

C.—*The Photodecomposition of Chlorine Water and of Aqueous Hypochlorous Acid Solutions. Part II.*

By ARTHUR JOHN ALLMAND, PERCY WALMSLEY CUNLIFFE,  
and ROBERT EDWIN WITTON MADDISON.

IN Part I of this investigation (J., 1925, 127, 822), we recorded our work on the factors affecting the proportions of the reaction products—oxygen and chloric acid. The present paper contains our results on the energetics of the reaction, and a suggested theory of the whole.

EXPERIMENTAL.

*Extinction Coefficients.*—These were determined by means of an ultra-violet spectrometer (Hilger), thermopile (Hilger), and galvanometer (Paschen), a quartz-mercury lamp being used as light source. The absorption cells were of the type already described (*loc. cit.*, p. 829), with crystal quartz ends. Two similar ones were employed, after being tested, when filled with distilled water, for equality of transmission over the wave-length range used.

One contained the solution under examination, the other distilled water; the ratio of the galvanometer deflexions therefore gave the fractional transmission of the solution. Cells of 5 and 0.5 cm. depth were used. No extraordinary accuracy is claimed for the results, in consequence of the difficulty experienced at that time in obtaining steady deflexions with the Paschen galvanometer at high sensitivity. Only those figures used in the subsequent calculations and discussion are therefore given. When values differed appreciably amongst themselves, those obtained from solutions with very low transmissions have been omitted. The units used are the mol., litre, and cm., together with Briggsian logarithms. The figures in the last two lines of the table we owe to Mr. H. J. Taylor.

TABLE I.

Solution.	Molecular extinction coefficient ( $k$ ).		
	365 $\mu\mu$ .	405 $\mu\mu$ .	436 $\mu\mu$ .
0.0145M-Cl <sub>2</sub> .....	9.25	—	0.56
0.0375M-Cl <sub>2</sub> .....	14.7	2.12	0.64
0.043M-Cl <sub>2</sub> .....	—	2.43	0.74
0.0645M-Cl <sub>2</sub> + 0.01N-HCl .....	—	2.99	0.96
0.0115M-Cl <sub>2</sub> + 0.5N-HCl .....	—	7.51	2.7
0.045M-Cl <sub>2</sub> + 0.5N-HCl .....	—	3.85	1.38
0.051M-Cl <sub>2</sub> + 0.01N-KCl .....	—	2.9	1.16
0.045M-Cl <sub>2</sub> + 0.5N-KCl .....	—	5.1	2.1
0.0495M-Cl <sub>2</sub> + 0.01N-H <sub>2</sub> SO <sub>4</sub> .....	—	2.6	0.84
0.045M-Cl <sub>2</sub> + 0.5N-H <sub>2</sub> SO <sub>4</sub> .....	—	3.4	1.2
0.054M-Cl <sub>2</sub> + 0.01N-Na <sub>2</sub> SO <sub>4</sub> .....	—	2.3	0.74
0.047M-Cl <sub>2</sub> + 0.5N-Na <sub>2</sub> SO <sub>4</sub> .....	—	2.0	0.75 ?
0.049M-Cl <sub>2</sub> + Sat. Na <sub>2</sub> SO <sub>4</sub> .....	5.6	1.16	0.46
0.049—0.9M-HClO .....	1.2	0.19	0.13
0.045M-HClO + 0.5M-Na <sub>2</sub> HPO <sub>4</sub> ...	5	0.61	0.22 ?
0.024M-HClO + 0.125M-Na <sub>2</sub> HPO <sub>4</sub>	4.16	0.60	0.40
0.040M-HClO + 0.125M-Na <sub>2</sub> HPO <sub>4</sub>	3.59	0.43	0.37

In addition,  $k_{313}$  for 0.49—0.9M-HClO and for 0.0375M-Cl<sub>2</sub> were found to be respectively 18.2 and about 47.

Certain points in the table call for comment. In chlorine water, free from any addition, the values of  $k$  increase with concentration. The addition of hydrochloric acid increases  $k$ , and the more so the greater the ratio  $[HCl]/[Cl_2]$ . On the other hand, addition of sodium sulphate decreases the extinction. The last two effects are both visible to the eye. In all solutions containing chlorine,  $k_{405}/k_{436}$  is near 3. Solutions of hypochlorous acid have smaller  $k$  values than those containing chlorine, and  $k_{405}$  and  $k_{436}$  are nearer one another. The addition of disodium hydrogen phosphate increases the extinction. In all solutions examined, whether of chlorine or hypochlorous acid, the ratio  $k_{365}/k_{405}$  is of the order 5—9. We regard the effect on  $k$  of the addition of sodium phosphate to hypochlorous acid as independent evidence that, in such solutions, the reaction  $HClO + HPO_4'' \rightarrow H_2PO_4' + ClO'$

takes place to an appreciable extent (*loc. cit.*, p. 825). The increase in the extinction with increasing ratio  $[\text{Na}_2\text{HPO}_4]/[\text{HClO}]$  would indicate  $k$  values for the hypochlorite ion greater than those for hypochlorous acid, and preliminary measurements indicate that  $k_{365}$  for this ion is about 9. The rise in extinction for chlorine solutions with increasing concentration is readily explicable by the changing degree of hydrolysis, the  $k$  values for chlorine being greater than those of hypochlorous acid. Assuming  $K = [\text{H}^+][\text{Cl}^-][\text{HClO}]/[\text{Cl}_2]$  to be  $3.8 \times 10^{-4}$  for our solutions (value interpolated from table on p. 508 of Lewis and Randall's "Thermodynamics"), we calculate the concentrations in the chlorine-water solutions given at the head of our table to be as follows :

