the same pyrex glass of which the cell was constructed. The ratio of the galvanometer readings for the two cases was taken as the transmission,  $I/I_0$ , of the solution. In Table I are given average values of the transmission for various solutions together with the absorption coefficients,  $\alpha$ , defined by the equation

$$-\log_{10} I/I_0 = \alpha C$$

where  $C$  is the concentration in moles per liter. As our photochemical experiments were made in the same cell that was used for the absorption coefficients, these values are sufficient for our purpose. The thickness of the cell was 1.06 cm., so that the absorption coefficients,  $\epsilon$ , defined by the equation

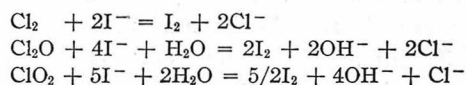
$$-\log_{10} I/I_0 = \epsilon Cd$$

where  $d$  is the thickness of the cell in centimeters, are  $\alpha/1.06$ . In the case of chlorine, absorption coefficients were also measured at the wave lengths 4358 Å. using a spectrograph and calibrated wire screens substantially as described by Winther.<sup>9</sup> The value of  $\alpha$  obtained by this method, 2.40, is in agreement with that given in Table I.

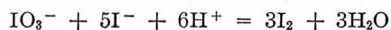
TABLE I

ABSORPTION COEFFICIENTS IN CARBON TETRACHLORIDE SOLUTION				
Substance	Moles per liter	Wave length, Å.	$I/I_0$	$\alpha$
Cl <sub>2</sub>	0.214	4358	0.308	2.40
	.0457	4047	.481	6.95
Cl <sub>2</sub> O	.0229	4358	.671	7.60
	.0676	4358	.296	7.82
	.0789	4358	.247	7.70
	.0229	4047	.686	7.13
	.0676	4047	.336	6.99
ClO <sub>2</sub>	.00115	4358	.595	197
	.00135	4358	.530	203
	.00115	4047	.195	616
	.000428	4047	.551	605

**Method of Analysis.**—The carbon tetrachloride solutions, which in the general case were presumed to contain chlorine, chlorine monoxide and chlorine dioxide, were treated in the following manner. A weighed amount of the solution was run into a flask containing an excess of potassium iodide acidified with a known excess of standard acid. The iodine liberated by the following reactions was titrated with thiosulfate



The unused excess of acid was then determined by adding a small amount of potassium iodate and titrating with thiosulfate the iodine liberated by the reaction



Calling  $a$  the number of equivalents of thiosulfate used per liter of sample in the first titration, and  $b$  the number of equivalents of acid neutralized per liter of sample as determined by the second titration, it is evident that

$$a = 2(\text{Cl}_2) + 4(\text{Cl}_2\text{O}) + 5(\text{ClO}_2) \quad (1)$$

$$b = 2(\text{Cl}_2\text{O}) + 4(\text{ClO}_2) \quad (2)$$

where the parentheses indicate molal concentrations.

In those cases (as in the absorption measurements or at the beginning of the photochemical exposures) where one or more of the three substances was known to be absent, these titrations sufficed; but when all three substances were present, an additional independent relation between their

<sup>9</sup> C. Winther, *Z. wiss. Phot.*, **22**, 125 (1923).

concentrations was necessary. This was afforded by a measurement of  $I/I_0$ , the fraction of light transmitted by the solution when placed in the cell used for determining the absorption coefficients. The additional relation is, then

$$-\log I/I_0 = \alpha_1(\text{Cl}_2) + \alpha_2(\text{Cl}_2\text{O}) + \alpha_3(\text{ClO}_2) \quad (3)$$

Simultaneous solution of Equations 1, 2 and 3 would give the desired analysis.

In practice it was found convenient to proceed slightly differently by using for the transmission measurements the radiation 4047 Å. For this wave length, the absorption coefficients of chlorine and chlorine monoxide are practically equal and much smaller than the coefficient for chlorine dioxide. If then no chlorine be allowed to escape from the solution during the photochemical reaction, any change in the transmission of the solution is ascribable to a change in  $(\text{ClO}_2)$ . If the solution initially contains no chlorine dioxide and has a transmission  $(I/I_0)_i$ , the concentration of chlorine dioxide corresponding to the transmission  $(I/I_0)_t$  found after illumination is given by

$$-\log (I/I_0)_t + \log (I/I_0)_i = \left( \alpha_3 - \frac{\alpha_1}{2} \right) (\text{ClO}_2) \quad (4)$$

From Table I,  $[\alpha_3 - (\alpha_1/2)]$  has the value 607. We have accordingly followed, by transmission measurements, the concentration of chlorine dioxide in a sample of chlorine monoxide under illumination; using the final value of  $(\text{ClO}_2)$  so obtained, we have determined the values of  $(\text{Cl}_2)$  and  $(\text{Cl}_2\text{O})$  at the end by titration.

The experiments themselves afford two controls on this method of analysis. (1) The total chlorine in the solution, given by  $(a - b)$ , should be the same before and after illumination; this was ordinarily found to be the case to 1% or better which, in view of the small samples involved, is probably satisfactory. (2) From the analysis of the final solution, its transmission for 4358 Å. may be calculated and compared with a measured value. The calculated and observed transmission for this wave length agreed on the average to about 3%.

**Measurement of Quantum Yields.**—The chlorine monoxide solution, prepared as previously described, was placed in a small all-glass container built like a wash bottle. The exit tube from this container was ground into one of the capillary arms of the reaction cell. The cell was filled by blowing into the inlet tube of the container through a drying tube. The cell was then weighed, emptied into the titration flask, reweighed and immediately refilled. The initial composition of the  $\text{Cl}_2\text{O}$  solution was then determined by titration of the first sample. The second sample was then illuminated with 4358 Å. During this illumination, the cap C (Fig. 1) was removed to give a larger light source.

The illumination was interrupted at intervals for the measurement of



(1) the transmissions of 4358 and of 4047 and (2) the intensity of the 4358 as used for the reaction. The transmissions were measured as previously described. The light intensity was measured by noting the galvanometer deflection with C removed and the glass plate K in front of the thermopile; in this case a shunt was placed across the galvanometer to keep the deflection on the scale.

The thermopile had been calibrated with the aid of a carbon lamp calibrated by the Bureau of Standards; in the thermopile calibration the quartz window, L, was removed from the thermopile and the shunt from the galvanometer. The effect of the shunt had been determined by noting the deflections produced by a convenient white light source with and without the shunt.

