CXVII.—The Photodecomposition of Chlorine Water and of Aqueous Hypochlorous Acid Solutions. Part I.

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SINCE Berthollet's discovery that chlorine water is decomposed when exposed to light, with evolution of oxygen and formation of hydrochloric acid, many papers have been published on the subject. None of these, however, deals with the reaction in a systematic fashion, and the present work, carried out during 1921-1924, is an attempt to fill up some of the gaps in our knowledge of this photolysis. The literature is too voluminous to give fully here. The majority of the papers are quoted in Mellor's "Inorganic and Theoretical Chemistry," Vol. II, p. 78. Other papers dealing with the reaction are those by McLeod (J., 1886, 49, 608), Richardson and others (Rep. Brit. Assoc., 1888, 89; 1889, 59; 1890, 263), Richardson (J., 1891, 59, 536), and Benrath and Schaffganz (Z. physikal. Chem., 1922, 103, 139). Little has been published on the photodecomposition of solutions of hypochlorous acid. Gav-Lussac (Annalen, 1842, 43, 153) and Williamson (ibid., 1855, 54, 133) both refer to the acid as being photosensitive. Foerster and Jorre (J. pr. Chem., 1899, 167, 81) confirm this, whilst stating that the photosensitivity is small. Pedler (J., 1890, 57, 613) carried out a few experiments on the subject, Clark and Iseley (J. Ind. Eng. Chem., 1920, 12, 1116) state that its photodecomposition in sunlight is monomolecular, and finally, a few observations are recorded by Benrath and Schaffganz (loc. cit.).

With respect to the decomposition of chlorine water, the main results of previous work can be summarised as follows. The reaction in the dark is inappreciable (Draper). The products of the photoreaction are generally given (more particularly in the earlier papers, though this is also the case in the quite recent work of Benrath and his pupils) as merely hydrochloric acid and oxygen. Popper (1885) was the first to notice that chloric acid can be formed in quantity. This observation was confirmed by Gore (1889), Klimenko (1889 and later), Pedler (1890), and Billitzer (1906), the formation of oxygen, according to the last author, being quite unimportant. Billitzer reports the production of perchloric acid, and Gore mentions hydrogen peroxide. According to Richardson (1891), the evolved oxygen is ozonised, but no hydrogen peroxide is produced. The presence of hydrochloric acid renders chlorine water far less sensitive (Bunsen and Roscoe and other subsequent workers), although, according to Billitzer, a small addition of acid acts as a positive

catalyst. The addition of other chlorides also retards the reaction, although less effectively than hydrochloric acid (Klimenko, Billitzer, Milbauer); so also do certain sulphates (Benrath and Schaffganz). Bromine acts as a positive catalyst (Milbauer). The evolution of the oxygen is subject to marked supersaturation effects (Berthollet). As will be seen, this circumstance probably accounts for the induction period and the "after effect" noted by Draper. The reaction goes more readily in violet light than in the rest of the visible spectrum (Davy). The temperature coefficient is 1.4 (Benrath and Tuchel).

De Saussure, assuming the validity of the $I \times t$ law, recommended the use of chlorine water as an actinometer liquid. According to Wittwer, the reaction is of the first order, and its rate is proportional to the intensity of the light. Bunsen and Roscoe, and, later, Billitzer, found no such relations, Billitzer saying that the reaction is autocatalytic. Finally, the actual primarily photosensitive constituent is imagined to be chlorine itself (earlier workers and Billitzer), hypochlorous acid (Pedler, Pebal, Jakowkin, Klimenko, and more particularly Dawson), and the ClO' ion (Benrath and Schaffganz).

Plan of Work.—It will be seen that, not only is there disagreement as to the mechanism of the reaction, but there are discordant statements even as to the chemical nature of the reaction products. No work has been done in monochromatic light, and the energetics of the reaction has not been touched. It is therefore to these points in particular that our attention has been directed.

The present paper is an account of our work on the reaction products and the factors affecting them. We adopted a working hypothesis which we subsequently found to have been previously developed up to a point by Jakowkin (Z. physikal. Chem., 1899, 29, 621) and by Dawson (Z. wiss. Phot., 1914, 14, 213). A solution of chlorine in water is, at the ordinary temperature, very considerably hydrolysed (Jakowkin, *loc. cit.*) according to the equation,

$$Cl_2 + H_2O \rightrightarrows HClO + H^{\bullet} + Cl'.$$

All evidence goes to show that the addition of chlorides and, in particular, of hydrochloric acid, retards its photodecomposition. This follows qualitatively from the above equation if the hypochlorous acid molecule is considerably more photosensitive than the chlorine molecule. It would appear reasonable to suppose that the primary decomposition reaction in the case of hypochlorous acid would be

$$HClO \longrightarrow HCl + O$$

and also that oxygen atoms would be formed at an early stage when

chlorine was the photosensitive substance. (Possible reaction mechanisms will be considered more closely in the second paper). The production of molecular oxygen and chloric acid would then be due to secondary reactions, the latter substance being formed as a result of the hypochlorous acid molecules acting as acceptors for the oxygen atoms. If, therefore, by addition of suitable nonphotosensitive substances, it could be arranged practically to exclude the presence from the solution during insolation of either hypochlorous acid molecules or of chlorine molecules respectively, one might expect in the first case a slow reaction with very little chlorate formation, and, in the second case, a more rapid reaction with a higher percentage of chloric acid in the product than would have been the case with ordinary chlorine water.