- (a)  $0.0035M\text{-Cl}_2 + 0.011M\text{-HClO}$  (total  $0.0145M$ ).  
 (b)  $0.0185M\text{-Cl}_2 + 0.019M\text{-HClO}$  (total  $0.0375M$ ).  
 (c)  $0.023M\text{-Cl}_2 + 0.02M\text{-HClO}$  (total  $0.043M$ ).

Combining these data by means of the equation  $\log I_0/I = d(C_{\text{HClO}} \cdot k_{\text{HClO}} + C_{\text{Cl}_2} \cdot k_{\text{Cl}_2})$ , where  $d$  = the depth of the solution, with the measured transmissions of the solutions and the  $k_{\text{HClO}}$  values given above, we have calculated the values for  $k_{\text{Cl}_2}$  given in the second column of Table II. The remaining columns contain

TABLE II.

Wave-length.	In chlorine water.	$k_{\text{Cl}_2}$ .		
		For gas.		
		(v. H. and S.).	(C. and R.).	(recent figs.).
313 $\mu\mu$	(77)	53	33.6	—
365	34; 29	27	20.6	24.7
405	4.4; 4.1; 3.2	4	4.6	4.4
436	0.96; 1.29; 1.94	2	3.7	1.9

$k$  values calculated for chlorine gas from (i) the accurate work of von Halban and Siedentopf (*Z. physikal. Chem.*, 1922, **103**, 71); (ii) some rough measurements made by one of us (P. W. C.) in conjunction with Dr. Reeve; (iii) more recent data obtained in this laboratory. The general nature of the agreement between the figures for dissolved and gaseous chlorine is of distinct interest.

*Measurements of Quantum Efficiency.*—A number of experiments were carried out, using one or another of several quartz-mercury lamps arranged to give "parallel" beams of known energy distribution and total energy flux, and filters intended to pass monochromatic radiation of wave-length 365  $\mu\mu$ .

The energy absorbed in the reaction cell was computed by means of the extinction coefficients given above, and the quantum efficiency

calculated from the degree of decomposition. The exact experimental procedure used was varied during the course of the work, but in outline the method was as follows. The mercury lamp was situated immediately behind a metal screen in which was cut a circular aperture of 1—2 cm. diameter. This diaphragm was placed at the focus of a quartz lens (diameter, 8 cm.; focal length, 10—11 cm.), and the resultant approximately parallel beam passed through a water cell (for absorbing heat rays) and a cell containing the filter solution, before falling on the reaction vessel. The cells used were all of the type already described (*loc. cit.*, p. 829), their ends consisting of crystal quartz plates. The reaction vessel was 5 cm. deep in every case. Any chlorine carried forward by the evolved oxygen was, as before, trapped in a potassium iodide solution, and the necessary correction applied.

The intensities of the beams used were by no means uniform over their whole cross-section. In order to obtain the total incident energy flux on the surface of the reaction vessel, the filter cell was filled with distilled water, and the thermopile-galvanometer deflexion read with the thermopile placed in a number of representative positions in the path of the beam, and in the plane which was later occupied during the actual measurements by the front of the reaction vessel. The thermopile-galvanometer combination (in some experiments a Coblenz pile and Broca galvanometer, in others a Moll pile and Gambrell galvanometer) had previously been calibrated by means of a standard Hefner lamp. The average *H.K.* intensity of the unfiltered beam was thus obtained, and this, when combined with its measured energy-distribution, determined as described elsewhere (*J. Physical Chem.*, 1925, 29, 713), with the spectral transmission of the filter used, with the insolated area of the solution under investigation, and corrected for reflexion at the front surface of the reaction cell, made it possible to calculate completely the intensity and the nature of the radiant energy flux entering the solution. The extinction coefficients of the different solutions were estimated for the beginning and end of the reaction by interpolation between the experimental figures already given, taking account of the change due to the production of hydrogen chloride by insolation. From these figures the initial and final absorptions were deduced, and the arithmetic mean was taken for the calculation of  $\gamma$ . In the case of chlorine in lithium chloride, no exact data were available, but both the appearance and photographs taken with a Judd Lewis photometer and quartz spectrograph indicated very high absorption.

Under the above experimental conditions, the lamps used gave beams of the following intensity and energy distribution.

TABLE III.

