[CONTRIBUTION FROM THE UNIVERSITY OF SASKATCHEWAN]

Photodecomposition of Chlorine Dioxide

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The photodecomposition of chlorine dioxide has been the subject of a number of researches[1,2] and led to the isolation of Cl_2O_6.[3] The mechanism suggested by Bodenstein and Schumacher[4] would lead to the formation of one mole of Cl_2O_6 for two einsteins of light absorbed. The photodecomposition in solution has also been studied[5,6] and appears to differ very considerably from the reaction in the gas phase.

Experimental

Chlorine dioxide was prepared and analyzed by the method of Bray[7] and purified by bubbling through a solution of sodium bicarbonate.[8] In the first series of experiments two similar cells were filled with the gas at the same concentration and at atmospheric pressure. The connecting tubes were then swept clear of chlorine dioxide by air or oxygen, and the concentration of the gas in the dark cell determined by analysis. This gave the initial concentration of the gas in the light cell which was usually less than 8% by volume. The gas in the light cell was analyzed at the end of the experiment by sweeping out with air or oxygen through neutral potassium iodide solution.

$$3ClO_2 + 5I^- \longrightarrow 2IO_3^- + 3Cl^- + 3I$$

Any chlorine present would liberate an equivalent amount of iodine. The iodine liberated was titrated against a standard thiosulfate solution. A known quantity of standard sulfuric acid was then added which decomposed the iodate.

$$IO_3^- + 6H^+ + 5I^- \longrightarrow 6I + 3H_2O$$

The iodine liberated was titrated with thiosulfate, then an excess of potassium iodate solution was added and the unused portion of the sulfuric acid found. This last afforded a double check on each analysis.

In most cases the solution was acidified before the initial titration.

$$ClO_2 + 5I^- + 4H^+ \longrightarrow Cl^- + 2H_2O + 5I$$

The excess H^+ was then determined by adding a slight excess of potassium iodate solution.

The course of reaction was followed by the pressure change on a sulfuric acid manometer connected between the two cells.

The manometer was read by a cathetometer which could be read to 0.001 cm.

The cells were cylindrical, of Suprax glass, 10 cm. in length and 5 cm. in diameter, with plane ends. The cells and all the connecting tubes were immersed in a thermostat (Fig. 1). The source of light used was a quartz atmospheric mercury arc lamp consuming 2.2 amperes at 136 volts. The optical arrangement in the first series of experiments is shown in Fig. 2. The light from the source was limited by a diaphragm with a 1.0-cm. opening and the rays made parallel by a 15.2-cm. condensing lens (A) of glass. B is the filter for obtaining monochromatic light and is placed immediately in front of the shutter (C).

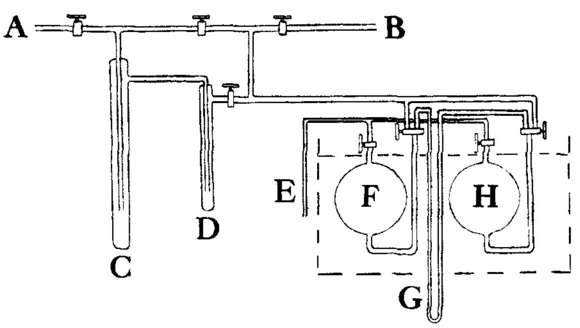

Fig. 1.—Apparatus used in wet cell experiments: A, oxygen inlet; B, air; C, ClO_2 generator; D, $NaHCO_3$ solution; E, to water pump and analysis apparatus; F and H, light and dark reaction cells; G, manometer.

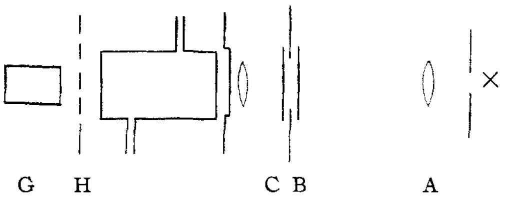

Fig. 2.—Optical arrangement. Mercury arc at X.