The total number of quanta,  $Q$ , entering the reaction mixture in  $t$  minutes was calculated by the following formula

$$Q = 60t \times d \times f_1 \times f_2 \times f_3 \times E \times A \times f_4 \times f_5 \times q = 9.2 \times 10^{15} \times t \times d$$

$d$  = galvanometer deflection in centimeters of scale as read with the shunt  
 $f_1$  = ratio of deflection without shunt to that with shunt  
 $f_2$  = ratio of deflection with thermopile in plane of diaphragm and at its center, to deflection with thermopile in position used (the beam was slightly convergent) = 0.942  
 $f_3$  = ratio of average deflection over area of diaphragm to deflection with thermopile at center of diaphragm = 0.925  
 $E$  = intensity of radiation giving unit scale deflection; ergs per sq. mm. per sec. per cm. scale deflection = 0.672  
 $A$  = area of diaphragm opening in sq. mm. = 573  
 $f_4$  = reciprocal of transmission of quartz plate = 1.065  
 $f_5$  = reciprocal of transmission of one surface of pyrex plate = 1.035  
 $q$  = number of quanta in one erg of radiation of wave length 4358 Å. =  $2.217 \times 10^{14}$

The results of a number of experiments made by illuminating pure or nearly pure chlorine monoxide solutions of various concentrations are given in Table II. The initial and final amounts of chlorine monoxide and chlorine in the solutions are given in Cols. 3 and 4. The amount of solution was always  $6.92 \pm 0.02$  cc. The amounts of chlorine dioxide present at various times (as computed from the transmission of  $\lambda 4047$ ) are given in Col. 5.

The total number of quanta having been absorbed by the system up to the time  $t$  (Col. 2) is given in Col. 9 and was calculated as follows. The number of quanta entering the reaction vessel in each interval of time was calculated from the average galvanometer deflection for that interval (Col. 8) as described above. This number was multiplied by  $[1 - (I/I_0)] [1 + r(I/I_0)]$  to give the number of quanta absorbed in the time interval. Here  $(I/I_0)$  is the average value of the transmission for  $\lambda 4358$  for the interval and  $r (= 0.035)$  is the fractional reflection of radiation back into the cell at the rear window. (It may be noted that the small correction

TABLE II  
 QUANTUM YIELD MEASUREMENTS

Expt.	Total time of illum., min.	Cl <sub>2</sub> O, milli-moles	Cl <sub>2</sub> , milli-moles	ClO <sub>2</sub> , milli-moles	$I/I_0$ for 4358 Å.	$I/I_0$ for 4047 Å.	Average def. for preceding interval	Total quanta absorbed $\times 10^{-19}$	Cl <sub>2</sub> O decomp. per quantum abs. by soln.	Cl <sub>2</sub> O decomp. per quantum abs. by Cl <sub>2</sub> O
1	0	0.158	0.000	0.00000	0.676	0.686	..	..	..	..
	170	..	..	.00338	..	.346	20.7	1.22	..	..
	240	.123	.035	.00399	.546	.306	18.7	1.76	1.20	1.72
2	0	.215	.005	.00000	.574	.579	..	..	..	..
	60	..	..	.00225	..	.367	26.9	0.675	..	..
	120	..	..	.00370	..	.275	22.2	1.28	..	..
	180	.176	.042	.00475	.454	.222	22.8	1.95	1.21	1.65
3	0	.375	.004	.00000	.383	.414	..	..	..	..
	30	..	..	.00225	.347	.270	22.2	0.394	..	..
	60	.352	.023	.00409	.315	.182	26.0	0.881	1.58	1.83
4	0	.298	.025	.00000	.462	.476	..	..	..	..
	30	..	..	.00164	.430	.342	20.2	0.313	..	..
	60	..	..	.00303	.402	.258	18.5	0.616	..	..
	90	.276	.044	.00394	.385	.215	16.7	0.900	1.48	1.77
5	0	.280	.006	.00000	.491	.510	..	..	..	..
	60	..	..	.00238	.439	.316	18.9	0.567	..	..
	120	..	..	.00449	.396	.206	25.5	1.40	..	..
	180	..	..	.00572	.369	.161	21.4	2.14	..	..
	240	.222	.059	.00714	.355	.121	22.5	2.94	1.20	1.70
6	0	.100	.006	.00000	.778	.781	..	..	..	..
	30	..	..	.00085	.745	.657	26.2	0.176	..	..
	60	..	..	.00138	.724	.592	25.7	0.363	..	..
	90	..	..	.00180	.707	.545	25.8	0.563	..	..
	120	.083	.018	.00214	.702	.507	25.6	0.776	1.33	1.82

$r(I/I_0)$  for rear-window reflection is not compensated in the absorption measurements.) The sum of the quanta absorbed in all intervals up to the time  $t$  is given in Col. 9.

The amount of chlorine dioxide formed in the various runs is shown in Fig. 2 plotted against the number of quanta absorbed. In a given run, the amount of chlorine dioxide formed increases less and less rapidly with the quanta absorbed as the exposure is prolonged. At least two reasons may be given for this: (1) chlorine dioxide already formed acts as an internal filter and partially screens its further formation; (2) chlorine dioxide is itself decomposed photochemically.<sup>10</sup> In addition there is the possibility of photochemical reaction between chlorine dioxide and chlorine monoxide.

When the various runs are compared with each other, it is found that for a given number of quanta absorbed, more chlorine dioxide has been formed the higher the initial concentration of chlorine monoxide. This effect

<sup>10</sup> H. Booth and E. J. Bowen, *J. Chem. Soc.*, 127, 510 (1925).

again could obviously result from internal screening in both the formation and decomposition of the chlorine dioxide.

The simplest conditions evidently prevail at the beginning of the exposure where the material is substantially all chlorine monoxide. The initial (quantum) rate of formation of chlorine dioxide appears to be not markedly, if at all, dependent on the concentration of chlorine monoxide. The initial slope of the curves gives directly a quantum yield of about 0.35 chlorine dioxide formed per quantum absorbed.

