159. *The Photodecomposition of Chlorine Dioxide Solutions.*

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THE photodecomposition of chlorine dioxide has been studied in the gaseous phase by Booth and Bowen (J., 1925, **127**, 510), and by Bodenstein, Harteck, and Padelt (*Z. anorg. Chem.*, 1925, **147**, 233), who showed that chlorine hexoxide is formed by the absorption of blue light. The spectrum of gaseous chlorine dioxide indicates that the decomposition $ClO_2 \longrightarrow ClO + O$ occurs by a "predissociation" mechanism at wave-lengths shorter than 3753 Å. (Finkelnburg and Schumacher, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 704; Urey and Johnston, *Physical Rev.*, 1931, **38**, 2131). Dissolved in carbon tetrachloride, chlorine dioxide decomposes with a quantum efficiency of about 1 at 4450 Å. (Bowen, J., 1923, **123**, 1199) and of 2 at 4150 Å. (Nagai and Goodeve, *Trans. Faraday Soc.*, 1931, **27**, 508). The reason for this difference is made clear in this paper. In aqueous solution the photodecomposition of chlorine dioxide is complicated by reactions with the solvent. Popper (*Annalen*, 1885, **227**, 161; **231**, 137), from experiments in sunlight, proposed the mechanism:

$$18ClO_2 + 9H_2O \longrightarrow 13HClO_3 + 5HCl + 3O_2$$

The work described below shows that this equation does not represent the reaction.

EXPERIMENTAL.

Chlorine dioxide, prepared from oxalic acid and potassium chlorate by the method of Bray (*Z. physikal. Chem.*, 1906, **54**, 569, 731), was passed into water or purified, dried carbon tetrachloride. At concentrations of solute less than about 2×10^{-5} g.-mol. per c.c., the solutions changed only very slowly in concentration in the dark if the bottles containing them were nearly filled, and the loss of gas on handling with pipettes was not so great as to be serious. The solutions were exposed in stoppered silica cells with transparent plane ends to the light from a mercury lamp. As the solutions were liable to lose gas during the decomposition, the time of exposure was minimised by condensing the light from the lamp with a liquid condenser which also acted as a filter. For the mercury lines 4360, 4050, and 3665 Å., this consisted of a double-walled spherical glass flask of 12·5 cm. outside diameter and 10·5 inside diameter (an unsilvered and unevacuated Dewar vessel) containing water in the inner vessel and a solution of cuprammonium ion (400 c.c. of 5% $CuSO_4,5H_2O$; 300 c.c. of ammonium hydroxide solution, *d* 0·880; 300 c.c. of water) in the space between the double walls. Such a condenser-filter permits of internal cooling if necessary and presents roughly a constant thickness of filter solution to the light passing through it. This solution transmitted only the above three mercury lines, which were separated by the use of the following additional filters: 3665 Å., Chance's black "ultra-violet" glass; 4050 Å., 1 cm. of 0·05*N*-iodine in carbon tetrachloride + Noviol O glass; 4360 Å., Noviol A glass. The region 3160—2700 Å. (average wave-length 3000 Å.) was obtained by the use of two quartz flasks placed one behind the other and acting as condensers, each 10 cm. in diameter and filled with a solution of pure nickel chloride (140 g. of $NiCl_2,6H_2O$ + 60 c.c. of HCl, *d* 1·19, in 2 litres). Infra-red radiation from the lamp housing was suitably screened off. The amounts of energy in the radiation employed and the light absorptions, which were total in all the experiments, were measured with a Moll surface thermopile and galvanometer, calibrated against a Hefner lamp (Gerlach, *Physikal. Z.*, 1913, **14**, 577). For the region 3160—2700 Å., both the thermopile and a special spectroscope, fitted with a sodium photoelectric cell and arranged to integrate the light received and record directly the number of quanta received at any wave-length, were used (Bowen and Tietz, J., 1930, 234). This instrument had been constructed and calibrated by Mr. J. H. Joffree.