After a second lens the slightly convergent beam fell on the front of the cell, the light passing through a glass window in the side of the thermostat. After traversing the cell, the light fell on the thermopile (G). Using this arrangement, energy measurements could be made at intervals during the experiment. Sometimes a shutter was inserted at H. The filters used to isolate the different wave lengths of light were: 5460 Å. Corning Nonex glass, heat resisting yellow shade, 2.8 mm. thick, together with Corning Didymium filter 4.97 mm. thick. This

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(1) Millon, *Ann.*, **45**, 281 (1843).

(2) Booth and Bowen, *J. Chem. Soc.*, **123**, 1199 (1923); **127**, 510 (1925).

(3) Bodenstein, Harteck and Padelt, *Z. anorg. allgem. Chem.*, **147**, 233 (1925).

(4) Bodenstein and Schumacher, *Z. physik. Chem.*, **B5**, 233 (1929).

(5) Nagai and Goodeve, *Trans. Faraday Soc.*, **27**, 508 (1931).

(6) Bowen and Cheung, *J. Chem. Soc.*, 1200 (1932).

(7) Bray, *Z. physik. Chem.*, **54**, 463, 579, 731 (1906).

(8) Luther and Hoffmann, *ibid.*, Bodenstein Band, 755 (1931).

filter gave very pure 5460 Å. light and transmitted none of the blue or ultraviolet. There was a transmission band from 5240 and 7370 Å., but since the source is almost entirely lacking in these higher wave lengths, it was neglected. The wave length 5460 Å. is not absorbed by the chlorine dioxide or by any chlorine that may be formed during the reaction, so that this wave length was used as a reference to check the intensity of the light source during an experiment.

4360 Å. 0.5 cm. thickness of cuprammonium solution (20 cc. of concd. ammonium hydroxide, 3 g. of copper sulfate, 130 cc. of distilled water). 0.5 cm. thickness of quinine sulfate solution. (30 g. per liter of quinine in 2 normal sulfuric acid soln.) The 3650 and 4360 Å. filters in conjunction gave no deflection on the thermopile. 5460 and 4360 Å. in conjunction gave 3 mm. deflection, showing that the 4360 Å. filter transmits 3% 5460 Å. since 5460 Å. transmits no 4360 Å.

3650 Å. Corning Ultra A glass filter 3.83 mm. thick. This filter transmits about 4% in the red (λ = 6820 to 7825 Å.).

The energy measurements were made with a 2-cm. Moll surface thermopile connected in series with a moving coil galvanometer. Readings were made by an optical lever of 2 meters radius. The thermopile contained a bright polished cone in front of the thermopile surface which reflected the light entering the window onto the surface. Since this feature introduced a 30% correction in the calibration,[9] a polished metal diaphragm 2 cm. in diameter was inserted over the cone 1 cm. from the sensitive surface. Thus in calibration all light measured was incident on the surface, and no correction factor was necessary. During the experiment the whole of the light was obtained on the thermopile surface.

Calibration.—The calibration of the thermopile was made against two standard carbon filament lamps from the Bureau of Standards, Washington, D. C.

It was found that 1 mm. deflection on the scale corresponds to 5.19×10^{-6} watts sq. cm., which is equivalent to 1.82×10^{15} quanta per minute at 3650 Å. The reflection correction is 9.3%.[10] 1 mm. $\equiv 1.99 \times 10^{15}$ quanta per minute. Using the equation $PV = nRT$, an expression can be obtained relating change in number of moles of gas with the movement of sulfuric acid in the manometer. When V = 184 cc., T = 20°C., P = 720 mm. and diameter of capillary of manometer = 1.83 mm.; 1 mm. $H_2SO_4 \equiv 8.6 \times 10^{17}$ molecules. A correction was applied for the slight volume change due to the movement of the manometer liquid.

It is shown later that when the gases are moist, one mole disappears from the gas phase for every mole of chlorine dioxide decomposed. The quantum efficiency γ is equal to the ratio: molecules decomposed/quanta absorbed. For moist gases

$$\gamma_{3650} = \frac{9.60 \times 10^{17}}{1.99 \times 10^{15}} = 432\ \frac{\text{mm. } H_2SO_4\text{/minute}}{\text{mm. deflection.}}$$

The corresponding factor for 4360 Å. is 362. The calibration was checked by quantitative experiments on the Cl_2O_3 photoreaction.