The addition of either hydrogen ions or chlorine ions to chlorine water will increase the chlorine concentration in the solution at the expense of that of the hypochlorous acid. Experiments were accordingly carried out with chlorine water in which the percentages of the reaction products were carefully estimated. Similar experiments were then done with chlorine dissolved in solutions of potassium chloride, lithium chloride, cadmium chloride, sulphuric acid, and hydrochloric acid of varying strengths, in order to study the effect of hydrogen ions and chlorine ions, separately and in conjunction with each other. Experiments were further done with chlorine dissolved in solutions of sodium sulphate and lithium sulphate, in order to test the effect of neutral salts, and with chlorine dissolved in bromine water and in solutions of copper sulphate, cobalt sulphate, and nickel sulphate, in connexion with later experiments on possible catalytic effects.

With the intention of affecting the Jakowkin equilibrium in favour of hypochlorous acid, experiments were carried out with chlorine water containing dissolved mercuric chloride, the idea being that, as the result of the reaction

$$\operatorname{HgCl}_{2} + 2\operatorname{Cl}' \longrightarrow \operatorname{HgCl}_{4}'',$$

the hydrolysis of chlorine would be made almost complete. Subsequent reference to Sherrill's work (Z. physikal. Chem., 1903, 43, 734; 1904, 47, 103) showed this not to be so, only a moderate diminution in chlorine-ion concentration being effected even by saturating the chlorine water with mercuric chloride. Measurements of Jakowkin himself led to the same conclusion.

A solution of hypochlorous acid, on insolation, immediately forms hydrochloric acid, with consequent production of chlorine in the solution. To avoid this, it is necessary to remove either the chlorine ions or the hydrogen ions as they are formed. Experiments

were done with addition of mercuric chloride to remove the chlorine ions. They were few in number, not very concordant, and are not recorded here, more particularly as, for the reason just stated, they were ill-adapted to achieve their purpose. In order to remove the hydrogen ions, the obvious course was to add to the solution the sodium salt—NaR—of a weak acid unaffected by light. The acid chosen, however, should not be so weak as to allow of the reaction

$HClO + R' \longrightarrow ClO' + HR$

setting in, as the photosensitivity of the sodium hypochlorite formed would then complicate matters. The necessary condition is that the salt used should be of an acid with a dissociation constant which, whilst small, is appreciably greater than that of hypochlorous acid. Sodium acetate and disodium hydrogen phosphate were chosen, and the products of photodecomposition in their presence investigated. Any formation of hypochlorite ion will take place according to the respective equations

$$\begin{array}{l} \text{HClO} + \text{Ac}' \longrightarrow \text{HAc} + \text{ClO'}.\\ \text{HClO} + \text{HPO}_4'' \longrightarrow \text{H}_2\text{PO}_4' + \text{ClO'}. \end{array}$$

The dissociation constants K_{HAc} and $K_{\text{H}_2\text{PO}_4}$ (Abbott and Bray, J. Amer. Chem. Soc., 1909, 31, 729) are respectively 1.8×10^{-5} and $1.95 imes 10^{-7}$ at 18°. The value for $K_{
m HCIO}$ is given as $3.7 imes 10^{-8}$ (Sand, Z. physikal. Chem., 1904, 48, 610), 6.7 × 10⁻¹⁰ (Noyes and Wilson, J. Amer. Chem. Soc., 1922, 44, 1630), and 1×10^{-8} (Soper, J., 1924, 125, 2227). When starting these particular experiments, we assumed the figure given by Noves and Wilson to be probably more nearly correct than that of Sand, in which case the condition necessary for practical non-formation of hypochlorite ions would be satisfied. It would seem, however, from Soper's work, that their value is certainly too low. Adopting the figure of 1×10^{-8} , an approximate calculation shows that, in a solution containing M/8-Na₂HPO₄ + M/20-HClO, about 28% of the hypochlorous acid is present as hypochlorite ions, and that this proportion is reduced to about 15% when the solution is half decomposed. Our results must therefore be considered in the light of this uncertain factor. With sodium acetate, no such difficulty arises, and the production of both hydrogen- and hypochlorite-ions should be satisfactorily repressed.

EXPERIMENTAL.

Preparation of Solutions.—Chlorine was prepared by the action of concentrated hydrochloric acid on either potassium dichromate or potassium permanganate crystals, the gas being washed by water (in the latter case also by a solution of potassium permanganate

prior to the water washing) and then passed into distilled water or into the appropriate solution. Hypochlorous acid was prepared by the method of Bostock and Taylor (J., 1912, 101, 451), viz., by distillation at a pressure of about 120-140 mm. of a mixture of bleaching powder, boric acid, and water. In some cases a solution of sodium hypochlorite was substituted for the bleaching powder. Unless the pressure were lowered well below the figure just given, the distillate was appreciably weaker, in spite of the higher hypochlorite concentration in the distilling flask. This difference is presumably due to the relative insolubility of the calcium borate resulting in the first case, and to boric acid being a weaker acid than hypochlorous acid (accepting Soper's figure for K_{HOO}). When insolating mixtures of hypochlorous acid and the above-mentioned salts, weighed quantities of the latter were dissolved in the hypochlorous acid solution.

Analytical Methods.—During the whole of the work, as will be seen later, the only decomposition products found, apart from hydrochloric acid, were chloric acid and oxygen.* In what follows, the concentrations of the different oxidising substances concerned are expressed as normalities of equivalent oxidising power. Thus "normal" solutions of chlorine, hypochlorous acid, and chloric acid contain respectively 35.5, 26.2, and 14.1 g./litre of the substance concerned. In the particular case of oxygen, supposing it to remain in solution, a normal solution would contain 8 g./litre, and it can be readily seen that, in correlating the quantity of oxygen produced during a given experiment with the corresponding loss in chlorine or hypochlorous acid, the following equation holds :

"Normality" of oxygen $= 4v/22 \cdot 4V$,

where V is the volume of the insolated solution, and v the volume of evolved oxygen at N.T.P.