Carbon Tetrachloride Solutions.—The solutions were analysed for chlorine dioxide and chlorine by the method described by Bowen (*loc. cit.*; Bray, *loc. cit.*), involving the liberation of iodine from neutral and acid potassium iodide solutions. The results obtained were as follows :

Calibration of thermopile–galvanometer combination :

Hefner lamp at 50 cm. distance ; receiving surface at thermopile = 2·0 sq. cm.

Galvanometer deflexion (mean) 3·0 divisions.

1 Division of galvanometer $= 60{\cdot}3 \times 10^{-6}$ cal. per sec.

TABLE I.

Wave-length, Å.	Conc. ClO_2, g.-mols./c.c. $\times 10^6$.	ClO_2 decomp., g.-mols./sec. $\times 10^9$.	Galvano-meter reading.	G.-mol. quanta per sec. $\times 10^9$.	Quantum efficiency.
4360	9·6	9·17	9·8	9·0	1·02
	8·5	9·6	9·8	9·0	1·07
	9·6	8·3	9·8	9·0	0·92
4050	9·5	7·5	4·0	3·4	2·2
	9·4	7·5	4·0	3·4	2·2
3665	10·0	40·0	23·0	18·0	2·2
	9·3	40·0	23·0	18·0	2·2
3000	8·5	25·8		12·5	2·06
	8·5	26·3		12·5	2·1

In the last two experiments the energy was measured with the special ultra-violet light integrating instrument.

Aqueous Solutions.—In Table II are results which show that the rate of photodecomposition is proportional to the light intensity. The amount of decomposition was estimated as in the previous section.

TABLE II.

Relative amount of decomposition ($\lambda = 3665$ Å.).

	Light intensity.		
Time, mins.	33.	47.	100.
5	6·5	9·0	20
10	13	18·5	40
Ratio, intensity/rate	2·54	2·53	2·50

In aqueous solution, for the investigation of the mechanism of decomposition, the concentrations of the following substances have to be determined : ClO_2, Cl_2, ClO_3', Cl', ClO_2', and ClO_4'. All measurements were made on decompositions of less than 20% of the total. The first two substances were estimated by drawing air through the solution and absorbing the chlorine dioxide and chlorine in potassium iodide solution, the iodine liberated from the neutral and then from the acidified solution being titrated. In the solution from which the volatile gases had been removed, the chloride ion was estimated by the Volhard method, and the chlorate (+ chlorite) ion by the same method after reduction with titanous sulphate solution. As a check on this method of estimation, in some experiments the chlorate ion was determined colorimetrically with a solution of aniline hydrochloride (Yoe, "Photometric Chemical Analysis," New York, 1928, p. 162). The chlorite ion was estimated by titration of the iodine liberated from an acid potassium iodide solution, and the perchlorate ion by the colorimetric method of Monnier (*Arch. Sci. phys. nat.*, 1916, **42**, 210), a solution of methylene-blue being used. The accuracy of all the methods was controlled by the use of standard solutions of all the ions concerned, and by the check afforded by the constancy of the quantity

$$[ClO_2] + 2[Cl_2] + [ClO_3'] + [Cl'] + [ClO_2'] + [ClO_4'] = K,$$

a diminution of which would indicate a loss of chlorine in some form. The amount of perchlorate formed was extremely small, less than 1% of the total decomposition, and attention was therefore confined to the other products.

In Table III are shown collected results on the proportions of the decomposition products. All concentrations are in g.-mols × 10^{-6} per c.c.

TABLE III.

$\lambda = 3665$ Å.

Time, mins.		$[ClO_2]$.	$2[Cl_2]$.	$[ClO_3']$.	$[Cl']$.	$[ClO_2']$.	*K*.
		$[ClO_3']$ estimated photometrically.					
0		16·82	0·25	0·67	0·176	0·22	18·136
	diff.	0·76	0·06	0·30	0·304	0·04	
15		16·06	0·31	0·97	0·48	0·26	18·08
	diff.	0·73	0·05	0·33	0·32	0·04	
30		15·33	0·36	1·30	0·80	0·30	18·09
		$[ClO_3']$ estimated by titration.					
0		6·35	0·025	0·56	0·10	0·030	7·065
	diff.	0·75	0·049	0·34	0·32	0·033	
2·5		5·60	0·074	0·90	0·42	0·063	7·057
	diff.	0·71	0·017	0·33	0·34	0·037	
5·0		4·89	0·91	1·23	0·76	0·10	7·071
0		11·80	0·09	0·208	0·04	0·016	12·154
	diff.	0·80	0·06	0·382	0·34	0·015	
3		11·00	0·15	0·59	0·38	0·031	12·151
	diff.	0·77	−0·05	0·39	0·36	0·024	
6		10·27	0·10	0·98	0·74	0·055	12·145