Preliminary Experiments. 18° Dry Gases.—Preliminary experiments on the photodecomposition of dry chlorine dioxide have already been described,[11] giving γ_{3650} of the order of 10 but the reaction is complicated by side reactions and quantitative results are of little value.[12] The erratic results obtained were at least partly due to imperfect drying of the cell walls since Cl_2O_6 reacts immediately with water.

This suggested doing the decomposition of chlorine dioxide with water present in the cell, somewhat after the manner of a Bunsen actinometer. In this way it is possible to eliminate uncertainties due to surface action and obtain reproducible results. The primary process and the effect of a number of variables can then be studied before proceeding with the reaction with dry gases.

Experiments with Moist Chlorine Dioxide, 18°.—In order to wet the walls of the cell thoroughly, the cell was filled with distilled water and all but a few cubic centimeters of the water sucked out. Water remained in the lower connecting tube. Chlorine dioxide was swept into the cell with oxygen or air. Since the gas bubbled through the water in the connecting tube, it was assumed to be saturated with water vapor. On leaving the gas in the cell overnight in the dark, the pressure change was less than 1 mm., so the dark reaction was practically nil. No attempt was made to remove the carbon dioxide that is formed with the chlorine dioxide.

On insolating with 3650 Å. there was a small increase in pressure (Budde and Draper effect), and after this the pressure in the light cell decreased at a uniform rate, 3650 Å. being strongly absorbed to quite low concentrations of chlorine dioxide. This points to a constant quantum yield since with constant intensity the light absorbed will be constant for 3650 Å., which is almost completely absorbed down to 0.5% chlorine dioxide. On cutting off the light there was a fall in pressure nearly equal to the Budde and Draper effect previously noted. It was later found that the Budde and Draper effect depends to a marked extent on the concentration of the chlorine dioxide when this is less than 0.3%. A curve showing this dependency was made. After allowing for the changing Budde and Draper effect and the changing percentage absorption in this region, it is found that the quantum yield is constant down to less than 0.05% of chlorine dioxide. The correction need only be applied when the absorption of 3650 Å. is varying ($ClO_2 < 0.3\%$) and demonstrates the value of taking energy measurements during the experiment.

The results in the presence of moisture were easily reproducible: *e. g.*, experiments 65, 66, 67, 68, 71 and 72 gave rates calculated for the same amount of light absorbed equal to 1.08, 1.06, 1.04, 1.09, 1.02, 1.05, *i. e.*, a constant quantum yield. In these experiments (ClO_2) varied between 1 and 8% and the wave length was 3650 Å.

When the light was cut off there was no change in pressure other than the inverse Budde and Draper effect. This is in marked contrast to the behavior with the cell dry. It is suggested that this is due to the removal of the active groups, such as ClO_3, ClO and Cl_2O_3 by the water on the cell walls and by the water vapor in the gas

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[9] Ridyard, "Proc. 7th Int. Cong. Phot.," 1928, p. 104.

[10] Allmand and Spinks, *J. Chem. Soc.*, 1658 (1931).

[11] Spinks, THIS JOURNAL, **54**, 1689 (1932).

[12] Schumacher, *Z. Elektrochem.*, **39**, 1 (1933).

phase. Shining the full light on the cell (no filter) caused a heavy mist to form which was afterward noted with 3650 Å. In the latter case the mist caused a 3% reduction in the transmission of 5460 Å., which is not a serious correction. At the end of an experiment the cell was swept out with air and the transmission checked.

As the presence of water in the bottom of the cell made it impossible to analyze the gases chemically, a curve was obtained experimentally of the percentage absorption of 4360 Å. against the percentage chlorine dioxide in the cell. The points lay on a fairly smooth curve and from it the initial percentage of chlorine dioxide in the cell could be obtained (Fig. 3). A similar curve for the percentage absorption of 3650 Å. against the percentage of chlorine dioxide was made.

Comparing this with the above 0.808 × 10^{-4} mole, pressure measurements show that 1 mole of chlorine dioxide disappears entirely from the gas phase for every mole of chlorine dioxide decomposed.

Analyses of residual gases at the end of an experiment show that no chlorine is formed by the photoreaction in the presence of moisture. This is supported by the fact that 3650 Å. is absorbed less than 1% when the chlorine dioxide is completely decomposed, indicating that there is no chlorine in the gas phase.