Chlorine and hypochlorous acid were determined by delivering a known volume of the solution under the surface of an acidified 5% solution of potassium iodide, and titrating with N/10-thiosulphate. A special experiment showed that solutions containing hydrochloric and chloric acids at concentrations of the order of those prevailing after insolation caused no detectable liberation of iodine from the potassium iodide. Owing to the volatility of chlorine, concordant results could only be obtained if great care were exercised during pipetting and transference. In the later work, the pipette designed by Jakowkin (*loc. cit.*) was used with advantage.

Chloric acid was determined by the Bunsen method, using

^{*} The paper of Richardson, in which the formation of ozonised oxygen is recorded, was not read until this work was finished, and the point has not yet been tested.

N/10-ferrous sulphate and N/10-potassium permanganate solutions. A certain amount of trouble was experienced at the start in dealing with partly decomposed solutions containing both free chlorine and chloric acid. Attempts to determine chlorine plus chlorate by the ferrous sulphate method failed. Titration of chlorate by titanous chloride gave an unsatisfactory end-point, the percentage error involved being too great in the case of the dilute solutions used. We then investigated the addition of substances which would destroy the hypochlorous acid or chlorine present, without either attacking the chlorate or leaving behind in the solution something which would subsequently vitiate the chlorate determination (as was the case when the chlorine was titrated with potassium iodide and sodium thiosulphate or with sodium arsenite). Manganous sulphate, urea, and oxalic acid were all found to be possible reagents. Oxalic acid was chosen, as it seemed feasible that, by its use, both Cl₂(HClO) and HClO₂ might be determined on a single sample. The general procedure was to pipette 10 c.c. of the solution into a conical flask, to add 20-40 c.c. of N/10-oxalic acid, and to warm slowly until nearly boiling, adding about 20-30 c.c. of dilute sulphuric acid towards the end of the heating, which should take at least 10 minutes. The excess of oxalic acid was then titrated with N/10-permanganate to a faint pink colour, and the chloric acid determined in the usual way. Appropriate experiments showed (a) that no formation of chloric acid took place during the reduction of the Cl_o(HClO), and (b) that, with the concentrations used, the above procedure resulted in no loss of chloric acid by interaction with the oxalic acid, as is the case with stronger solutions (Bray, Z. physikal. Chem., 1906, 54, 463, 569, 731). Losses of the order of 5-10% of the total soon, however, appeared if the solutions were too concentrated or too rapidly heated during the oxalic acid treatment, and, until this was appreciated, concordant results were not obtained.

Further experiments showed that the presence of mercuric chloride and of the other salts added during the work did not affect the accuracy of the chlorate determination, with the exception of 2N-sodium acetate, when the results were about 1% too low. It was mentioned above that it seemed possible to determine both chlorate and HClO(Cl₂) on the same sample by this method, the condition being of course quantitative oxidation of the oxalic acid according to the equations

$$\begin{array}{l} \mathrm{H_{2}C_{2}O_{4}+HClO} \longrightarrow \mathrm{HCl}+2\mathrm{CO_{2}+H_{2}O} \\ \mathrm{H_{2}C_{2}O_{4}+Cl_{2}} \longrightarrow 2\mathrm{HCl}+2\mathrm{CO_{2}}. \end{array}$$

Using an *uninsolated* solution of hypochlorous acid, this was found to be the case, very concordant results being obtained from

analyses by the oxalic acid, iodide and thiosulphate, and sodium arsenite methods. With *insolated* solutions of hypochlorous acid or with chlorine water, however, the results were found to average about 4% too low, due in all probability to volatilisation of chlorine before complete reaction. In the great majority of the experiments, including all those carried out with chlorine water, separate samples were used for the Cl₂(HClO) and HClO₃ determinations.

Dark Experiments.—The following solutions, of oxidising power varying between 0.05N and 0.12N, were sealed up in glass tubes, kept in the dark for periods varying between 2 and 20 days, and subsequently titrated : Hypochlorous acid dissolved in water, in M/4-disodium hydrogen phosphate and in N/2-sodium acetate; chlorine dissolved in water and in 5% mercuric chloride, 10% nickel sulphate, 10% cobalt sulphate, and 5% lithium sulphate. As always, the greatest care had to be exercised in the manipulation and transference of the solutions containing chlorine, if significant results were to be obtained, these being very readily masked by volatilisation losses caused during pouring, pipetting, etc. The results showed losses in $Cl_{0}(HClO)$ titre varying between 0.002N— 0.009N per 24 hours, except in the cases of the chlorine-cobalt sulphate and hypochlorous acid-sodium acetate mixtures. Such small figures show that the dark reaction can be neglected when carrying out the light experiments. In the case of the two exceptions, the titre fell per day by amounts varying between 0.02N-0.075N. A black precipitate was formed in the cobalt sulphate solution. The results in the case of the hypochlorous acid-sodium acetate mixture will be guoted later.

Apparatus.-All the definitive experiments were carried out with 110-volt Cooper-Hewitt quartz mercury lamps of the straight tube Two kinds of insolation cell were used. The first and pattern. simpler type consisted of a clear silica flask of about 130 c.c. capacity, closed by a rubber stopper. In the first experiments, the light from the lamp passed successively through a 1 cm. quartz water-cell and an aperture in a hollow copper screen, a stream of water at constant temperature being taken through the screen and a copper condenser on the neck of the flask, finally running out over the surface of the flask to waste. It was found later that a stream of tap-water playing over the surface of the flask sufficed to keep the temperature The rubber stopper carried two capillary tubes. constant. One of these in the earlier experiments led down to the bottom of the flask, and was used for saturating the photolyte with oxygen beforehand, a process which was soon discontinued. It was closed by pressure tubing and a screw-clip during insolation. The second was fused on to a three-way tap at the top of a small, water-jacketed

gas burette, provided with a levelling tube and filled with potassium iodide solution. To avoid the manipulation errors already referred to, the chlorine solutions used were finally prepared in the flask, a sample being withdrawn for analysis before insolation.