Lamp No.	Total intensity.	Fraction of total intensity.			
		313 $\mu\mu$ .	365 $\mu\mu$ .	405 $\mu\mu$ .	436 $\mu\mu$ .
1	25.9 H.K.	0.086	0.188	0.070	0.129
2	27.87	0.069	0.180	0.078	0.151
3	39.72	0.078	0.190	0.068	0.152

The filter employed for Expt. 1, Table V, consisted of 1 cm. of 0.03125% Diamond Fuchsine (Cassella). In Expts. 2 and 3, 5 mm. of 0.0625% Acid Fuchsine (B. D. H.) were used, and in Expts. 4—8, 5 mm. of a 0.075% solution of the same substance. This change from the Cassella to the B. D. H. dyestuff proved to be unfortunate, as subsequent measurements showed the latter to absorb diffusely, and to pass high proportions of the violet and blue lines. Although this unfavourable circumstance is partly corrected by the higher proportion of the 365  $\mu\mu$  component in the unfiltered beam, and by its greater absorption in the solutions used, the result is that the  $\gamma$  values obtained in these experiments are only average figures, corresponding to a mean wavelength which lies between 365—405  $\mu\mu$  and varies from experiment to experiment. The transmissions of the actual solutions (determined by the Hilger thermopile and Paschen galvanometer) are given in Table IV.

TABLE IV.

Expt.	Filter.	Fractional transmission of			
		313 $\mu\mu$ .	365 $\mu\mu$ .	405 $\mu\mu$ .	436 $\mu\mu$ .
1	1 cm. 0.03125% Diamond Fuchsine.	0.013	0.365	0.013	Nil.
2, 3	0.5 cm. 0.0625% Acid Fuchsine.	Nil.	0.234	0.333	0.115
4—8	0.5 cm. 0.075% Acid Fuchsine.	Nil.	0.175	0.267	0.075

The calculation is given in full for the simplest case only (Expt. 1) where the small amounts of absorbed energy belonging to lines other than 365  $\mu\mu$  were neglected (error involved about 2%).

Lamp used : No. 1. Fraction of 365  $\mu\mu$  energy absorbed : 1.0. Duration of expt. : 41.5 hours. Average surface of insulated solution : 31.6 cm.<sup>2</sup>.

Energy in unfiltered beam incident on cell =  $a = 25.9$  H.K.

Ergs in unfiltered beam incident on cell =  $a = 25.9 \times 945/\text{cm.}^2/\text{sec.}$

Ergs of 365  $\mu\mu$  in unfiltered beam incident on cell =  $b = a \times 0.188/\text{cm.}^2/\text{sec.}$

Ergs of 365  $\mu\mu$  in filtered beam incident on cell =  $c = b \times 0.365/\text{cm.}^2/\text{sec.}$

Ergs of 365  $\mu\mu$  in filtered beam incident on solution =  $d = c \times 0.95/\text{cm.}^2/\text{sec.}$

Ergs of 365  $\mu\mu$  in filtered beam incident on solution =  $e = d \times 31.6/\text{sec.}$

Ergs of 365  $\mu\mu$  incident on and absorbed by solution in course of run =  $f = e \times 41.5 \times 3600$ .

Quanta of 365  $\mu\mu$  incident on and absorbed by solution in course of run =  $g = f \div (6.57 \times 822 \times 10^{-16})$ .

$$= 1.40 \times 10^{21}.$$

Molecules of chlorine decomposed in course of run =  $0.00366 \times 6.06 \times 10^{23}$ .

$$= 2.22 \times 10^{21}.$$

Hence  $\gamma = 2.22/1.40 = 1.59$ .

TABLE V.

No. of expt.	Lamp. used.	Initial conc. of $\text{Cl}_2(\text{HClO})$ , $M.$	Duration of insol. ation (hrs.).	Loss in titre by decom- position, $M.$	$\text{HClO}_3$ yield (%).	Initial fraction of incident energy absorbed.		Final fraction of incident energy absorbed.		Absorbed quanta ( $\times 10^{-20}$ ).		Molecules decom- posed ( $\times 10^{-20}$ ).	$\gamma$ .			
						365 $\mu\mu.$	405 $\mu\mu.$	436 $\mu\mu.$	365 $\mu\mu.$	405 $\mu\mu.$	436 $\mu\mu.$			365 $\mu\mu.$	405 $\mu\mu.$	436 $\mu\mu.$
1	1	$\text{Cl}_2$ water. 0.0503	41.5	0.02305	46	1.0	—	As at start.	14.0	—	—	22.2	1.59			
2	2	"	23.0	0.01515	62	0.977	0.466	0.172	0.984	0.499	0.198	7.01	2.37	0.65	20.35	2.03
3	2	"	30.0	0.02535	61	1.0	0.807	0.386	1.0	0.808	0.411	9.33	5.18	1.84	34.0	2.08
4	3	$\text{Cl}_2$ water + 0.004N. HCl.	27.0	0.0052	56	1.0	0.741	0.373	1.0	0.749	0.386	9.48	4.30	1.54	6.96	0.45
5	3	$\text{Cl}_2$ water + 0.6N. HCl.	48.25	0.0012	—	1.0	0.88	0.535	As at start.	16.93	9.07	3.87	1.61	0.054		
6	3	$\text{Cl}_2$ water + 0.5N. LiCl.	46	0.00615	39	1.0	1.0	1.0	As at start.	16.15	9.83	6.90	8.24	0.25		
7	3	$\text{Cl}_2$ water + 0.33M. $\text{Na}_2\text{SO}_4$ .	26.75	0.0040	—	0.967	0.495	0.204	As at start.	9.08	4.30	1.54	5.36	0.42		
8	3	HClO + 0.125M. $\text{Na}_2\text{HPO}_4$ .	69	0.0300	86	0.872	0.226	0.204	0.695	0.156	0.112	19.0	2.8	1.6	40.2	1.72

Table V contains the results of our measurements, for which the accuracy claimed does not exceed 10—15%.