The above results are typical of other series made at 3665 Å. and at 4360 Å. The proportions of the products were found to be independent of the wave-length. In Fig. 1 the last series of Table III is shown graphically.

Table IV contains measurements of the quantum efficiency of decomposition in aqueous solutions at different wave-lengths, the method of following the total change being as for the solutions in carbon tetrachloride.

Fig. 1.

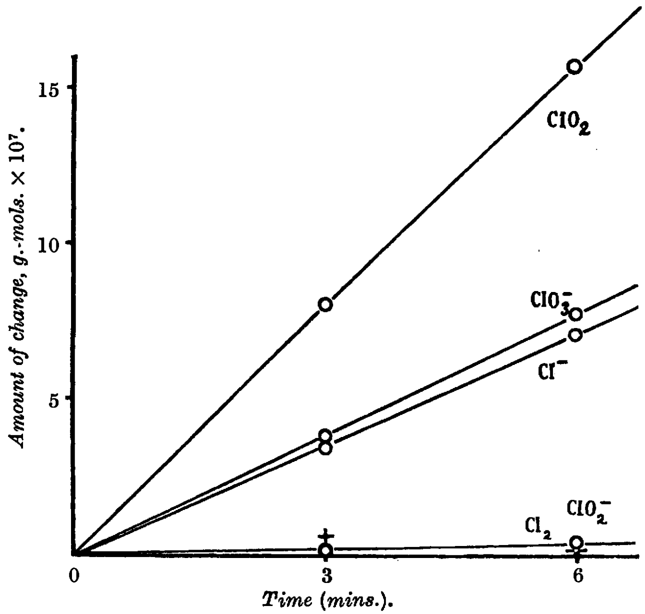


TABLE IV.

Wave-length, Å.	Conc. of ClO_2, g.-mols./c.c. × 10^6.	ClO_2 decomp. per sec., g.-mols. × 10^{-9}.	Galvano-meter reading.	G.-mol. quanta per sec. × 10^9.	Quantum efficiency.
4360	8·7	1·53	9·8	9·0	0·17
	13·7	2·04	9·8	9·0	0·23
	13·7	2·00	9·8	9·0	0·22
4050	8·7	1·70	4·0	3·4	0·50
	13·7	1·73	4·0	3·4	0·51
3665	8·7	12·8	22·0	17·1	0·75
	13·6	12·8	22·0	17·1	0·75
	13·6	13·5	22·0	17·1	0·79
3000	13·7	16·35	26·0	16·4	1·0
	13·7	12·3		12·5	1·0

The last result in the above table was obtained by the use of the instrument for integrating the ultra-violet light received.

Discussion.

The two significant results from the above measurements on aqueous solutions of chlorine dioxide are that the main products of photochemical decomposition are chloric acid and hydrochloric acid in equimolecular proportion, and that the quantum efficiency rises from 0·2 at 4360 Å. to 1·0 at 3000 Å. These facts can be explained by making use of the observation that chlorine dioxide in the gaseous state exhibits the phenomenon of predissociation at 3753 Å. (Finkelnburg and Schumacher, *loc. cit.*). The primary process probably is therefore

$$ClO_2 + h\nu \longrightarrow ClO_2^{\times} \longrightarrow ClO + O$$

In contrast with the behaviour observed with chlorine dioxide in the gaseous phase or in solution in carbon tetrachloride, the ClO molecule apparently does not attack other ClO_2 molecules. This is probably because it combines with water to give an acid :

$$ClO + H_2O \longrightarrow H_2ClO_2.$$

If this compound be assumed to react with more ClO,

$$H_2ClO_2 + ClO \longrightarrow HClO_3 + HCl,$$

the nature and proportion of the products are explained.