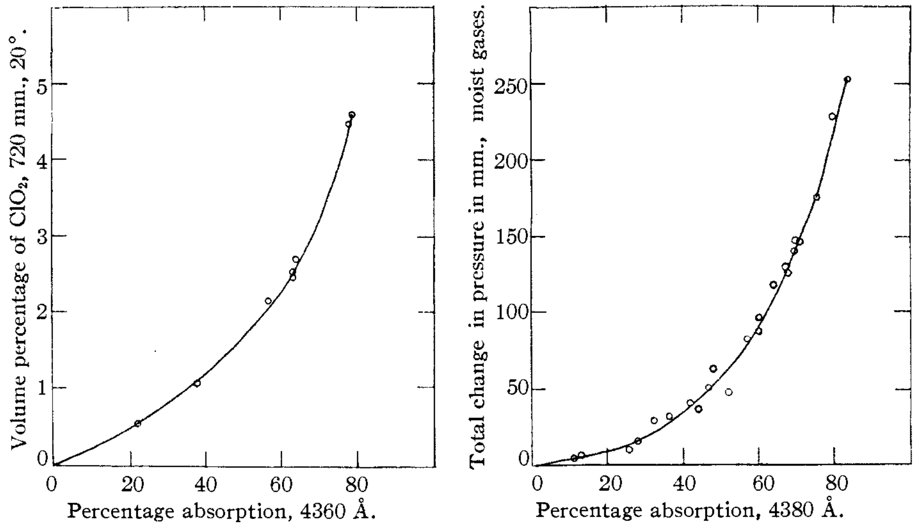

Fig. 3.

A series of experiments was then run in which the total pressure change due to decomposition of the chlorine dioxide was found for different percentage absorptions of chlorine dioxide (Fig. 3). From the absorption measurements the percentage of chlorine dioxide at various stages of the experiment could be calculated.

CHANGE IN PRESSURE PER PERCENTAGE OF CHLORINE DIOXIDE PRESENT

ClO_2, %	Moles $ClO_2 \times 10^4$	Absorption, % 4360 Å.	ΔP (mm. H_2SO_4)	Diff.
4	3.232	78	200	
				55
3	2.424	70.5	145	
				58
2	1.616	59.0	87	
				59
1	0.808	37	28	
				28
0	0	0	0	

The average change in pressure per percentage of chlorine dioxide is 57.5, neglecting the last reading; 57.5 mm. pressure change is equivalent to the disappearance of 57.5·1.42 × 10^{-6} mole = 0.813 × 10^{-4} mole.

Knowing that decomposition of 1 mole of chlorine dioxide results in a decrease in volume of 1 mole, quantum yields can be calculated from energy measurements and changes in pressure as already indicated. The difference in value at less than 1% chlorine dioxide may be due to inaccuracy at these low concentrations but is more probably due to chlorine dioxide escaping from the water into the gas phase under these conditions. This would be negligible at the beginning of the experiment where gas and solution are in equilibrium.

Variation of Wave Length in Presence of Moisture.—Rates of reaction were obtained using filters for 3650 and 4360 Å. in a series of eleven experiments in which (ClO_2) varied from 1 to 8.6%. Energy measurements were made at the same time and relative quantum efficiencies calculated: $\gamma_{4360}/\gamma_{3650} = 0.86 \pm 0.07$. The average value for the quantum efficiency from ten experiments is 3.7 for 3650 Å. and 3.1 for 4360 Å.

Variation of Intensity in Pressure of Moisture.—Nine experiments were performed in which the light intensity was varied between four- and ten-fold by interposing wire gauzes directly in front of the light filter.[13] The exact position of the gauze was found to be not critical, and from the ratio of the thermopile readings with and without the gauze in place, the ratio of intensities was found. Within the limits of experimental error, the rate of decomposition is directly proportional to the intensity for chlorine dioxide concentrations up to 8%.