It will be noticed that  $\gamma$  for decomposition of chlorine water is much lowered by the addition either of hydrochloric acid or of the two neutral salts tested, results predicted by the observations of Bunsen and Roscoe (*Pogg. Ann.*, 1855, **96**, 373), Milbauer (*Z. physikal. Chem.*, 1914, **86**, 564), Benrath and Schaffganz (*ibid.*, 1922, **103**, 139), and others. The effect of the very small initial addition of hydrochloric acid in Expt. 4 is striking, and probably connected with the decreased yield of chloric acid remarked on in Part I of this work. Whilst, however, the addition of a chloride, besides lowering  $\gamma$ , decreases the yield of chloric acid and increases both extinction and the partial pressure of chlorine above the liquid, in the case of sodium sulphate the decreased quantum efficiency is accompanied by a decreased extinction and lowered partial pressure of chlorine, whilst the yield of chloric acid is practically unaffected (Part I, p. 834). Hypochlorous acid is seen to be, at all events, not more photosensitive than chlorine water under the conditions prevailing, whereas the reverse behaviour was originally anticipated (Part I, pp. 823, 824). It will be noted that  $\gamma$  in Expt. 1 is considerably lower than in Expts. 2 and 3. We think this may be connected with the low percentage of chloric acid found in the products, considerably the lowest of any ever obtained by us with chlorine water, and confirmed by several titrations during the course of the experiment. Qualitatively, it would suggest the presence of hydrochloric acid in the original chlorine water, perhaps due to insufficient washing of the gas.

*Quantum Efficiency and Wave-Length.*—Three experiments were carried out in which chlorine water was exposed under comparable conditions to monochromatic light of wave-lengths 313  $\mu\mu$ , 365  $\mu\mu$ , and 436  $\mu\mu$ , of known relative, but not absolute, intensity. The filters employed were, respectively:

(a) 5 mm. of 0.0125% Diamond Fuchsine + 5 mm. of 0.0125% Auramine O.

(b) 1 cm. of 0.03125% Diamond Fuchsine.

(c) 5 mm. of 0.0857% Victoria Blue + 5 mm. of 4% quinine sulphate.

The results are in Table VI.

The figures stand in the usual order of increasing  $\gamma$  with increasing frequency, but we lay no stress on this, in view of the probable experimental error. The results might equally well be interpreted as indicating that  $\gamma$  is independent of  $\lambda$ .

TABLE VI.

Wave-length.	Relative incident intensity.	Average fraction absorbed.	Relative absorption rate (watts).	Initial titre. ( <i>M</i> ).	Loss in titre during 30 hrs.	Relative quanta absorbed.	Relative $\gamma$ ( $\gamma_{365} = 1$ ).
313 $\mu\mu$	2.0	1.0	2.0	0.0445	0.0074	2.09	1.02
365	6.36	1.0	6.36	0.0515	0.0268	7.75	1.00
436	8.40	0.366	3.07	0.0497	0.0130	4.46	0.84

*Discussion.*

Any proposed reaction mechanism must account for the experimental facts described in this and in the preceding paper, of which the following are the most important.

(i) The yields of chloric acid during the photolysis of hypochlorous acid and of chlorine water are nearly the same; they are considerably increased by adding sodium phosphate, less so by lithium sulphate, slightly raised by sodium sulphate, and slightly diminished by sulphuric acid; they are depressed by adding strongly dissociated chlorides, which are effective in the order  $\text{HCl} > \text{KCl} > \text{LiCl}$ .

(ii) The same chlorides increase the extinction coefficients of chlorine water, the order of effectiveness now being  $\text{LiCl} > \text{KCl} > \text{HCl}$ . At the same time the partial pressure of the chlorine rises, as shown by the amounts volatilised during the insolutions.

(iii) Lithium and sodium sulphates decrease both volatility of chlorine and extinction coefficient; the addition of sulphuric acid hardly affects the former, whilst slightly increasing *k*.

(iv) The three electrolytes so far tested (hydrogen chloride, lithium chloride, and sodium sulphate) all decrease  $\gamma_{365}$  for decomposition of chlorine water, the first being by far the most effective in this respect.  $\gamma_{365}$  for the photolysis of a hypochlorous acid solution containing sodium phosphate is lower than that for chlorine water.