In carrying out an experiment, the flask was almost filled with the solution under study, put into connexion with the gas burette, and the latter levelled off and read after temperature equilibrium had been reached. The lamp was then lighted, the insolation proceeded with, and burette readings taken at intervals. When the volumes of oxygen collected became too large, they were discharged into the air by the three-way tap, and readings re-started without interrupting the insolation. Sometimes this was carried to completion—sometimes interrupted for a few moments in order to pipette out a sample for analysis, in which case it was necessary to disconnect the burette from the flask. At the end of the experiment, any iodine liberated from the potassium iodide in the burette by chlorine carried over with the oxygen was titrated, and a correction applied.

A large number of experiments were done with this apparatus. The use of a rubber stopper is open to objection. The necessity of disconnecting flask and burette for the purpose of withdrawing a sample for analysis was a disadvantage. So also was the comparatively large dead-space left in the apparatus after removing a sample for titration before insolation, as the chlorine contained in the vapour phase thus produced only slowly diffused along into the potassium iodide solution in the gas burette, rendering the correction correspondingly uncertain. The results were less concordant amongst themselves than those obtained with the cell now to be described, although agreeing sufficiently with the latter.

The cell used in the later experiments consisted of a rectangular glass block $10 \times 10 \times 5$ cm., through which had been drilled a horizontal cylindrical hole, 7.5 cm. in diameter. This hole was closed back and front by circular windows of crystal quartz, cemented to the plane surface of the glass block by a hard pitch composition, special experiments showing that no appreciable reaction took place between dissolved chlorine and the very small surface of cement exposed to its action. In the top of the cell, two openings were drilled. One, closed by a ground-glass stopper, served for the introduction of a pipette for taking samples, etc. The other was closed by a water-sealed, ground-glass joint, bearing a capillary tube connexion sealed on to the gas burette. A similar cell, 2 cm. in depth, served as a water-filter to cut out heat rays. In some experiments, it was directly attached to the front quartz plate of the reaction vessel, thus forming a compound cell, and economising a quartz plate. Experiments showed that, in this case, there was never more than 0.5° difference between the temperature of the water flowing through the filter and that of the liquid in the reaction cell.

As the work proceeded, continual minor improvements in technique were made. The most concordant results were obtained when the dead-space in the insolation cell was reduced to a minimum (about 3 c.c.).* The solution under investigation was prepared in a stock bottle, and siphoned off into the cell. The latter was first of all rinsed out several times with about 10 c.c. of the liquid, and a vapour phase thus established. It was then filled and, after pipetting out 20 c.c. for analysis, refilled from the stock bottle. In addition, the gas leaving the cell was caused to pass *through* two small traps containing potassium iodide solution, the gas burette being filled with water. After the completion of the experiment, any chlorine in the connecting tubes was gently blown through the potassium iodide traps, the first of which in practice sufficed for complete absorption.

Supersaturation Effects.—It was at first thought that it might be possible to follow the rate of reaction during insolation by means of the volume of oxygen collected at any instant, but it was soon found that this was out of the question, owing to the remarkable extent to which supersaturation occurred. The rate of evolution of gas was, of course, low at the start, owing to the necessity of first saturating the photolyte. It usually increased to a more or less constant value after 2-3 hours. If insolation were interrupted before complete decomposition, then gas continued to come off at the same rate for another 2-3 hours, and only after many hours' standing did the volume become constant. If insolation were continued until all the HClO(Cl₂) had reacted, the rate of collection of gas became less towards the end, corresponding with the decreased light absorption and rate of decomposition. But the liberation of oxygen after the light was cut off still persisted. Careful experiments showed that there was no change taking place in the electrolyte, the oxidising titre of which remained quite unaltered in the dark. The reaction therefore does not exhibit an "after effect." Saturation with oxygen beforehand made no essential difference, not even to the initial time required for the rate of gas evolution to become approximately constant.

The nature of the surface of the containing vessel, on the other hand, had an effect. Gas could be seen coming off at definite points

^{*} At the beginning of the work the dead-space was carefully shielded from light, in order to avoid the possibility of the reaction $2Cl_2 + 2H_2O \rightarrow 4HCl + O_2$ taking place in the vapour phase. Work done in another connexion in the laboratory showed this precaution to be unnecessary.

on the surface, and the delayed evolution was more marked with experiments carried out in the smooth silica flasks than was the case when using the composite cells with their inner surface of groundglass. When sand or powdered quartzite was added to the insolation cell, the rate of gas evolution was still further increased, but its appearance in quantity subsequent to the insolation was never eliminated.

The consequence of the phenomenon was that the sum of the amount of oxygen collected as gas and of that contained in the chloric acid found after the experiment was very seldom (within the experimental error) equal to that calculated from the loss in titre of Cl_o(HClO), even when the solution was left standing for hours after the experiment. The deficiency could easily amount to 30% of the whole. As the formation of perchloric acid had been reported by Billitzer, we tested for this substance in the insolated solution after neutralisation with alkali, using the reaction with methylene-blue described by Monnier (Ann. Chim. Analyt., 1916, 20, 237). None was ever found, nor, it may be mentioned here, did the usual tests ever show the presence of hydrogen peroxide.* the formation of which had been mentioned by Gore. In order to get more positive evidence. experiments were done in which the solution was either allowed to stand for very considerable periods after the insolation, or in which the apparatus was vigorously shaken before the final reading was taken. The following are specimens of the results obtained.