Bromine Sensitized Decomposition of Chlorine Dioxide.[14]—Chlorine dioxide does not absorb 5460 Å. to any appreciable extent and shows no sign of reaction when insolated with light of this wave length. On the addition of bromine to the insolated system, a sensitized reaction takes place. The reaction proceeds both in the wet and dry gases and in carbon tetrachlorine solution, and appears to be quite similar to the direct photolysis taking place at lower wave lengths. Quantitive data were obtained in experiments using moist gases, and water in the bottom of the cell. Chlorine-free chlorine dioxide was passed into the cell with oxygen and bromine, the percentages of chlorine dioxide and bromine being roughly indicated by the percentage absorption of 4360 and 5460 Å. The thermostat was kept at 16° and reaction rates obtained for different wave lengths as in the wave length variation experiments. Relative quantum efficiencies were obtained and in a few cases the absolute value of the quantum efficiency was measured. It was found to be the same value as that obtained for the direct reaction at 4360 and 3650 Å. Experiments in which the chlorine was not removed from the chlorine dioxide behaved similarly to the others. No change in 5460 Å. transmission took place and this is in accord with the experiments of Gray and Style on bromine-chlorine mixtures.[15] In these experiments the Budde and Draper effect was usually quite large, while there was practically no mist formation, and no dark reaction. Over the small range of concentration used (Br_2, 6 to 1%; ClO_2, 4 to 1%) the rate was directly proportional to the amount of light absorbed and independent of the concentration of the ClO_2, *i. e.*, the quantum efficiency was constant. Taking $\gamma\,3650 = 1$, the following table of relative quantum efficiencies was obtained. $\gamma\,5460$ is seen to be very nearly equal to $\gamma\,3650$ and $\gamma\,4360$.

BROMINE SENSITIZED REACTION

Expt.	113	114	115	123	124	125	127	Mean
(Br_2), %...	2.5	6	4	2	3	1.5	4	
5460 Å....	1.0	0.83	0.99	1.27	0.85	1.12	0.8	1.01
4360 Å....					0.8	0.99	0.8	0.86
3650 Å....	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Summarizing, one may say that in presence of moisture and under the above conditions, the rate of photodecomposition of chlorine dioxide is proportional to the light absorbed and gives a constant value of the quantum yield slightly greater than 3 for 3650 and 4360 Å. This also holds for 5460 Å. where the reaction is sensitized by bromine.

Analysis of Mist Solution.—Since it appeared from the preceding experiments that the products of the reaction in the wet cell dissolved completely in water, an analysis of the resulting solution was made. Moist chlorine dioxide was passed slowly through the light absorption cell and insolated with light from the mercury arc lamp, either full light or with the interposition of a filter. A heavy mist formed and the products were removed from the resulting gases by passing through an absorption tower containing distilled water and glass beads. The resulting solution was freed from chlorine dioxide with a stream of air. As a preliminary experiment chlorine dioxide was passed through water for three hours in the dark. The solution was freed from chlorine dioxide by a stream of air and analyzed for the same constituents as are found in the mist solution. All tests were negative. The mist solution was first tested for Cl^- by acidifying a portion with dilute nitric acid and adding silver nitrate. A slight cloudiness of silver chloride was observed which is probably due to HClO.

The solution liberated iodine from potassium iodide, which indicates ClO^- or ClO_2^-. The solution bleaches litmus solution but not in the presence of sodium arsenite. This indicates ClO^- and not ClO_2^-. The absence of ClO_2^- may also be inferred from the fact that the solution does not decolorize dilute potassium permanganate solution. The presence of ClO^- is confirmed by the odor of the solution. The delicacy of the above tests for ClO_2^- is not known and it is possible that a small amount of ClO_2^- is present.

Brucine (2% solution) gave a positive test for ClO_4^-.

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[13] Forbes, *J. Phys. Chem.*, **32**, 482 (1928).

[14] Spinks, THIS JOURNAL, **55**, 428 (1933).

[15] Gray and Style, *Proc. Roy. Soc.* (London), **A126**, 607 (1930).

Addition of potassium chloride to the solution, followed by partial evaporation, gave crystals of potassium chlorate, indicating ClO_3^-. Reduction of the solution with ferrous sulfate also gives more Cl^- than corresponds to the ClO^-.