(v) The actual value of  $\gamma_{365}$  for pure chlorine water under the conditions of experiment is about 2, and it varies but little with frequency between the limits 313—436  $\mu\mu$ .

(vi) There is obviously a close similarity between the two photolyses.

Many possible reaction mechanisms have been considered and dismissed as involving unlikely assumptions or as leading to conclusions inconsistent with the experimental results. Thus, for hypochlorous acid photolysis, combinations of the following were considered.



	Mechanism.	$\gamma$ .	Yield of chloric acid (%).
(a)	$\begin{cases} \text{HClO} + h\nu \longrightarrow \text{HCl} + \text{O}, \\ \text{HClO} + \text{O} \longrightarrow \text{HClO}_2, \\ \text{HClO}_2 + \text{HClO} \longrightarrow \text{HClO}_3 + \text{HCl}. \end{cases}$	3	100
(b)	$\begin{cases} 2\text{HClO} + 2h\nu \longrightarrow 2\text{HCl} + 2\text{O}, \\ 2\text{O} \longrightarrow \text{O}_2', \\ \text{O}_2' + \text{HClO} \longrightarrow \text{HClO}_3. \end{cases}$	1.5	100
(c)	$\begin{cases} 2\text{HClO} + 2h\nu \longrightarrow \text{HCl} + 2\text{O}, \\ \text{O} + \text{HClO} \longrightarrow \text{HClO}_2, \\ \text{O} + \text{HClO}_2 \longrightarrow \text{HClO}_3. \end{cases}$	1.5	100
(d)	$\begin{cases} 2\text{HClO} + 2h\nu \longrightarrow 2\text{HCl} + 2\text{O}, \\ 2\text{HClO} + 2\text{O} \longrightarrow 2\text{HClO}_2, \\ 2\text{HClO}_2 \longrightarrow \text{HClO}_3 + \text{HClO}. \end{cases}$	1.5	100
(e)	$\begin{cases} \text{HClO} + h\nu \longrightarrow \text{HCl} + \text{O}, \\ \text{O} + \text{HClO} \longrightarrow \text{HCl} + \text{O}_2. \end{cases}$	2	0
(f)	$\begin{cases} 2\text{HClO} + 2h\nu \longrightarrow 2\text{HCl} + 2\text{O}, \\ 2\text{O} \longrightarrow \text{O}_2. \end{cases}$	1	0

Similar schemes were considered for chlorine water, in which  $\text{Cl}_2 + \text{H}_2\text{O}$  took the place of  $\text{HClO}$ , as also mechanisms involving as primary reactions dissociation of the chlorine molecule, either directly or after collision between an activated and a normal molecule.

We have finally been led to suggest the following reaction mechanisms.

	For hypochlorous acid.	For chlorine water.
	$A \text{ HClO} + h\nu \longrightarrow \text{HCl} + \text{O},$	$\text{Cl}_2, \text{H}_2\text{O} + h\nu \longrightarrow 2\text{HCl} + \text{O},$
{	$B \frac{1}{2}(2\text{O} \longrightarrow \text{O}_2'),$	$\frac{1}{2}(2\text{O} \longrightarrow \text{O}_2'),$
	$C \text{ HClO} + \text{O} \longrightarrow \text{HCl} + \text{O}_2',$	$\text{Cl}_2, \text{H}_2\text{O} + \text{O} \longrightarrow 2\text{HCl} + \text{O}_2',$
{	$D \text{ HClO} + \text{O}_2' \longrightarrow \text{HClO}_3,$	$\text{Cl}_2, \text{H}_2\text{O} + \text{O}_2' \longrightarrow \text{HClO}_3 + \text{HCl},$
	$E \text{ O}_2' \longrightarrow \text{O}_2.$	$\text{O}_2' \longrightarrow \text{O}_2.$

By  $\text{Cl}_2, \text{H}_2\text{O}$  is meant, not necessarily a molecule of a "chemical" chlorine hydrate, but rather a grouping of molecules of these two substances in sufficiently close association to render possible the reactions ascribed to it.

The maximum attainable value of  $\gamma$  (processes  $A, C, D$ ) will be 3, with a 100% yield of chloric acid. Processes  $A, B, E$  [(f) above] will result in  $\gamma = 1$  and  $\text{HClO}_3 = 0\%$ ; processes  $A, B, D$  [(b) above] in  $\gamma = 1.5$  and  $\text{HClO}_3 = 100\%$ ; and processes  $A, C, E$  [(e) above] in  $\gamma = 2$  and  $\text{HClO}_3 = 0\%$ . Let  $a$  be the fraction of absorbed quanta resulting in the process  $A$ ,  $b$  and  $c$  the fractions of the total oxygen atoms produced by  $A$  reacting in accordance with  $B$  and  $C$ , respectively ( $b + c = 1$ ), and  $d$  and  $e$  the fractions of activated  $\text{O}_2'$  molecules reacting in  $D$  and  $E$ , respectively ( $d + e = 1$ ). Then it is clear that the observed quantum efficiency will be higher the greater  $a, c/b$ , and  $d/e$ , whilst the chloric acid yield will depend solely on  $d/e$ . The proposed mechanism thus allows of a very low  $\gamma$  value accompanying a 100% yield of chloric acid,

but, on the other hand, excludes the possibility of  $\gamma$  exceeding 2 unless chloric acid is produced. It also brings out clearly the essential similarity between the hypochlorous acid and chlorine-water photolyses.