Initial	Final corrected	Corrected loss in	Titre of chloric acid	${f Titre} {f of}$	Chloric acid plus
titre.	titre.	titre.	formed.	oxygen.	oxygen.
0.095N-HClO	0.0025N	0.0925N	0.059N	0.032N	0.091N
$0.0935N-Cl_2$	0.0047N	0.0888N	0.0563N	0.0313N	0.0876N

It was further shown, on several occasions, that, after complete decomposition of a solution of hypochlorous acid, all the chlorine originally present as hypochlorous acid (allowing for losses by volatilisation) was to be found in the solution either as chloric acid or as hydrochloric acid, thus showing that any formation of perchloric acid was negligible. It seems therefore reasonable to suppose that supersaturation is solely responsible for the observed phenomena, and that there is neither an "induction period" nor an "aftereffect," as Draper had imagined.

Certain remarkable experiments should, however, be especially mentioned, in which chlorine water and chlorine water containing

^{*} Observations of Anderson and Taylor (J. Amer. Chem. Soc., 1923, 45, 1215) render it unlikely that appreciable amounts of hydrogen peroxide could exist under our experimental conditions.

dissolved mercuric chloride were insolated in a silica flask. Practically no gas could be seen coming off from the solutions during irradiation and, in the whole set of about twenty-five experiments, more than 2 c.c. of oxygen were never collected during any single insolation, although amounts of up to 50 c.c. would have been anticipated from the subsequent analyses for chloric acid and negative tests for perchloric acid. After completion of the experiments, the solutions were in some cases boiled or evacuated. but not more than an extra c.c. of gas was ever obtained. This curious non-appearance of gas remains unexplained. It is, of course, possible to imagine the gas being given off from the liquid surface as single molecules or small aggregates, instead of being liberated as visible bubbles. It is also true that the neck of the flask was closed by a rubber stopper, which might conceivably react with any "activated" oxygen or ozone, but the suggestion would seem inadequate to explain such a complete elimination of the appearance of oxygen. It may be added that of course the possibilities of a leak or of the presence of some reducing agent in the apparatus were carefully gone into. In any case, the striking feature of the experiments to the eve was the absence of visible oxygen evolution. \mathbf{It} is hoped to follow up the subject further. In the meantime, it may be mentioned that relevant data are contained in the recent papers by Metschl (J. Physical Chem., 1924, 28, 427) and by Kenrick, Wismer, and Wyatt (ibid., p. 1314).

Results.

The figures which follow represent the percentages of chlorine or hypochlorous acid which, on reaction, gave chloric acid as a product. The remainder, in absence of any positive test for perchloric acid or hydrogen peroxide, is assumed to have decomposed, giving oxygen.

Chlorine Water.—Several series of measurements, during which the experimental technique was gradually improved, were carried out, involving nearly fifty different insolations.

	Type of	No. of	Extreme	Mean
Series.	apparatus.	expts.	values.	value.
1	Flask	9	$56 \cdot 3 - 68 \cdot 3$	$62 \cdot 5$
2	Cell	6	$57 \cdot 4 - 62 \cdot 3$	60.1
3	Flask	3	58 - 66	63
4	Flask	13	51 - 76	60·4
5	Cell	3	55 - 63	60
6	Cell	12	59 - 63	61.3

The general mean is 61.2% of chloric acid, which is also practically the mean of the last and most concordant series. The strengths of the solutions insolated varied between 0.158N and 0.0175N, and

the degree of decomposition from about 15% to completion. The extreme values for the chloric acid figures were obtained either when the technique had not been fully developed, or when the titration values were very small, and the errors correspondingly great. We therefore feel justified in concluding that the proportions of the products are not sensibly affected either by the initial concentration or by the extent of decomposition.

Chlorine in Hydrochloric Acid Solution.*-

Conc. of HCl	0.004N	0.01N	$0{\cdot}1N$	0.5N
Chloric acid %	56	55.5	31.7; 29; 27	22.5; 10; 14

Chlorine in Potassium Chloride Solution.*---

Cone. of KCl	$0 \cdot 1N$	0.5N
Chloric acid %	51.9; 60; 63; 45	44·3; 29; 21; 15; 26

Chlorine in Mercuric Chloride Solution.—As with chlorine water, several series of measurements were done, the concentration of the mercuric chloride always being 5%. As aqueous mercuric chloride is reported by some observers to be photosensitive, with formation of calomel and evolution of oxygen (e.g., Pougnet, Compt. rend., 1915, 161, 348), solutions containing the salt alone were insolated beforehand, but no trace of decomposition could be detected. This agrees with the observation of Lesure (J. Pharm. Chim., 1910, 1, 569).

	Type of	No. of	$\mathbf{Extreme}$	Mean
Series.	apparatus.	expts.	values.	value.
1	Flask	3	55 - 68	60.3
2	Flask	13	57 - 79	65
3	Cell	4	65 - 66	65.2
4	Cell	3	$62 - 63 \cdot 5$	$62 \cdot 8$

The general mean gives 64.1% of chloric acid.