Qualitative analysis thus indicates the formation of ClO^-, ClO_3^- and ClO_4^- by the photodecomposition of chlorine dioxide in the gas phase in the presence of water vapor. Owing to the low concentration of the resulting solution, quantitative analysis was a matter of some difficulty. Eventually ClO^- was determined by titration of the iodine liberated by potassium iodide.

$$2H^+ + ClO^- + 2I^- \longrightarrow I_2 + Cl^- + H_2O$$

ClO_3^- was determined by reducing another portion of the solution by boiling for twenty minutes with acid ferrous sulfate in an atmosphere of carbon dioxide and back titration of unused ferrous sulfate with potassium permanganate.

$$ClO_3^- + 6Fe^{2+} + 6H^+ \longrightarrow Cl^- + 6Fe^{3+} + 2H_2O$$
$$ClO^- + 2Fe^{2+} + 2H^+ \longrightarrow Cl^- + H_2O + 2Fe^{3+}$$

ClO^- is known from the iodine titration and hence ClO_3^- can be calculated by difference. An alternative method was used to get ClO_3^-. The solution was boiled with ferrous sulfate and Cl^- estimated by precipitation of silver chloride by silver nitrate after oxidizing any Fe^{2+} by nitric acid and boiling. (This treatment also dissolved any basic iron hydroxide formed.) The precipitated silver chloride was weighed in a Gooch crucible.

The two methods agreed fairly well and six analyses gave a mean ratio: $ClO_3^-/ClO^- = 1.08/1$. The results showed a mean variation of 8% (1.26, 0.89, 1.05, 0.97, 1.16, 1.20). The analysis for ClO_4^- was more difficult and the results obtained were quite erratic, indicating (ClO_4^-) of the same order as (ClO_3^-). Owing to the possible interactions and decompositions of the oxyhalogen acids it was not thought profitable to extend the quantitative analyses further.

Spectroscopic Data and Discussion of Experiments with Wet Gases.—The absorption spectrum of chlorine dioxide shows a convergence limit at 2560 Å. and a region of predissociation beginning at 3750 Å.[16,17,18,19,20]

It is considered that at the convergence limit chlorine dioxide dissociates into $ClO + O(^1D)$. The energy of activation of $O(^1D)$ is 45 k. cal., so that the energy required for the dissociation of $ClO_2 \longrightarrow ClO + O(^3P)$ is $111 - 45 = 66$ k. cal. This corresponds to a wave length of 4360 Å. Actually the upper limit for predissociation is 3750 Å., so that this is another case of the predissociation region giving only the upper limit for the heat of dissociation.[21,22]

From the above spectroscopic data it is evident that 3650 Å. is within the region of predissociation. Hence the primary light action at this wave length would be: $ClO_2 + h\nu \longrightarrow ClO + O$. The products would have 11 k. cal. excess energy. This dissociation is followed by the reaction $ClO_2 + O + M \longrightarrow ClO_3 + M$. 4360 Å. is in the band region, the primary action resulting in the formation of an activated molecule: $ClO_2 + h\nu \longrightarrow ClO_2'$. If one remembers the slight uncertainty in the value for the heat of dissociation of chlorine dioxide, it is possible that the activated chlorine dioxide molecule has just enough energy to be able to dissociate on collision: $ClO_2' + M \longrightarrow ClO + O + M$. The equal efficiencies of 3650 and 4360 Å. would then be explained if nearly all the activated chlorine dioxide molecules dissociated on collision. Schumacher and Finkelnburg have suggested an alternative mechanism for the band region which leads to the same result. $ClO_2' + ClO_2 \longrightarrow ClO_3 + ClO$. It is interesting to note that the same similarity of action in the regions of band absorption and predissociation is found for nitrosyl chloride, acetaldehyde and formaldehyde, while other substances, notably nitrogen dioxide and benzaldehyde, show a very marked change in photoreactivity in passing from the one region of the spectrum to the other. For the photoreaction, in the presence of moisture the following actions are postulated

$$ClO_2 + h\nu \longrightarrow ClO + O$$
$$ClO_2 + O + M \longrightarrow ClO_3 + M$$
$$2ClO_3 \longrightarrow Cl_2O_6$$
$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$
$$ClO + ClO_2 \longrightarrow Cl_2O_3$$
$$Cl_2O_3 + H_2O \longrightarrow 2HClO_2 \longrightarrow HClO + HClO_3$$

This would give (a) a quantum yield of 3 independent of concentration and light intensity, (b) 1 mole disappearing from the gas phase for every mole of chlorine dioxide decomposed, (c) no chlorine formed, (d) $HClO$, $HClO_2$, $HClO_3$ and $HClO_4$, formed in solution. This is sub-

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(16) Goodeve and Wallace, *Trans. Faraday Soc.*, **26**, 255 (1930).