Further consideration of these reaction stages suggests the probability that  $b$  is negligible compared with  $c$ , except in very dilute solutions (see later). We therefore put  $b = 0$ ,  $c = 1$ , for purposes of calculation, and thus arrive at the simple relations

$$\gamma = 2a + ad = a(2 + d)$$

$$\text{HClO}_3 \text{ yield (\%)} = 100 \times 3ad / (2a + ad) = 100 \times 3d / (2 + d)$$

which, given  $\gamma$  and the chloric acid yield, allow us to calculate both  $a$  and  $d$ —or  $d$  alone, if only the chloric acid yield is available. Table VII contains, for the experiments of Table V, the values of  $a$  and  $d$ , whilst Table VIII contains  $d$  values for different solutions, calculated from the chloric acid yields given in Part I.

TABLE VII.

Expt.	1.	2.	3.	4.	5.	6.	7.	8.
$a$ .....	0.67	0.80	0.83	0.18	0.026	0.11	0.17	0.61
$d$ .....	0.37	0.53	0.52	0.47	0.1	0.3	0.53	0.81

TABLE VIII.

Solution.	HClO.	HClO + M/8- Na <sub>2</sub> HPO <sub>4</sub> .	HClO + M/4- Na <sub>2</sub> HPO <sub>4</sub> .	Cl <sub>2</sub> water.	Cl <sub>2</sub> water + 2N-Li <sub>2</sub> SO <sub>4</sub> .	
$d$ .	0.52	0.81	0.73	0.52	0.65	
Solution.	Cl <sub>2</sub> water +N/4- Li <sub>2</sub> SO <sub>4</sub> .	Cl <sub>2</sub> water +Na <sub>2</sub> SO <sub>4</sub> .	Cl <sub>2</sub> water +N/10- H <sub>2</sub> SO <sub>4</sub> .	Cl <sub>2</sub> water +N/2- H <sub>2</sub> SO <sub>4</sub> .	Cl <sub>2</sub> water +N/10- KCl.	
$d$ .	0.54	0.53	0.5	0.47	0.51	
Solution.	Cl <sub>2</sub> water +N/2- KCl.	Cl <sub>2</sub> water +N/2- LiCl.	Cl <sub>2</sub> water +N/250- HCl.	Cl <sub>2</sub> water +N/100- HCl.	Cl <sub>2</sub> water +N/10- HCl.	Cl <sub>2</sub> water +N/2- HCl.
$d$ .	0.22	0.3	0.47	0.46	0.22	0.1

*The d Coefficients.*—These express the fraction of O<sub>2</sub>' molecules which collide with HClO molecules or Cl<sub>2</sub>,H<sub>2</sub>O groupings and thereby produce a molecule of chloric acid;  $1 - d$  represents the fraction of such molecules which either undergo such a collision without result, or else become deactivated before collision. Clearly, if this mechanism holds good, the chloric acid yield would be expected eventually to diminish with fall of concentration, unless some kind of a compensating influence were active; and the shorter the average life of the activated molecule, the higher the concentration at which this effect would be anticipated. No definite sign of this falling off has so far been found in our experiments (*loc. cit.*, p. 833), which may indicate that the life of the O<sub>2</sub>' molecule under the conditions prevailing was, in general, long enough to ensure a normally effective collision before deactivation. In dilute solutions

of chlorine water, however, a compensating influence of the kind mentioned may be active, *viz.*, an increased proportion of hypochlorous acid molecules resulting from greater hydrolysis, for the high  $d$  values with solutions of hypochlorous acid containing sodium phosphate suggest that hypochlorous acid molecules are better acceptors for  $O_2'$  molecules than are the  $Cl_2, H_2O$  groupings under the experimental conditions. Indeed, the difference is probably greater than appears from the above figures, for, as has been seen, there is reason to suppose that a proportion of hypochlorite ions, increasing with concentration of sodium phosphate, is present in these solutions, and other measurements point to their being comparatively bad acceptors for  $O_2'$  molecules.

The effect of *sulphates* is interesting, and can be considered in conjunction with the concomitant changes in the degree of volatility of the chlorine and in the extinction. We suggest that addition of sulphuric acid slightly increases the free chlorine concentration (when added in small amounts, at all events, in accordance with the Jakowkin equilibrium). The observed results are consistent with this view and with our hypothesis on the relative efficiencies of the acceptors  $HClO$  and  $Cl_2, H_2O$ . In the case of lithium and sodium sulphates, we assume the reaction  $H^+ + SO_4'' \rightarrow HSO_4'$  to take place, a change probably responsible for the results of Thomas and Baldwin (*J. Amer. Chem. Soc.*, 1919, **41**, 1981) on the effect of the addition of sulphates on the hydrogen-ion concentration (activity) in 0.1*N*-hydrochloric acid. This would cause the displacement of the Jakowkin equilibrium in the direction of increasing chlorine hydrolysis and a greater hypochlorous acid concentration; this, in turn, would account for the changes in volatility of chlorine, extinction, and yield of chloric acid.