Chlorine in other Chloride Solutions.—

Solution	0.01M-CdCl ₂	0.1M-CdCl ₂	0.5M-CdCl.	0.5N-LiCl
Chloric acid %	55·7	$57 \cdot 9$	44.6 -	39

Chlorine in Sulphuric Acid Solution.—

Conc. of H ₂ SO ₄ .	Chloric acid $\frac{0}{10}$.
0.1N	57.6; 64.2 ; 49.5 ; 62 ; 63 ; 57 ; 63 (mean figure 59.5)
0.5N	52.6; 48; 57; 59; 60; 61 (mean figure 56.3)

There appeared to be a certain tendency in this case for solutions containing higher initial chlorine concentrations to give lower chloric acid percentages.

* Many of the titration figures for chlorate were here exceedingly small -the percentages given in italics correspond to the largest, and hence presumably to the most trustworthy, titrations.

Chlorine in Sodium Sulphate Solution.—

Conc. of Na ₂ SO ₄	0.01M	$0 \cdot 1M$	0.33M	Saturated
Chloric acid %	$63 \cdot 2$	60.0	$62.5;\ 62;\ 62$	61.7
, -		Mean figure	61.9	

Chlorine in Lithium Sulphate Solution.-

Conc. of Li ₂ SO ₄	0.25M	0.5M	1M	2M
Chloric acid %	63	67	69	73; 73

The colour of solutions of chlorine in aqueous sodium and lithium sulphates is far less pronounced than is the case with chlorine water alone, or with chlorine dissolved in dilute solutions of sulphuric acid or of halides.

Chlorine in other Solutions.-

 Added solute
 Bromine
 0.5%CuSO4
 0.5%CoSO4
 0.5%NiSO4

 Chloric acid % 61.3 64; 63; 64 61.5; 56 59; 67

An experiment with chlorine dissolved in 0.5% manganous sulphate resulted in the rapid formation of a black precipitate, the same slowly occurring in the dark. In certain circumstances, the solution in cobalt sulphate behaved similarly.

Hypochlorous Acid.—Five experiments gave $65\cdot3$; $63\cdot4$; 57; 58; $60\cdot2\%$ of chloric acid (mean figure $60\cdot8$).

Hypochlorous Acid in Sodium Phosphate Solution.—Two experiments gave 81% in 0.25M- and 86% in 0.125M-disodium hydrogen phosphate.

Hypochlorous Acid in Sodium Acetate Solution.-It was mentioned earlier that experiment showed the dark reaction in this case to be considerable, a 0.1N-hypochlorous acid solution in 0.5N-sodium acetate losing about half its titre in 9 days. It soon became apparent that the light reaction itself was more complex than those hitherto Two insolations were made of solutions of about the same studied. composition as above. They rapidly lost their titre when exposed to light, but no evolution of oxygen could be detected in the one case, and the merest trace in the other, whilst subsequent analyses showed only 12 and 18%, respectively, of the original oxidising power as chloric acid. Chlorination or oxidation of the sodium acetate or of the acetic acid formed in the reaction naturally suggested itself, and the usual tests were applied for monochloroacetic, succinic, and oxalic acids. All were negative, although an appropriate amount of the substance concerned gave a positive result under the conditions of experiment. However, on boiling with alcoholic potash, after adding a drop of aniline, a faint but unmistakable smell of carbylamine was noticed, which pointed to the This observation probably means that presence of chloroform. hypochlorous acid chlorinates acetic acid or sodium acetate in light

to give trichloroacetic acid, the chloroform either being formed during the carbylamine test, or possibly being produced by the further action of light on the trichloroacetic acid *in statu nascendi*. The formation of the monochloro- and dichloro-acids is presumably transitory, as no trace of oxalic acid, which would be the final product of their photolysis under the experimental conditions, was found.

In order roughly to check the results, another insolation was carried out in which, after partial decomposition of the hypochlorous acid and determination of the chloric acid (which amounted to 24% of the loss in HClO titre), the chloride concentration of the solution which had been used in the chlorate analysis was determined by titration. The result, of course, represented the total chlorine present in the original solution, less that fixed (presumably) as trichloroacetic acid. The figures were (expressed as gram-atoms or gram-ions per litre)

	Cl in original HClO	0.0622
	Cl as HČlO after insolation	0.0250
	Cl converted to HClO ₃	0.0029
	Cl' found on titration	0.0397
Hence	Cl as Cl' after insolation	0.0397 - 0.0250 - 0.0029 = 0.0118
	Cl fixed as $CCl_3 \cdot CO_2H$ (?)	0.0622 - 0.0397 = 0.0225

Another portion of the insolated solution was then taken, hydrolysed by 12.5% sodium hydroxide, and another chloride titration carried out. This figure (corrected for a blank test on the sodium hydroxide) should be a measure of the chloride formed during the insolation and by the hydrolysis, plus that produced on heating the alkaline sodium hypochlorite, in accordance with the reaction

 $3ClO' \longrightarrow 2Cl' + ClO_3'$.

The result was 0.0542N. If we add the figures for the chlorine converted to chlorate ion during the insolation (0.0029N) and during the hydrolysis (0.0083N), if the above equation is correct), we get a total of 0.0654N, compared with the figure of 0.0622N in the 0.1244N-hypochlorous acid taken. The discrepancy of 5% is reasonable considering the assumptions made. Thus, for example, it is conceivable that, during the hydrolysis, further chlorination of the acetate by hypochlorite ions may have occurred, or possibly decomposition in accordance with the equation

 $2\text{ClO'} \longrightarrow 2\text{Cl'} + \text{O}_2$,

either of which reactions would have caused a discrepancy in the sense found.