In carbon tetrachloride solution the limiting quantum efficiency is about 2. The mechanism is probably

$$ClO_2 + h\nu \longrightarrow ClO_2^{\times} \longrightarrow ClO + O$$

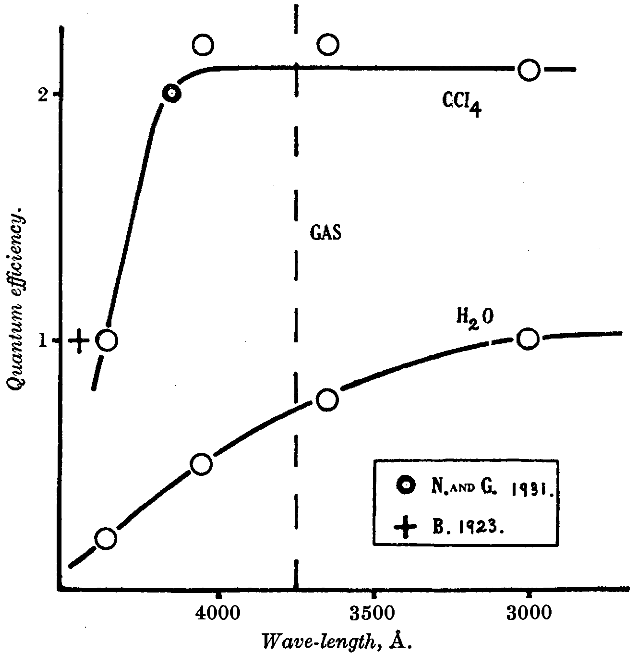
followed by

$$ClO + ClO_2 \longrightarrow \ ? \longrightarrow Cl_2 + \tfrac{3}{2}O_2$$

The quantum efficiency of the gaseous decomposition is similar to that for the solution, but no hexoxide has been detected in the decomposition in solution (Bowen, *Trans. Faraday Soc.*, 1931, **27**, 513). Since the gaseous decomposition occurs readily below the spectroscopic predissociation limit, it seems likely that predissociation produces excited products which can be produced in the unexcited state below the limit by collision.

The influence of the solvent on the phenomenon of predissociation is interesting (Fig. 2). In this connexion the limiting value of the quantum efficiency is immaterial; the two important matters are the change in the position of the limit and its sharpness. In solution the chlorine dioxide molecule undergoes predissociation at lower energy values than in the gas owing to the altered energy relationships produced by change of environment. The lack of sharpness of the limit is a measure of the variable distorting influence of the solvent on different dissolved molecules; in the gas the theoretical curve should be as indicated by the broken line in Fig. 2. From Fig. 2 it can be seen that the cause of the apparent discrepancy between the results of Nagai and Goodeve and of Bowen for carbon tetrachloride solutions (*locc. cit.*) is the difference of wave-length used. The quantum efficiency falls off at wave-lengths well to the red end of the gaseous predissociation limit, though its change with wave-length is sharper than with water. Allmand ("Discussion on the Critical Increment of Homogeneous Reactions," 1931, 22) discusses two possible solvent effects on the quantum efficiencies of photo-reactions : the deactivating effect of the solvent through collisions, and "inner filter" action. The second type of process seems out of question in this case owing to the closeness of the extinction coefficients of chlorine dioxide in carbon tetrachloride and in aqueous solution, while with the first type it is difficult to explain the photo-reaction of the aqueous solutions at the longer wave-lengths. A more probable explanation seems to be that in a polar solvent such as water the dissolved molecules are distorted to varying degrees, so that at long wave-lengths a certain fraction are capable of dissociating, the fraction depending on the degree of distortion.

Fig. 2.



In the thermal decomposition of aqueous solutions of chlorine dioxide much more chlorate than chloride is formed (proportions about 4 : 1). The mechanism of the thermal decomposition must therefore be essentially of a different character, as would be expected since it must involve non-electronically excited molecules activated to high values of vibrational energy, while the photoprocess involves the production of electronically excited molecules.

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