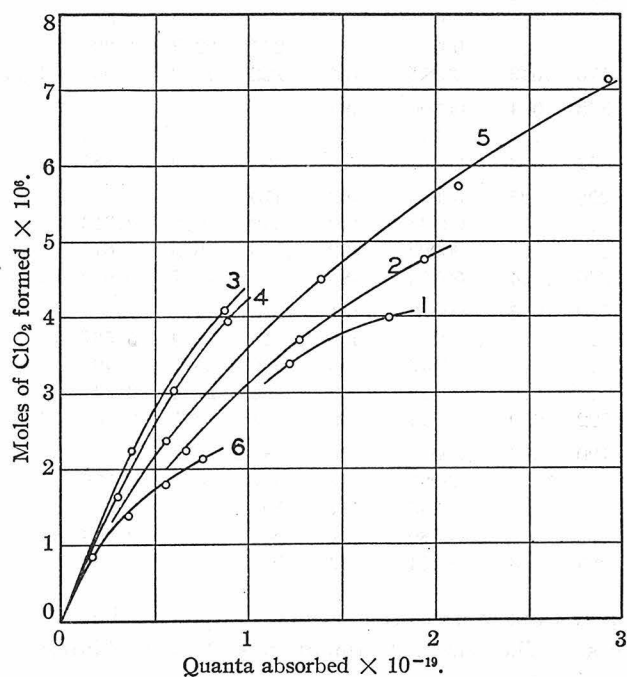


Fig. 2.—Amount of ClO<sub>2</sub> formed vs. number of quanta (4358 Å.) absorbed. The numbers on the curves are the experiment numbers of Table II. The initial concentrations of Cl<sub>2</sub>O increase in the order 6, 1, 2, 5, 4, 3.

Our method of analysis supplied a knowledge of the chlorine monoxide present at only the beginning and end of a run. The number of molecules of chlorine monoxide decomposed in each entire run per quantum absorbed, irrespective of the absorbing substances, was computed from Cols. 3 and 9 and is given in Col. 10. It may be seen that in Expts. 3 and 4, where the exposures were shortest and the proportion of chlorine dioxide at the end smallest, the yields were highest, *viz.*, 1.58 and 1.48, as against values around 1.2 in longer exposures. This suggests that shorter exposures would lead to still higher values for the initial yield; for after the decomposition of only a small amount of chlorine monoxide, the chlorine

dioxide which had been formed played a considerable part in the light absorption. However, on account of the small titration differences already involved, experiments resulting in smaller decompositions did not appear feasible.

We have, therefore, calculated the number of molecules of chlorine monoxide decomposed per quantum absorbed by the chlorine monoxide. At any moment, the fraction of the absorption due to chlorine dioxide is  $\alpha_3(\text{ClO}_2)/[\alpha_1(\text{Cl}_2) + \alpha_2(\text{Cl}_2\text{O}) + \alpha_3(\text{ClO}_2)]$ . The denominator is equal to  $-\log(I/I_0)$  for  $\lambda 4358$ . Hence the fraction of the entering quanta which are absorbed by other than chlorine dioxide is

$$\left[1 - \frac{\alpha_3(\text{ClO}_2)}{-\log(I/I_0)}\right] [1 - I/I_0][1 + r(I/I_0)]$$

Values of this last expression were calculated for each time interval using average values of  $(\text{ClO}_2)$  and  $(I/I_0)$ ; these were multiplied by the number of quanta entering in the interval and summed over the entire run. The ratio of the number of molecules of chlorine monoxide decomposed to this sum is given in Col. 11. Strictly this is the yield per quantum absorbed by  $\text{Cl}_2\text{O} + \text{Cl}_2$ ; however, the quantity of free chlorine was never large and its absorption coefficient for 4358 is small. These yields are comparatively constant, showing possibly a slight tendency to increase with decreasing exposure; the mean for the three longest runs is 1.69, while the mean for the three shortest runs is 1.81. In view of the uncertainty of extrapolation and of the small titration differences, it seems not impossible that the value for zero exposure and hence for pure chlorine monoxide solution may be as high as 2.

### Summary

The effect of light of wave length 4358 Å. on solutions of chlorine monoxide in carbon tetrachloride has been investigated. It has been found that the decomposition of chlorine monoxide is accompanied by the formation of considerable chlorine dioxide. In solutions 0.014 to 0.054 molal in chlorine monoxide, the initial rate of formation of chlorine dioxide has been found to be about 0.35 molecule of chlorine dioxide per quantum absorbed. The initial rate of decomposition has been found to be at least 1.8 molecules of chlorine monoxide per quantum absorbed.

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THE PHOTOCHEMICAL REACTION OF IODINE WITH CYCLOHEXENE  
IN BENZENE SOLUTION

Many cases of photochemical halogenation of hydrocarbons with chlorine and bromine have long been known and studied, but few iodinations of such compounds have hitherto been known. Badger and Urmston<sup>1</sup> recently found that iodine reacted with normal hexene vapor on illumination with visible light. In the present paper a study of the reaction of iodine with cyclohexene in benzene solution is described.

Preliminary Experiments.

It was found that when benzene, cyclohexane, or carbon tetrachloride solutions of iodine and cyclohexene were illuminated with visible light, the iodine disappeared, and on sufficiently long illumination the solutions were bleached completely. An attempt was made to titrate the iodine remaining in a partially bleached solution, but it was found that iodine was liberated from the product of the light reaction when the solution was poured into potassium iodide solution. If some of the completely bleached solution was poured into potassium iodide solution the free iodine color immediately appeared. Also, when one of the bleached solutions was evaporated on a watch glass in a current of air, there was precipitation of iodine.

It seems then, that the product of the reaction is unstable out of solution. Completely bleached solutions were kept for long periods of time, however, without any evidence of the re-appearance of iodine, even in the dark.

Since the product of the reaction is colorless it is possible to follow the disappearance of the iodine by measuring the change in light absorption. This is the method used in this study. The radiation 4358 Å of a quartz mercury arc was used for the photochemical reaction and the absorption measurements.

With the iodine concentrations that were convenient to use, the rate of the thermal reaction was found to be small for low concentrations of cyclohexene, but at 0.1 molal the thermal rate begins to amount to 2 or 3 per cent. In an experiment 0.0523-v.m. in cyclohexene with an initial concentration of iodine of 0.00159-v.m., a portion of the solution was kept in the dark during illumination of the other portion. In 143 minutes the illuminated sample bleached down to 0.00105-m, while the solution kept in the dark dropped in concentration to 0.00158-m. Other experiments with lesser concentrations of cyclohexene showed also, practically no thermal reaction. These experiments and all the following photochemical experiments were carried out at a temperature of 23-24.5°C.

### The Materials.

Benzene. Benzene was chosen for the solvent in the study of this reaction because it is easier to purify than carbon tetrachloride and because it is a similar liquid to cyclohexene. Commercial c.p. benzene was treated essentially by the method of Victor Meyer <sup>2</sup>, which consists of treating with an excess of pure bromine for several hours with frequent agitation, washing with sodium hydroxide until the bromine is removed, washing with water, drying with calcium chloride, and distilling. The product was distilled with an all glass distilling apparatus with a fractionating column, and a middle portion used. When iodine was dissolved in this benzene and the solution illuminated for three hours with the radiation 4358 of the mercury arc, no change in the light absorption was detected.

