

precipitates which were allowed to stand over for a twenty-four hour period gave uniformly good results. This was due to the complete transformation of the arsenate into the oxalate during this period of standing.

Recommended Procedure

Accurate results were obtained from the following procedure. The solution was made alkaline with ammonium hydroxide and a few drops excess added. After the addition of an excess of ammonium oxalate to the boiling solution, it was kept at incipient boiling temperature and occasionally stirred for ten minutes. After standing for an hour the precipitate was filtered off, washed with distilled water containing a small amount of ammonium hydroxide, transferred on the paper to the precipitation beaker, dissolved in 30 cc. of dilute sulfuric acid, diluted to 100 cc. and titrated rapidly with a 0.10 *N* potassium permanganate solution.

Summary

1. Calcium oxalate may be precipitated quantitatively in the presence of the arsenate ion.

2. The solution may be made alkaline either before or after the addition of ammonium oxalate, and a small excess of ammonium hydroxide added.

3. The best temperature for precipitation is 90–100°

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

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That chlorine monoxide, Cl_2O , is sensitive toward light has long been recognized. In recent years several quantitative investigations of the photochemistry of this compound have been undertaken. Bowen¹ 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 measured² 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.

¹ E. J. Bowen, *J. Chem. Soc.*, **123**, 1199 (1923).

² Bowen, *ibid.*, **123**, 2330 (1923).

The gaseous reaction was studied more extensively by Bodenstein and Kistiakowsky.³ 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_2 formation) has been discussed by Schumacher and Wagner.⁴ They have shown that for 4350 Å. the absorption process may be either $\text{Cl}_2\text{O} + h\nu \longrightarrow \text{Cl}_2 + \text{O}$ or $\text{Cl}_2\text{O} + h\nu \longrightarrow \text{ClO} + \text{Cl}$, and regard the latter as more probable. The character of the absorption spectrum of gaseous Cl_2O ⁵ 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.⁶ 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.

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

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

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

⁶ 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.⁷ 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

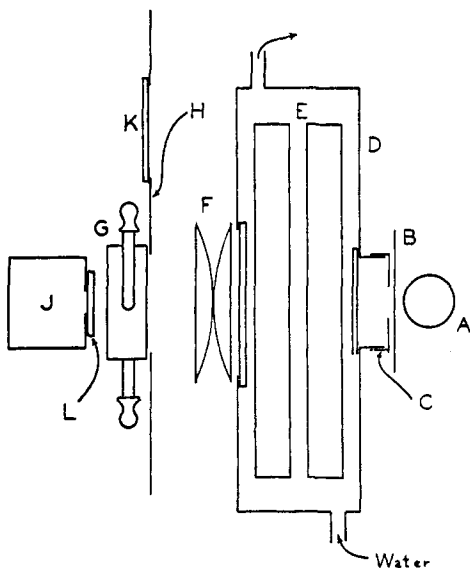


Fig. 1.—Plan view of photochemical apparatus.

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.⁸ To isolate λ_{4358} , a 4-mm. piece of Corning G 585

⁷ W. C. Bray, *Z. physik. Chem.*, **54**, 592 (1906).

⁸ 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, α , 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, ϵ , defined by the equation

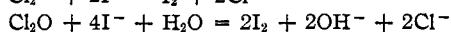
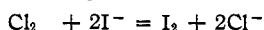
$$-\log_{10} I/I_0 = \epsilon Cd$$

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.⁹ The value of α 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	α
Cl ₂	0.214	4358	0.308	2.40
	.0457	4047	.481	6.95
Cl ₂ 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 ₂	.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

⁹ 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 (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 $(I/I_0)_f$ found after illumination is given by

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

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 (ClO_2) so obtained, we have determined the values of (Cl_2) and (Cl_2O) 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 Cl_2O 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. = 2.217×10^{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 ± 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 ₂ O, milli-moles	Cl ₂ , milli-moles	ClO ₂ , milli-moles	I/I_0 for 4358 Å.	I/I_0 for 4047 Å.	Av. galv. defl. for preceding interval	Total quanta abs. $\times 10^{-19}$	Cl ₂ O decomp. per quantum abs. by soln.	Cl ₂ O decomp. per quantum abs. by Cl ₂ O
1	0	0.158	0.000	0.00000	0.676	0.686
	17000338	..	.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
	6000225	..	.367	26.9	0.675
	12000370	..	.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
	3000225	.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
	3000164	.430	.342	20.2	0.313
	6000303	.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
	6000238	.439	.316	18.9	0.567
	12000449	.396	.206	25.5	1.40
	18000572	.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
	3000085	.745	.657	26.2	0.176
	6000138	.724	.592	25.7	0.363
	9000180	.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.¹⁰ 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

¹⁰ 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.

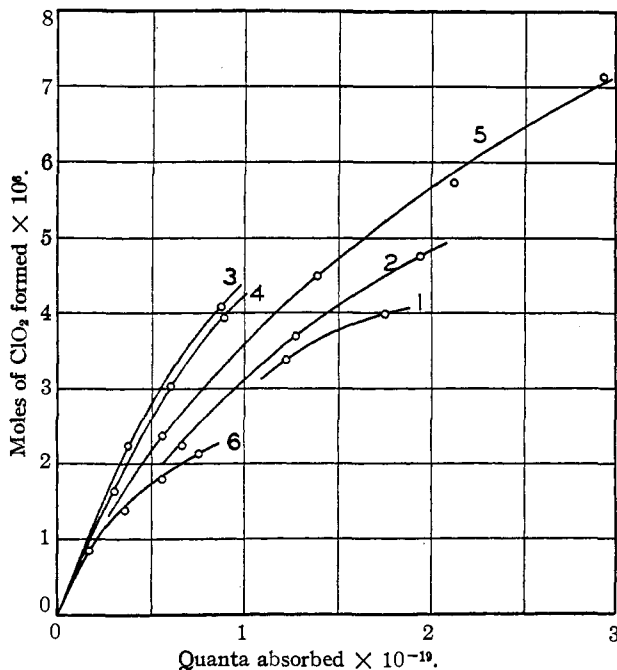


Fig. 2.—Amount of ClO_2 formed vs. number of quanta (4358 \AA .) absorbed. The numbers on the curves are the experiment numbers of Table II. The initial concentrations of Cl_2O increase in the order 6, 1, 2, 5, 4, 3.

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 (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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