(17) Goodeve and Stein, *ibid.*, **25**, 738 (1929).

(18) Schumacher and Finkelnburg, *Z. physik. Chem.*, Bodenstein Band, 704 (1931).

(19) Urey and Johnston, *Phys. Rev.*, **38**, 2131 (1931).

(20) Urey and Johnston, *Ind. Eng. Chem.*, **23**, 1241 (1931).

(21) Herzberg, *Z. Physik*, **61**, 604 (1931).

(22) Franck, *Z. physik. Chem.*, **18B**, 88 (1932).

stantially in agreement with the facts. The oxide Cl_2O_3 has been mentioned fairly often in the literature in connection with the reactions of the oxides of chlorine but so far no very definite evidence has been adduced for its existence. It is therefore in all probability very unstable. According to the above mechanism, the ratio $HClO_3/HClO_2 = {}^1/_4$ but one would not expect to find this ratio in the mist solution owing to the decomposition $2HClO_2 \longrightarrow HClO + HClO_3$. If this goes to completion $ClO_3^-/ClO^- = {}^3/_2$, which is approximately in agreement with the analyses of the mist solution. For the reaction in aqueous solution Bowen[6] suggests $ClO + H_2O \longrightarrow H_2ClO_2$ and $ClO + H_2ClO_2 \longrightarrow HClO_3 + HCl$. The absence of an appreciable test for Cl^- together with tests for ClO^- and the quantum yield of 3 speak against the occurrence of these reactions in our case unless ClO first takes part in some chain reaction. The bromine sensitized reaction with wet gases appears to follow the same course as the direct reaction. With a sufficiently large quantum one could postulate that the activated bromine molecule transfers its energy by collision to a chlorine dioxide molecule which then dissociates. The energy at 5460 Å. is, however, far too small for this (54 k. cal.). The following is therefore suggested, parallel to the suggestion of Finkelnburg and Schumacher for the band region

$$\begin{aligned} Br_2 + h\nu &\longrightarrow Br_2' \\ Br_2' + ClO_2 &\longrightarrow ClO_2' + Br_2 \\ ClO_2' + ClO_2 &\longrightarrow ClO_3 + ClO \qquad \text{(A)} \end{aligned}$$

and then as before. This mechanism gives the same quantum yield and products as in the direct photolysis, in agreement with the experimental data. The assumptions underlying this mechanism are interesting. First of all, the exchange of energy between Br_2 and chlorine dioxide must be quite specific[23] and take place at almost every collision, while the activated bromine molecule must not lose its energy to foreign molecules such as oxygen. Second, reaction (A) must take place before ClO_2' is deactivated. One might expect this reaction to take place in the thermal decomposition but Schumacher and Stieger[24] lean more to

$$ClO_2 \longrightarrow ClO + O \qquad \text{(B)}$$

taking place as a wall reaction.

If (A) takes place, as would appear probable, in the bromine sensitized reaction, it certainly requires far less energy than (B) and would probably have a much lower activation energy. The thermal reaction is very sensitive to change in temperature.

The question of the relation between activation energy and the energy which must be possessed by one of two colliding molecules before reaction takes place also comes in and unfortunately very little seems to be known about this, except that molecules can sometimes be excited by quanta far greater than the ordinary activation energy without any reaction taking place.

Experiments with Dry Gases.—In these experiments the cells were dried as thoroughly as possible by careful heating while passing a stream of dry air through them. Vacuum stopcocks moistened with phosphoric acid were used and phosphorus pentoxide drying tubes were connected to the entrance and exit of the cells. No difference in the results could be detected whether the cells were swept out with dried oxygen or air. The initial concentration of chlorine dioxide could be determined from the percentage absorption of 4360 Å. The gases in the light cell at the end of an experiment could be analyzed chemically by bubbling through potassium iodide solution. At 17° the behavior was much the same as in the preliminary experiments. On insolation the pressure decreased, at first rapidly and then slowly until the rate of change of pressure was zero. On continuing the insolation the pressure increased, the rate of increase of pressure finally becoming quite rapid until the whole of the chlorine dioxide had decomposed. It is thought that this increase in pressure is at least partly due to the photodecomposition of Cl_2O_6 deposited on the walls in the first part of the reaction.