Cyclohexene. The cyclohexene used was an Eastman product. It was redistilled and boiled at 82.2°C. at 748-mm.

Iodine. Commercial c.p. iodine was ground up with a large excess of potassium iodide and calcium oxide, and sublimed from this mixture. The sublimate was then resublimed twice at 50-60°C.

Stock solutions of iodine in benzene, and cyclohexene in benzene were made up by weighing the materials into volumetric flasks and diluting with benzene at 20°C.

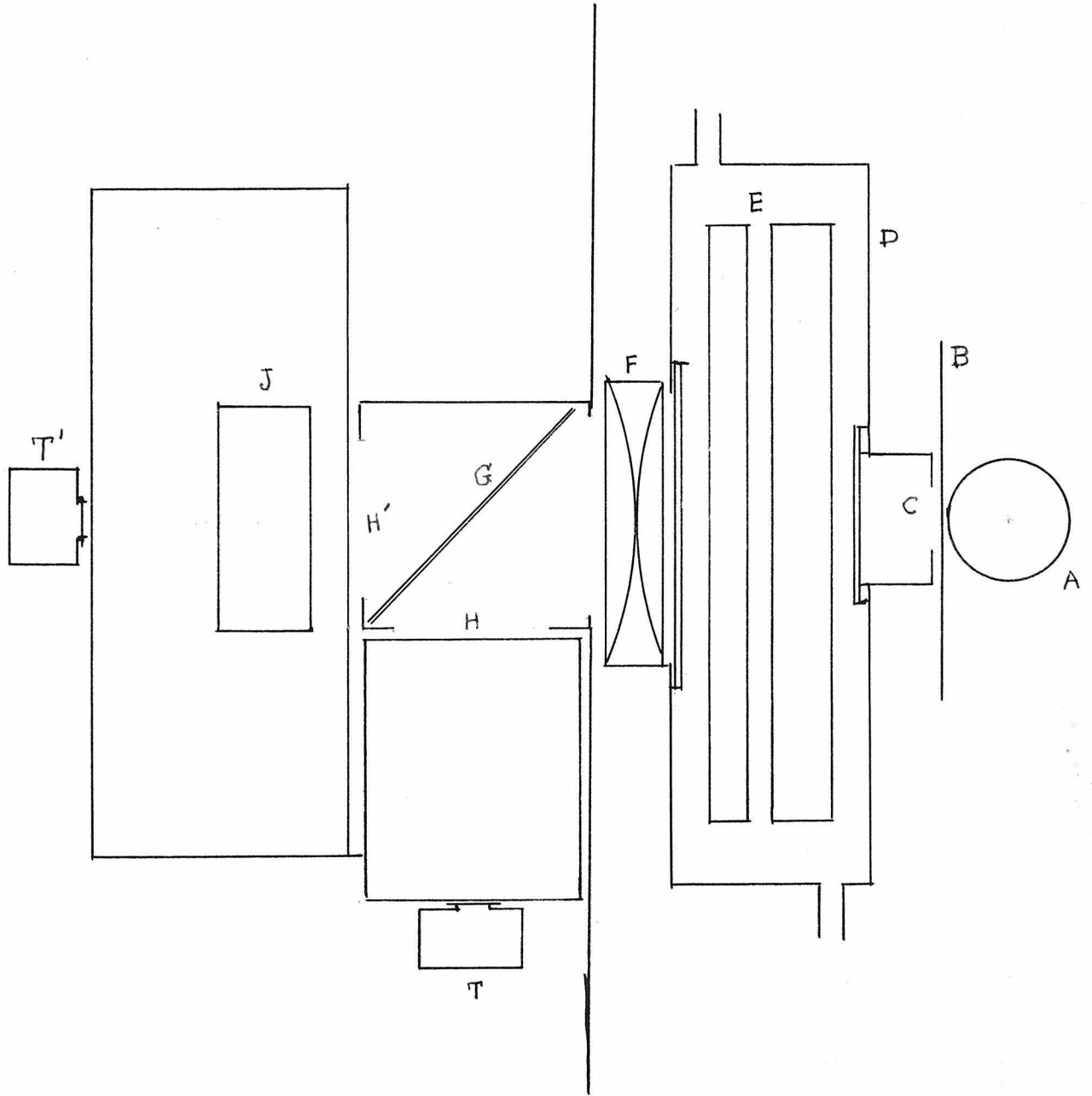


Fig.1-Plan view of the photochemical apparatus



These stock solutions were of such a concentration as to make it convenient to prepare solutions for the experiments by using the stocks and pure benzene.

#### The Apparatus.

The arrangements for illuminating the solutions and measuring the transmissions are shown in plan in Fig.1. Light from the quartz mercury arc A, operated from a D.C. generator with voltage regulator, passed when the shutter B was opened, through a rectangular slit  $\frac{3}{8}$  inch wide and 1 inch long. It then passed through the filter box D through which water was flowed. The light filters E were submerged in this box. The light was collimated by the lenses F, and the beam partially transmitted and partially reflected by the two glass plates G, set at an angle of  $45^\circ$  to the beam. These plates were fairly plane, being the plates of a photographic filter. They were shimmed apart slightly to prevent interference. The two light beams then passed through the two holes, 1 inch in diameter in the diaphragms H and H', which were so placed as to be reflections of each other across the plane of the reflecting plates. The light passing through these diaphragms passed through glass windowed troughs, two inches thick, filled with xylene, whose index of refraction is close to that of pyrex glass and benzene, and struck the two thermopiles T and T'. The correct position for the thermopiles was determined by getting real images of the

filament of a small lamp placed a suitable distance before the lenses F, and moving the thermopiles until the two images fell simultaneously on the windows of the thermopiles. It is seen that the light path is identical for the two parts of the split beam on the way to the thermopiles. The cell J was clamped in a brass holder that fitted into the trough in the transmitted beam, thus making it possible to remove it and replace it in exactly the same position. The cell was pyrex with parallel faces. It was 2.15-cm. thick and 3.5-cm in diameter, with a neck for filling fitted with a ground glass stopper. The thermopiles were connected to two galvanometers whose deflections were read on a single glass scale. A reflection factor was determined by inserting the cell in position filled with pure benzene, and reading the deflections of the two galvanometers. The ratio of the deflection caused by the thermopile in the transmitted beam to that caused by the one in the reflected beam was taken as the reflection factor. The factor varied somewhat, but rarely was more than 2% from 2.90, and in most cases it was 2.90 within 1%.