One further experiment was done, in which a dilute--0.5%-solution of sodium acetate was used, and the mixture with 0.045Nhypochlorous acid exposed to daylight for $10\frac{1}{2}$ hours. The chloric

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acid percentage of the loss in hypochlorous acid titre was now found to be 72, a very different figure from those given by strong sodium acetate solutions. Chloride determinations were carried out as above, and good agreement was found with the calculated figure. It would thus appear definitely as if, on insolating these solutions, two reactions proceed simultaneously—photodecomposition of the hypochlorous acid, resulting in the production of much chloric acid and little oxygen, and chlorination of the added acetate, the latter reaction naturally occurring to a greater extent the higher the percentage of acetate present. Time has not yet permitted of a further investigation of these results.

Effect of Wave-length.—Experiments carried out in sunlight, diffused daylight, and in monochromatic light of wave-lengths 313, 365, and 436 $\mu\mu$ showed no appreciable difference in the proportion of the products formed.

Effect of Surface.—Two experiments on solutions of hypochlorous acid indicated that, in presence of the highly developed surface furnished by adding pure silica powder to the contents of the insolation vessel, the proportion of chloric acid in the product was considerably reduced. In the present lack of confirmatory experiments, we prefer to lay no stress on this observation.

Discussion.

A detailed discussion of the mechanism of the reaction is best postponed until the measurements on the energetics have been Certain conclusions can, however, be drawn at this described. The results obtained with the solutions of hypochlorous acid stage. in disodium hydrogen phosphate, viz., an increase in the chloric acid yield from 61 to 83%, support our assumption that oxygen atoms are the primary product of photolysis, and that molecules of hypochlorous acid present will act as acceptors for these oxygen atoms, or possibly for "activated" oxygen molecules, the final result being formation of chloric acid. That the addition of disodium hydrogen phosphate to the hypochlorous acid solutions did, in fact, prevent the formation of hydrochloric acid and thus of free chlorine during the insolation is made very probable by the fact that such solutions remained colourless throughout the experiment. Further, when chlorine was passed into a solution of disodium hydrogen phosphate, the initial yellow colour disappeared on standing for a short time, and on addition of potassium iodide, the solution behaved like hypochlorous acid, *i.e.*, it required added mineral acid in order to liberate its full amount of iodine. The uncertainty as to whether there was appreciable formation of hypochlorite ions has already been mentioned. One fact, however, speaks against this, as Mr.

M. Holmes, working in this laboratory on the photodecomposition of sodium hypochlorite solutions, found only 11-12% chlorate formation, indicating that hypochlorite ions are not very avid acceptors of oxygen atoms (or "activated" oxygen molecules). The results with sodium acetate solutions are perhaps less conclusive, in consequence of the simultaneous photochlorination which is going on. Nevertheless, the amount of oxygen set free in this case is negligible compared with the quantity of chloric acid produced. It is also noticeable that solutions of chlorine in aqueous lithium sulphate, which became more nearly colourless as the concentration of the salt was increased, gave corresponding progressively increasing yields of chloric acid.

When we consider the results obtained with chlorine water, however, particularly those given by solutions of chlorine in dilute hydrochloric acid, the facts by no means completely fit the original hypothesis. This was, briefly, that the only products, or practically so, of the photo-reaction between chlorine itself and water are *oxygen* and hydrochloric acid, and therefore that, if by addition of hydrochloric acid to the chlorine water beforehand, the amount of hypochlorous acid in the photolyte could be made negligible, there should be only a correspondingly minute quantity of chloric acid present after insolation. This, however, is not so.

The value of the Jakowkin equilibrium constant, $K = [Cl_2]/[H^*][Cl'][HClO]$, is about 2500 at 20°, concentrations being expressed as mols./litre (Gröh, Z. physikal. Chem., 1913, 81, 695; see also Lewis and Randall, "Thermodynamics," p. 508). Assuming complete dissociation of any hydrochloric acid added or formed by hydrolysis, we have calculated the approximate concentrations (before insolation) of the various constituents present in 0.1N (0.05M)-chlorine, dissolved in water and in 0.01N-, 0.1N-, and 0.5N-hydrochloric acid. The results are contained in the following table, together with the percentage yield of chlorate experimentally found :—

Solution insolated.	Fraction of chlorine hydrolysed.	[HCl].	[HClO].	[Cl ₂].	Percentage chloric acid yield.
0·05M-Cl.	0.45	0.0225	0.0225	0.0275	61
+ 0.01N-HCl	0.35	0.0275	0.0175	0.0325	55*
+ 0.1N-HCl	0.04	0.102	0.002	0.048	29^{+}
,, + 0.5N-HCl	0.001.	0.500	0.000075	0.0499	14†
* One ins	olation only.		† " Best '	' values.	

It is clear that the chloric acid yield falls off far less rapidly than is likely to have been the case if it were solely produced by interaction between primarily formed oxygen and hypochlorous acid molecules present at concentrations demanded by the Jakowkin G G 2 constant. It would appear possible that hypochlorous acid is one of the intermediate products of reaction of photo-activated chlorine molecules with water, this photo-product acting as an acceptor for the oxygen. A somewhat similar mechanism was proposed by Billitzer. The effect of an increased concentration of hydrogen chloride would, of course, then be, by re-formation of chlorine, to lower the "stationary state" concentration of the hypochlorous acid, and thereby to decrease the opportunity for formation of chlorie acid.

With regard to the results obtained with the other salts, addition of either potassium chloride, lithium chloride, or cadmium chloride lowers the chloric acid yield, but in a lesser degree than does hydrochloric acid, a result to be anticipated (qualitatively) from the Jakowkin equation. Potassium chloride would appear (in 0.5Nsolution) to have the greatest effect, but the experiments are too few to enable any definite conclusions to be drawn. There is no doubt, however, that the action of sulphuric acid is, in this respect, much less than that of potassium chloride. This in itself is enough to show that the Jakowkin equation is by no means the only determining factor. The different ions appear to have specific effects, a view which is supported by the marked difference between the mode of decomposition of chlorine dissolved in sodium sulphate and in lithium sulphate solution.