The temperature of the thermostat was then raised to 31° and the experiments repeated. At this temperature, using concentrations of chlorine dioxide up to 8%, the dark reaction was negligible, the pressure changing less than 1 mm. in one hour. On insolating the gas there was an induction period lasting about six minutes during which time the pressure usually decreased slightly. After this the pressure increased rapidly and uniformly until the whole of the chlorine dioxide had decomposed. The gas remaining at the end of the experiment was chlorine, the amount corresponding approximately to its formation from chlorine dioxide according to the equa-

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(23) Franck, *Z. physik. Chem.*, **20B**, 460 (1933).

(24) Schumacher and Stieger, *ibid.*, **7B**, 363 (1930).

tion: $2ClO_2 \longrightarrow Cl_2 + 2O_2$. As the total increase in pressure was lower than the theoretical, soft glass cells were put into the apparatus which could be strongly heated with a free flame during the drying process. The photoreaction at 31° with these cells gave the theoretical increase in pressure and an amount of chlorine corresponding exactly with the above equation, *e. g.*, experiment 152. Change in pressure corresponds to the increase in volume of 4.38×10^{-5} mole. An analysis of gas showed 8.64×10^{-5} mole of chlorine formed. Using 3650 Å. and 3% chlorine dioxide, the rate of increase of pressure corresponds to a quantum yield of 12, indicating a chain reaction.

Cutting off the light before complete decomposition gave a comparatively small after effect, showing that the amount of Cl_2O_6 present at 31° is comparatively small. One or two experiments on intensity variation indicate that the reaction at 31° is probably of the $I^{1/2}$ type.

For the photoreaction with dry gases and 3650 Å. we have

$$ClO_2 + h\nu \longrightarrow ClO + O$$
$$O + ClO_2 + M \longrightarrow ClO_3 + M$$
$$2ClO_3 \longrightarrow Cl_2O_6$$
$$ClO + ClO \longrightarrow Cl_2 + O_2$$

There is also the possibility $ClO + ClO_2 \longrightarrow Cl_2O_3$.

At low temperatures Cl_2O_6 is comparatively stable and condenses out on the walls. This is the case at 17° and the reaction proceeds with a decrease in pressure; Cl_2O_6 is subsequently decomposed photochemically if insolation is continued or thermally if left in the dark. At higher temperatures the thermal decomposition of Cl_2O_6 is rapid, with the result that only a small concentration of Cl_2O_6 is built up: $Cl_2O_6 \longrightarrow Cl_2 + 3O_2$. Hence at 31° the reaction proceeds with an increase in pressure and the formation of $Cl_2 + O_2$. That the decomposition of Cl_2O_6 is very sensitive to temperature changes is confirmed in a recent note by Norrish.[25] According to Schumacher[26] $ClO + ClO \longrightarrow Cl_2 + O_2$ has a low activation energy and would therefore be expected to take place quite readily. The few quantitative experiments which have been done so far, indicate a chain reaction both at 17 and at 31° but a mechanism compatible with the data at hand is lacking. It is hoped to continue the work on this interesting problem.

Summary

By studying the photodecomposition of gaseous chlorine dioxide in the presence of moisture, troublesome dark reactions can be avoided.

It is found that in the presence of moisture one mole disappears from the gas phase for each mole of chlorine dioxide decomposed by light. For low concentrations of chlorine dioxide γ is independent of concentration and light intensity. γ is slightly greater than 3 for 3650 Å. and the ratio of quantum efficiencies at 4360 to 3650 Å. is 0.86:1.

The aqueous solution formed by the interaction of the products of photolysis with water has been analyzed and a mechanism advanced to account for the results in the presence of moisture.

The sensitized reaction in the presence of bromine and using 5460 Å. has also been studied and gives a quantum yield equal to that at 3650 Å. With dry gases the reaction is very sensitive to temperature changes. At 15° the main reaction is accompanied by a decrease in pressure and the formation of Cl_2O_6. At 30° the reaction takes place with an increase in pressure and the formation of chlorine and oxygen. The photolysis of dry chlorine dioxide is a chain reaction.

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[26] Hamann and Schumacher, *Z. physik. Chem.*, **17B**, 293 (1932).