#### The Filters.

To remove the infra-red, a 1-cm. layer of copper<sup>6%</sup> sulfate<sup>3</sup> solution was used. To isolate 4358, a 2-mm. piece of Noviol A, followed by a 4-mm. piece of Corning G 585 was used. On photographing with the spectrograph the radiation transmitted by these

filters showed only the weak neighboring lines 4347 and 4339 in addition to 4358.

#### Absorption Coefficients.

The absorption coefficient of iodine in benzene solution was determined for the radiation 4358, using the apparatus and filters described above. The ratio of the galvanometer deflection from the thermopile in the transmitted beam to that of the one in the reflected beam multiplied by the reflection factor was taken as the transmission  $I/I_0$  of the solution. In Table 1. are given values of the transmissions of solutions of various concentrations together with the absorption coefficients,  $\alpha$ , defined by the equation.

$$-\log_{10} I/I_0 = \alpha cd$$

where  $c$  is the concentration in moles per liter, and  $d$  is the thickness of the cell, 2.15-cm.

Table 1.

Mols $I_2$ per liter	$I/I_0$	
.001779	.1914	187.8
.001334	.2822	191.6
.000889	.4280	192.8
.000553	.6057	189.8

Using a visual spectrophotometer Getman<sup>4</sup> got for  $\epsilon = 1/d \log I/I_0$  0.09 for 4400 and 0.05 for 4300 with 0.0005 m. solutions of iodine in benzene. These values give for  $\alpha$  as calculated above the values 180 at 4400 and 100 at 4300.

### Rate Measurements.

Before starting any experiment the reflection ratio was checked. The solution of the desired concentration of iodine and cyclohexene was introduced into the cell and the transmission measured. The solution was then illuminated, and the illumination interrupted at definite intervals of time and the transmission re-measured. From these measurements, and the known absorption coefficient and cell thickness, the concentration could be determined at convenient time intervals during a run.

Due to the fact that the diaphragm before the cell was smaller than the cell, only a part of the solution was illuminated. It was found necessary to stir the solution to keep the concentration uniform as is shown by the fact that after a period of illumination, if a transmission measurement was made, then the solution stirred, and a second measurement made, the second transmission was lower than the first. Furthermore, the reaction is very rapid, especially near the beginning, and concentration differences were likely to be also caused by this fast change in part of the relatively thick layer illuminated. The stirring was done by hand by inserting a small glass rod into the cell through the neck. The concentration change during a short period of illumination was small, so it was considered sufficient to stir before each transmission measurement.

Oxygen was found to have some inhibiting effect on the rate of the reaction. In one experiment the solution was stirred by

bubbling in oxygen from a tank, and it was found that the reaction was considerably retarded. Solutions handled in air, however, showed a rate only a little different from those in which an effort was made to exclude air. In all the experiments that will be discussed here, air was excluded from the solution as well as possible in the following manner.

The benzene was put into an all glass wash bottle arrangement and heated with nitrogen bubbling through, and the container was kept closed by mercury traps except when filling the cell. Strong stock solutions were made up so that 1-c.c. or less of the stocks was needed to make the experimental samples up to the desired concentrations. The cell was calibrated to a mark on the neck and held 23.4 c.c. In making up a solution for a run, the cell was filled with nitrogen, and some benzene forced over into it with nitrogen. The stock solutions were then measured in, and the cell filled to the mark with the air free benzene. The amount of oxygen thus admitted to the sample was that dissolved in the small quantity of the stock solutions.

#### The Results.

The results of a number of experiments made by illuminating solutions of the same initial concentration of iodine and varying concentrations of cyclohexene are given in Tables 2, 3, 4, and 5.

The amount of iodine disappearing in the various runs is shown in Fig. 2 plotted against  $\sum \sqrt{I_0} \times \Delta t$ . The  $I_0$  here is taken as the deflection of the galvanometer connected to the thermopile in the reflected beam. The numbers on the curves are the experiment numbers of the Tables. The initial concentrations of cyclohexene were in the ratio 3,5,7,10, for the curves 20, 15, 19, and 16 respectively. The cyclohexene concentration was high enough in each case compared to the iodine disappearing, to be considered essentially constant throughout the run. The circles lying on or close to curve 19 is a run in which the concentrations of the reactants are the same as in experiment 19, but the intensity of the light was diminished by a little more than 50% by placing a screen in the light beam just before the lenses. The agreement of these two experiments, 18 and 19, indicates that the reaction goes at a rate proportional to the square root of the intensity. The results of this experiment, 18, are given in Table 6.

Fig. 2  
 The ratio of the cyclohexene concentrations  
 are 3, 5, 7, 10 for expts. 20, 15, 19, 16.