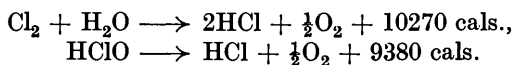
The influence of *chlorides* is more complex. From a consideration of the data, it would appear to be two-fold—a lowering of the  $d$  coefficients due to the chlorine ion, and an opposed effect, depending on the kation, running parallel with an increase in extinction and volatility (*i.e.*, chlorine activity), and increasing as we pass from hydrochloric acid through potassium chloride to lithium chloride (order of increasing "hydration"). More will not be suggested at this stage, as we think that our results with chlorine water in chloride solutions need further elucidation and confirmation from several points of view. In addition, the formation of chlorine ions during insolation is a complicating factor.

*The  $\alpha$  Coefficients.*—Those for chlorine water without any addition (Expts. 1—3) are seen to exceed that for hypochlorous acid in sodium phosphate solution (Expt. 8). In view of the fact that hydrochloric acid, which lowers these coefficients very considerably,

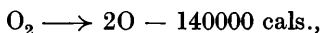
is produced during the reaction, it does not seem unreasonable to imagine that, if the effect due to this acid could be eliminated,  $a$  might be unity. It has already been mentioned that the nature of the results in Expt. 1 suggests that some acid was present from the commencement. Whether the lower value in Expt. 8 means that hypochlorous acid is primarily less photosensitive than chlorine water is doubtful. The presence of hypochlorite ions and also of the strong electrolyte sodium phosphate in the solution probably both play a part in lowering  $a$ . For we interpret the results of Expts. 3—7 in the sense that *strong electrolytes in general lower the efficiency of our primary photo-reaction resulting from quantum absorption*. Hydrochloric acid seems to be particularly effective, and 0.5*M*-lithium chloride more so than 0.33*M*-sodium sulphate. In this connexion, the marked retarding effect of chlorides, and particularly of hydrochloric acid, in photochemical reactions other than chlorine-water decomposition, is noteworthy. Examples are to be found in papers by Lemoine (*Ann. Chim.*, 1895, 6, 433), Hatt (*Z. physikal. Chem.*, 1918, 92, 513), Baur and Rebmann (*Helv. Chim. Acta*, 1922, 5, 221), and Benrath and Obladen (*Z. wiss. Phot.*, 1922, 22, 47, 65).

Finally, it may be remarked that the mechanism outlined above, if substantiated, will enable a clear distinction to be made (for the first time, as far as we are aware) between the *quantum efficiency* and the *quantum sensitivity* (respectively  $a$  and  $\gamma$  in this paper) as distinguished by Winther (*Trans. Faraday Soc.*, 1926, 21, 608). Until this is confirmed, we have preferred to term  $\gamma$  the *quantum efficiency*, as is usual.

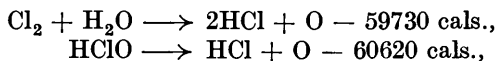
*Thermochemical Relations.*—For  $a$  to be unity, every absorbed quantum must cause reaction, which will probably only be the case if  $Nh\nu$  is appreciably greater than the energy absorption required by the primary reaction per mol. of hypochlorous acid or of  $\text{Cl}_2, \text{H}_2\text{O}$  ( $Q$ ). If they approach one another closely, then a value of  $a$  less than unity may be anticipated, although it is now generally agreed that  $Q$  may exceed  $Nh\nu$  and reaction still occur in the case of absorbing molecules of particularly high individual energy content. In the present case we have (Thomsen's "Thermochemische Untersuchungen," p. 185):



Assuming that

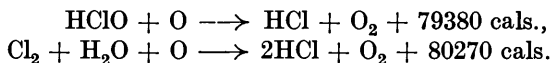


we get



these figures corresponding to  $\lambda = 475 \mu\mu$  and  $\lambda = 468 \mu\mu$  respectively. The longest wave-length used in our work was  $436 \mu\mu$ , corresponding to 65040 cal. Hence it would appear that, as far as the size of the absorbed quantum is concerned,  $a$  should be unity in all cases. It will be remembered that our values of  $\gamma$  only showed slight and doubtful variations with wave-length between the limits 313—436  $\mu\mu$ , which is in accordance with the above.

The  $C$  reactions are both strongly exothermic, apart from any excess energy derived from the primarily absorbed quantum which the oxygen atoms may carry. We have



Finally the  $D$  reactions, with *unactivated* oxygen, would both be somewhat endothermic :



but with the oxygen molecules carrying at any rate a proportion of the reaction energy liberated in  $C$ , their exothermic nature would appear highly probable.