From the figures with mercuric chloride solutions, we feel justified in concluding that the percentage of chloric acid is slightly increased. This result can be construed (qualitatively) in the light of the Jakowkin equation, as a rough calculation based on the results of Luther and of Sherrill shows that the chlorine-ion concentration in a completely photolysed 0.05M-chlorine solution is reduced by about half when the solution contains 5% of added mercuric chloride, owing to the formation of HgCl₄" ions.

One further striking result should be commented upon. There is no doubt at all that the presence of small concentrations of hydrochloric acid (say 0.1N or less) added to chlorine-water solutions before insolation depresses the yield of chloric acid. On the other hand, no diminution in this yield during the insolation of a chlorinewater solution was ever observed, in spite of the fact that the concentration of hydrogen chloride was continually increasing. Still more remarkable is the fact that the percentage of chloric acid produced during photolysis of a solution of hypochlorous acid is identical with that given by chlorine water. Putting, for the sake of simplicity, the percentage of chloric acid given by 0.1N-solutions of both substances as 60 (actually 61), the stoicheiometric equations for the two photodecompositions are :

 $\begin{array}{l} 0.05 \mathrm{Cl}_2 + 0.05 \mathrm{H}_2 \mathrm{O} \longrightarrow 0.01 \mathrm{HClO}_3 + 0.09 \mathrm{HCl} + 0.01 \mathrm{O}_2 \\ 0.05 \mathrm{HClO} \longrightarrow 0.01 \mathrm{HClO}_3 + 0.04 \mathrm{HCl} + 0.01 \mathrm{O}_2 \end{array}$

equations which apparently hold whatever the degree of decomposition, and the former of which corresponds to that given by Popper for the decomposition of chlorine water. Thus a reduction of the final hydrochloric acid acidity by more than half makes no difference in the yield of chloric acid, while, on the other hand, if the final acidity is doubled by working with chlorine solutions with 0.1N-hydrochloric acid added, or suppressed by adding disodium hydrogen phosphate to hypochlorous acid solution, the chlorate percentage falls to about 30 or rises to more than 80, respectively.

Using the same value of the Jakowkin equilibrium constant and the same assumptions as previously, we have calculated the values of [HCl] in a number of solutions before insolation, half way through the insolation, and after complete decomposition. The results are contained in the following table.

Solution insolated.	[HCl] at start.	[HCl] after 50% decomp.	[HCl] at end.	Yield of chloric acid %.
0.05M-HClO + Na ₃ HPO ₄				83
0.05M-HClO		0.013	0.04	61
0.05 <i>M</i> -Cl ₂	0.0225	0.0487	0.09	61
H = 0.01N-HCl	0.0275	0.0575	0.10	55
+ 0.1N-HCl	0.102	0.1455	0.19	29
, + 0.5N-HCl	0.500	0.545	0.59	14

It is difficult at first sight to see why the solutions of 0.05M-hypochlorous acid and 0.05M-chlorine should give the same yield of chloric acid when the HCl acidity conditions are so different. We are inclined to attribute it to the fact that, as soon as decomposition of the hypochlorous acid has commenced, chlorine will be formed in the first layers of the cell. The solutions were not stirred during the experiments, owing to the volatility of the substances present. Consequently the first and absorbing layers will be different in composition from the solution in the rest of the cell, which is unaffected or only weakly affected by light. They will always contain more acid than the latter, and a high chlorine concentration in comparison with their hypochlorous acid content. Chlorine, moreover, absorbs far more strongly than hypochlorous acid. So that the solution is really being insolated under conditions which, both in respect of acidity and of nature of absorbing molecules, correspond far more closely to those in a chlorine-water solution than at first sight they appear to do. This seems a very possible explanation of the results observed.

With regard to the first stage of the reaction in these experiments, we have no doubt that both the hypochlorous acid and the chlorine

molecules are primarily photosensitive. All the experiments go to show this, and we cannot agree with the view expressed by Benrath and Schaffganz that the hypochlorite ion is the sole responsible photosensitive agent. Its concentration in 0.05M-hypochlorous acid is of the order of 2×10^{-5} and in 0.05M-chlorine about 10^{-8} equivalents/litre. Further experiments in this laboratory have shown that the quantum efficiency for the decomposition of a 0.06N-solution of sodium hypochlorite is about the same as for hypochlorous acid and for chlorine water, and we regard it as in the highest degree unlikely that this agreement would be obtained if, in all these solutions, the hypochlorite ion, with its widely different concentrations, were the sole photosensitive component.

Summary.

(1) The apparatus and experimental methods used in the investigation of the photodecomposition of chlorine water and hypochlorous acid solutions are described.

(2) It is shown that, except when substances are added which cause secondary reactions, the sole products of decomposition are hydrochloric and chloric acids and oxygen.

(3) Results are tabulated showing the percentage yield of chloric acid obtained in photolysis of chlorine water; chlorine water containing certain added acids, salts, etc.; hypochlorous acid; and hypochlorous acid containing added disodium hydrogen phosphate or sodium acetate.

(4) Secondary reactions were found with chlorine water containing manganese sulphate or cobalt sulphate (sometimes), and with mixtures of hypochlorous acid and sodium acetate.

(5) The results show that both the hypochlorous acid and the chlorine molecule are photosensitive, the latter possibly giving hypochlorous acid as a primary product. The evidence indicates that some at all events of the ions present in the salts used have a specific effect on the proportions of the products.

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