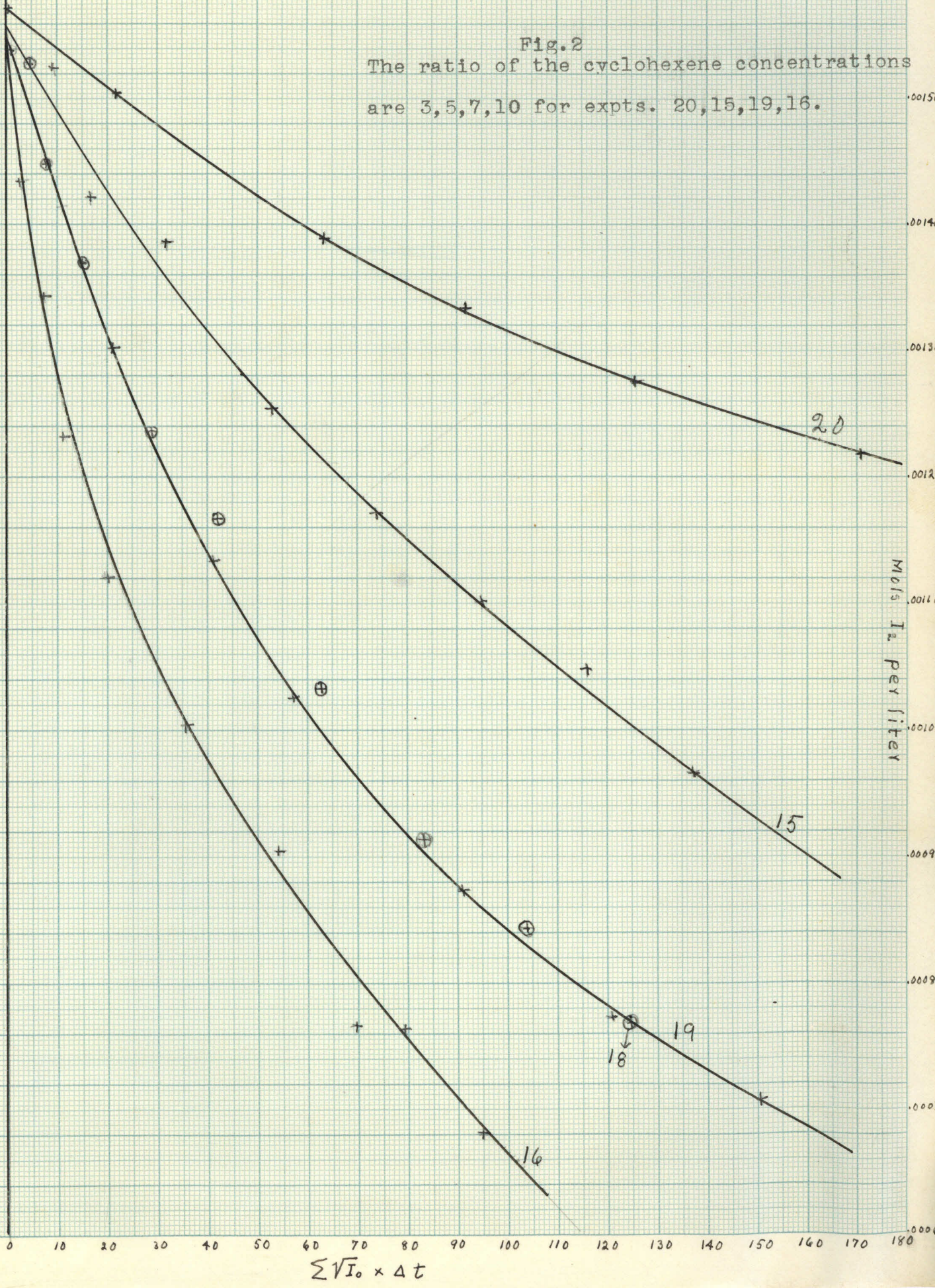


Table 2.

Experiment 20. Cyclohexene concentration = 0.03201-v.m.

Tot. time of ill. in min.	$I_0$	$I/I_0$	Concn. $I_2$ at time $t$ in millimols	$\sum \sqrt{I_{0i}} \Delta t$
0.5	3.96	0.2262	1.575	.99
5.0	3.65	.2372	1.524	9.77
11.5	3.69	.2420	1.504	22.22
19.0	3.61	.2535	1.455	36.55
34.5	2.75	.2700	1.389	64.25
50.0	2.90	.2840	1.335	90.25
71.0	3.11	.2997	1.277	126.65
96.0	3.24	.3175	1.219	171.15
121.0	3.42	.3260	1.188	216.75
150.0	3.58	.3285	1.178	270.95
180.0	3.65	.3478	1.122	326.95



Table 3.

Experiment 15. Cyclohexene concentration = 0.0533-v.m.

Tot. time of ill. in min.	$I_0$	$I/I_0$	Concn. $I_2$ at time $t$ in millimols	$\sum \sqrt{I_0 \cdot \Delta t}$
0.5	4.73	0.2160	1.625	1.09
2.0	4.63	.2385	1.520	4.33
4.0	4.60	.2555	1.448	8.63
8.0	4.57	.2621	1.422	17.16
15.0	4.53	.2795	1.384	32.08
25.0	4.38	.3065	1.255	53.18
35.0	4.34	.3318	1.170	74.08
45.0	4.44	.3537	1.101	95.01
55.0	4.46	.3721	1.047	116.09
65.0	4.64	.4020	0.966	137.40
85.0	4.48	.4145	0.934	180.16
95.0	4.61	.4285	0.897	201.46
105.0	4.44	.4420	0.866	222.71

Table 4.

Experiment 19. Cyclohexene concentration = 0.07462-v.m.

Tot. time of ill. in min.	$I_0$	$I/I_0$	Concn. $I_2$ at time $t$ in millimols	$\sum \sqrt{I_0} \times \Delta t$
0.5	3.73	0.2363	1.530	.97
6.0	3.66	.2638	1.413	11.50
11.5	3.66	.2930	1.301	22.00
22.0	3.64	.3425	1.135	42.02
32.5	3.56	.3892	1.000	61.94
48.0	3.67	.4380	0.875	91.36
63.5	3.71	.4825	0.773	121.11
79.0	3.74	.5135	0.706	151.00

Table 5.

Experiment 16. Cyclohexene concentration = 0.1066-v.m.

Tot. time of ill. in min.	$I_0$	$I/I_0$	Concn. $I_2$ at time $t$ in millimols	$\sum \sqrt{I_0} \cdot \Delta t$
0.5	4.00	0.2370	1.528	1.00
2.0	4.00	.2585	1.435	4.00
4.0	4.00	.2821	1.341	8.00
6.0	3.93	.3130	1.231	11.98
8.0	3.98	.3318	1.172	15.95
10.0	3.97	.3500	1.122	19.94
18.0	4.21	.3861	1.009	36.10
25.0	4.19	.4265	0.904	50.44
32.0	4.10	.4860	0.764	64.69
39.0	4.42	.4875	0.762	79.13
46.0	4.59	.5270	0.678	94.95
53.0	4.45	.5370	0.658	109.83
63.0	4.42	.5750	0.587	130.85
75.0	4.28	.5900	0.558	156.07
90.0	4.28	.6145	0.516	187.09

Table 6.

Experiment 18. Cyclohexene concentration = 0.07462-v.m.

Tot. time of ill. in min.	$I_0$	$I/I_0$	Concn. $I_2$ at time $t$ in millimols	$\sum \sqrt{I_0} \cdot \Delta t$
0.5	1.90	0.2342	1.540	.69
6.0	1.86	.2579	1.438	8.23
11.5	1.79	.2752	1.368	15.67
22.0	1.66	.3118	1.235	29.57
32.5	1.54	.3335	1.165	42.85
48.0	1.87	.3779	1.031	63.03
63.5	1.81	.4230	0.912	83.93
79.0	1.71	.4520	0.843	104.53
94.5	1.69	.4835	0.769	124.73

In Tables 7 to 9 inclusive, are given the results of a set of experiments at the lower iodine concentrations shown. The cyclohexene concentrations in experiments 23, 21, and 22 being the same as in experiments 15, 19, and 16, respectively. The iodine concentrations plotted against  $\sum \sqrt{I_0} \times \Delta t$  are shown in the curves of Fig.3. Table 10 and curve 24 show an experiment having the same cyclohexene concentration as experiment 22, but with a much lower initial iodine concentration. An experiment having the same initial concentration of reactants as experiment 22, but illuminated with diminished intensity, is given by Table 11 and curve 26. The agreement of this curve with curve 22 is not so good as in the experiments at higher iodine concentrations.