*Order of Reaction.*—As long as the course of the reaction is represented by processes  $A$ ,  $C$ , and  $D$ , the order will be between 0 and 1, increasing as the solution becomes more dilute, or as we pass from light of strongly absorbed to light of weakly absorbed wave-lengths. If, however, the solution becomes so dilute that  $B$  becomes more important than  $C$ , then  $n$  will increase still further. For the extreme case ( $c$  negligible compared with  $b$ ), we have

$$\begin{aligned} (A) \quad & -d[\text{HClO}]/dt = +d[\text{O}]/dt = k_a I_0 \epsilon [\text{HClO}] \\ & (\epsilon \text{ is the molecular extinction coefficient of HClO}), \\ (B) \quad & -d[\text{O}]/dt = 2d[\text{O}_2']/dt = k_b [\text{O}]^2, \\ (D) \quad & -d[\text{O}_2']/dt = -d[\text{HClO}]/dt = k_d [\text{O}_2'] [\text{HClO}], \\ (E) \quad & -d[\text{O}_2']/dt = k_e [\text{O}_2']. \end{aligned}$$

Whence, for the complete reaction,

$$- \frac{d[\text{HClO}]}{dt} = k_a I_0 \epsilon [\text{HClO}] \left\{ 1 + \frac{k_d [\text{HClO}]}{2(k_e + k_d [\text{HClO}])} \right\}$$

which corresponds to an order greater than unity and increasing as  $[\text{HClO}]$  decreases. Any change in  $k_a$ ,  $\epsilon$ , etc., during insolation would of course complicate matters, *e.g.*, an increase in  $\epsilon$  would decrease, or a decrease in  $k_a$  would increase, the apparent order of the reaction.

Certain experiments carried out under uniform conditions of illumination from start to finish, with titrations made at intervals,

have allowed of a calculation of the *average apparent* order of the reaction by means of the equation

$$(1/C_1^{n-1} - 1/C_2^{n-1})/(1/C_2^{n-1} - 1/C_3^{n-1}) = (t_1 - t_2)/(t_2 - t_3),$$

where  $C_1, C_2, C_3$  represent concentrations at the times  $t_1, t_2, t_3$ . The results are in Table IX.

TABLE IX.

Expt.	Solution.	Light.	$t_3 - t_1$ (hours).	$C_1$ (normality).	$C_3$ (normality).	$n$ .
1	HClO.	Unfiltered.	4	0.114	0.070	0.25
—	"	"	4	0.091	0.052	0.6
2	Chlorine.	"	23.25	0.067	0.001	1.2
3	"	"	23.5	0.084	0.003	1.2
4	"	"	22.25	0.056	0.001	1.2
5	"	436 $\mu\mu$	36.25	0.099	0.069	1.0
6	"	365 $\mu\mu$	31	0.103	0.048	0.0

Whilst demonstrating the complexity of the photolysis, they are in general agreement with the above deductions. In (6), the absorption is complete throughout, and the rate of reaction very uniform, in spite of the 50% decrease in concentration and the gradually increasing acidity, which would be expected to lower the quantum efficiency. On the other hand, in (5), where, in spite of the partial decomposition, the absorption slightly increases during the experiment (increase in  $\epsilon$ ), and where  $n$  was found to be very close to unity, it would seem that either the concentration or, more probably, the acidity effect (decrease in  $k_a$ ) must be playing a compensating part. In (1) where absorption is only complete for the ultra-violet components of the light,  $n$  increases during the course of the reaction, although the absorption of visible light is also increasing (increase in  $\epsilon$ ). Here the same acidity effect appears to enter. And in (2), (3), and (4), where the rate of decomposition falls off rapidly towards the end of the reaction, it would seem likely that both  $k_a$  (acidity) and concentration influences play a part.

Further work is in progress from several points of view on the questions raised in this paper, particularly on the marked influence of hydrochloric acid on the course of the reaction, a factor which we consider responsible for the non-reproducible nature of some of the experiments, and on the general effect of strong electrolytes on our coefficients  $a$  and  $d$ .

#### Summary.

(1) Data are presented on the extinction coefficients of aqueous solutions of chlorine and of hypochlorous acid, both in absence and in presence of certain electrolytes.

(2) The results are recorded of quantum efficiency measurements made during the photodecomposition of such solutions.

(3) A detailed mechanism is suggested for such photodecomposition, which attempts to correlate the nature and proportions of the decomposition products with the observed quantum efficiencies, with the variations in the extinction of the solutions, with their chlorine partial pressures, and with the order of the reaction.

(4) This mechanism permits of the efficiencies of the primary and secondary reactions being separately determined, and allows of the analysis (up to a point) of the nature of the retarding effect exerted by strong electrolytes on the photodecomposition.

The experimental work in this paper was carried out during the years 1921—1924. Of the authors, one (P. W. C.) wishes to acknowledge the help afforded by a bursary granted him by the British Cotton Industry Research Association, and another (R. E. W. M.) similarly wishes to acknowledge the grant made him by the Advisory Council of the Department of Scientific and Industrial Research. Some of the quartz apparatus employed was purchased out of a grant made to the laboratory by Messrs. Brunner Mond and Co., Ltd., to whom we express our indebtedness.

UNIVERSITY OF LONDON,  
KING'S COLLEGE.

[Received, December 15th 1926.]

---