A different type of experiment was performed to give additional evidence for the proportionality of the rate to the square root of the intensity. In this experiment the intensity was changed by a much greater amount than could be used in the two experiments cited above. A solution 0.1066-v.m. in cyclohexene, and 0.000972-v.m. in iodine was made up. Sample I was illuminated for 20 minutes with radiation from a 500 watt tungsten lamp. This light was filtered by a copper sulfate cell as was used in the other experiments, and then passed through a 4-mm. piece of Noviol 0, and a 4-mm. piece of corning G.585. This combination of filters transmits light from about 3800 to 4800 with the maximum of transmission at about 4200. Most of the radiation transmitted lies between 4000 and 4600. The transmission of the solution after illumination was determined with the regular apparatus described above. Sample II of this solution was illuminated for 40.7 minutes with a calibrated screen transmitting 0.2395% interposed between the cell and source. Sample III was illuminated in the same way, with the screen in, for 83.5 minutes. The concentration of sample I dropped to 0.0004<sup>28</sup>~~8~~-m., sample II to 0.000466-m, and sample III to 0.000331-m. This experiment serves to indicate that the rate is more nearly proportional to the square root of the intensity than to the first power.

Fig. 3

The ratio of the cyclohexene concentrations  
in expts. 23, 21, and 22 is as 5,7,10.

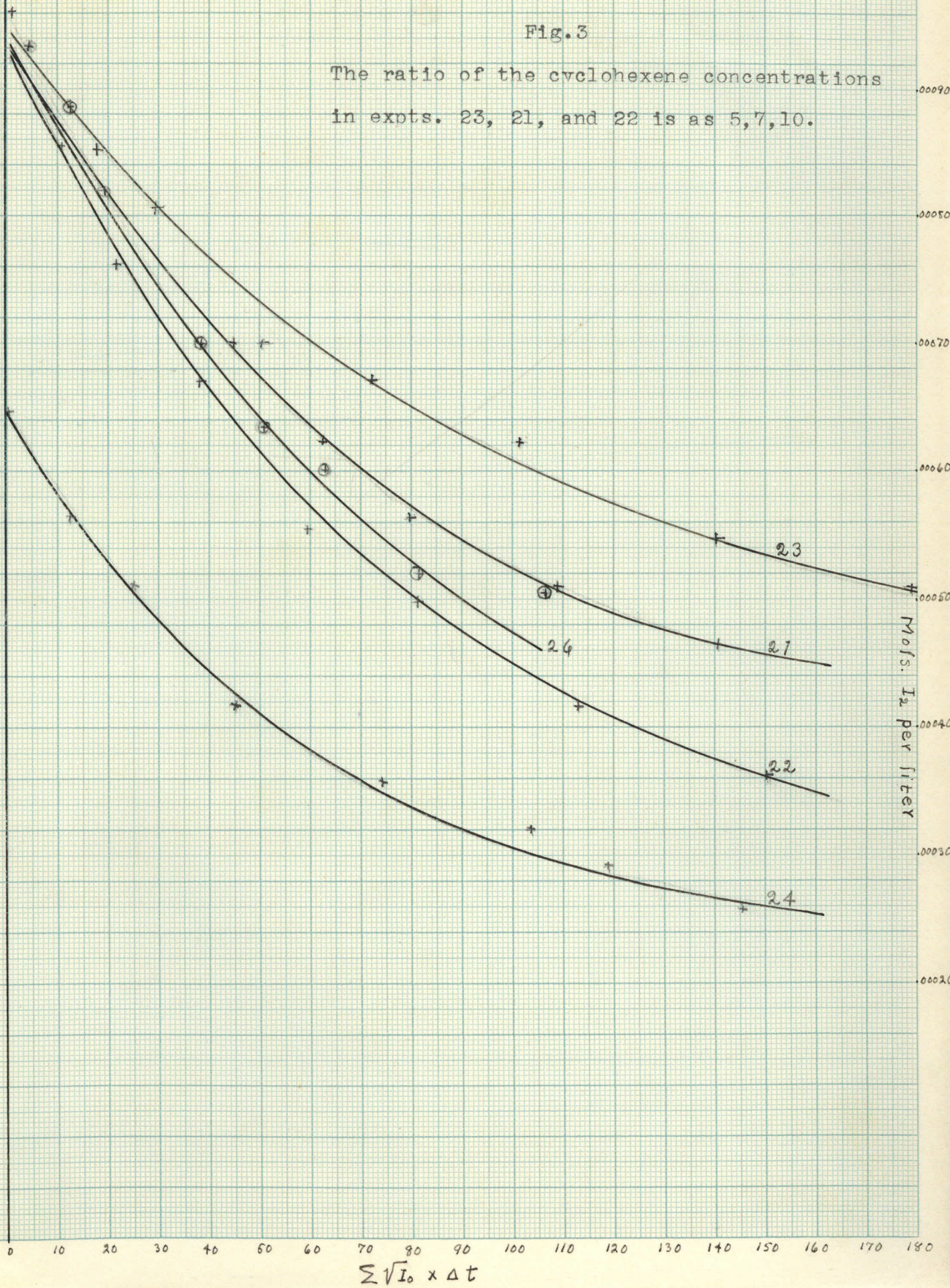


Table 7.

Experiment 23. Cyclohexene concentration = 0.0533-v.m.

Tot. time of ill. in min.	$I_0$	$I/I_0$	Concn. $I_2$ at time $t$ in millimols	$\sum \sqrt{I_0} \cdot \Delta t$
0.5	3.80	0.4040	0.962	.97
2.0	3.96	.4165	.928	3.93
9.0	3.93	.4470	.853	17.84
15.0	3.83	.4665	.807	29.66
26.0	3.73	.5165	.700	51.68
37.0	3.82	.5315	.672	72.49
52.0	3.75	.5600	.624	101.70
72.0	3.75	.5945	.548	140.45
92.0	3.86	.6180	.510	179.43

Table 8.

Experiment 21. Cyclohexene concentration = 0.07462-v.m.

Tot. time of ill. in min.	$I_0$	$I/I_0$	Concn. $I_2$ at time $t$ in millimols	$\sum \sqrt{I_0} \cdot \Delta t$
0.5	3.30	0.4175	0.923	.91
6.0	3.40	.4418	.867	10.96
11.5	3.41	.4660	.800	21.11
22.0	3.41	.5140	.703	40.49
33.5	3.54	.5545	.626	61.90
43.0	3.40	.5880	.564	79.62
59.0	3.65	.6175	.511	109.64
75.0	3.62	.6440	.467	140.07

Table 9.

Experiment 22. Cyclohexene concentration 0.1066-v?m.

Tot. time of ill. in min.	$I_0$	$I/I_0$	Concn. $I_2$ at time $t$ in millimols	$\sum \sqrt{I_0} \cdot \Delta t$
0.5	3.37	0.4150	0.931	.92
6.0	3.45	.4470	.854	11.07
11.5	3.26	.4875	.762	21.13
20.0	3.36	.5345	.665	38.43
31.0	3.34	.5920	.556	59.56
43.0	3.40	.6240	.500	81.57
60.0	3.48	.6740	.418	113.07
80.0	3.45	.7090	.364	150.27
100.0	3.38	.7340	.328	187.17

Table 10.

Experiment 24. Cyclohexene concentration = 0.1066

Tot. time of ill. in min.	$I_0$	$I/I_0$	Concn. $I_2$ at time $t$ in millimols	$\sum \sqrt{I_0} \cdot \Delta t$
0.5	3.36	0.5435	0.646	.92
7.0	3.37	.5865	.564	12.87
14.0	3.37	.6170	.512	25.73
25.0	3.19	.6735	.418	45.63
31.0	3.31	.6835	.404	56.43
41.0	3.24	.7125	.359	74.53
52.0	3.19	.7396	.320	94.25
66.0	3.38	.7600	.297	119.55
80.0	3.42	.7825	.260	145.35
100.0	3.39	.7980	.239	182.25



Table 11.

Experiment 26. Cyclohexene concentration = 0.1066-v.m.

Tot. time of ill. in min.	$I_0$	$I/I_0$	Concn. $I_2$ at time $t$ in millimols	$\sum \sqrt{I_0 \cdot \Delta t}$
0.5	1.39	0.4000	.972	.59
4.0	1.56	.4140	.934	4.85
10.0	1.46	.4340	.886	12.72
16.0	1.37	.4615	.819	19.87
32.0	1.40	.5170	.700	38.72
42.0	1.58	.5480	.636	50.92
52.0	1.51	.5650	.602	63.34
67.0	1.57	.6110	.522	81.96
87.0	1.50	.6250	.507	106.76

Quantum Yields.

A calculation of the quantum yield was made from the data of two representative experiments, 16 and 22. The yields being the molecules of iodine disappearing per quantum absorbed in the first 10 minutes of illumination for experiment 16, and for the first 11.5 minutes for experiment 22. An average value of the absorption for the interval was used. The thermopile used in the transmitted beam in the experiments was calibrated with the aid of a carbon lamp calibrated by the Bureau of Standards. In the calibration the quartz window of the thermopile was removed, the junctions being left bare.

The total number of quanta,  $Q$ , entering the solution in  $t$  minutes was calculated by the following formula

$$Q = 60t \times (d \times f) \times f_2 \times f_3 \times E \times A \times f_4 \times f_5 \times q = 5.67 \times 10^{15} \times (d \times f) \times t \times d$$

$(d \times f)$  = the deflection of the ~~galvanometer~~ in the reflected beam times the reflection factor, 2.860 for experiment 16, and 2.923 for 22.

$f_2$  = ratio of deflection of thermopile in plane of diaphragm and at its center to deflection in position used = 0.073

$f_3$  = ratio of average deflection over diaphragm to deflection at center of diaphragm = 0.9

$E$  = intensity of radiation giving unit scale deflection, ergs per sq. mm. per sec. per cm. scale deflection = 1.299

$A$  = area of diaphragm in sq. mm. = 490.9

$f_4$  = reciprocal of transmission of quartz plate = 1.065.

$f_5$  = reciprocal of transmission of two surfaces of glass plate = 1.035

$q$  = quanta in one erg of radiation of  $\lambda = 4368 = 2.217 \times 10^{11}$

The factors  $f_1$  and  $f_2$  were not determined for this particular diaphragm and thermopile, but ~~is~~<sup>are</sup> values close to those obtained for a similar arrangement, and ~~are~~<sup>is</sup> probably not in error by more than a few per cent.

The total number of quanta absorbed by this system is obtained by multiplying this quantity  $5.67 \times 10^{15}$  by the time interval, the average deflection of the reflected beam galvanometer times the reflection factor, and  $(1-I/I_0)$ . The  $I/I_0$  is the average value of the transmission over the interval. The number of molecules of iodine disappearing during the interval, were calculated from the data of Tables 5 and 9, for experiments 16 and 22 respectively. The yields thus obtained were 9.3 molecules per quantum absorbed for experiment 16, and 4.2 for experiment 22, which had a smaller initial iodine concentration, and went at a considerably lower rate. These results indicate that the reaction is a chain reaction.

### Discussion of the Results.

A comparison of the slopes of the curves 20, 15, 19, and 16 of Fig.2 shows that the rate of disappearance of iodine falls off rapidly with decreasing cyclohexene concentration. In fact, if slopes are taken at points on the curves where the same amount of iodine has disappeared, and the amount of products are the same, there is indication that the rate is proportional to the square of the cyclohexene concentration. If, however, slopes are taken in the same manner at points on the curves 23, 21, and 22 of Fig.3, i.e. at the same cyclohexene concentration and lower iodine concentrations, the effect of the cyclohexene is found to approximate the first power.

Similarly, it is seen from the slopes of the earlier parts of the curves 22 and 24 of Fig.3 and 16 of Fig.2, that the rate falls off rapidly with decreasing iodine concentration. The rate changes by a higher power of the iodine concentration than can be accounted for by any reasonable mechanism we have been able to propose.

It seems probable, on the basis of experiments 18 and 19, and the result of the experiment described above in which the intensity was cut down to one fourth, that the rate is proportional to the square root of the intensity.

There is also evidence of considerable inhibition by the products in this reaction. A comparison of the slopes of the curves 23 and 24 at a point where the iodine concentration is

the same in both, but the concentration of products much larger in 23, shows that the rate is decreasing much faster in 24 than in 23. Similar comparisons with other experiments show the same effect.

In view of the peculiar effect of the cyclohexene concentration, and the very large effect of iodine concentration on the rate of this reaction, no explanation of the kinetics has been attained.

#### Summary.

The effect of the concentrations of the reactants and of the light intensity on the rate of the photochemical reaction of iodine with cyclohexene in benzene solution have been studied. The rate was found to decrease very rapidly with the cyclohexene concentration, and also to fall off rapidly with decreasing iodine concentration. The rate is approximately proportional to the square root of the intensity. Quantum yields were calculated for two of the experiments where the iodine concentrations were initially 0.001528-m. and 0.000931-m. The yields were for these concentrations 4.3 and 5.8. It is evident that the reaction is a chain reaction.

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