

centrated to about  $\frac{1}{3}$  its volume. Any precipitate formed is dissolved by the addition of more hydrochloric acid.

2. Solid sodium or potassium bromate is added to the cold solution in small portions with stirring (under a watch glass to prevent loss by spattering) until the liquid assumes an intense color of bromine.

The solution obtained in 1 or 2 is heated nearly to boiling, and a slight excess of ammonium hydroxide is added gradually with constant stirring. After settling, the ammonium uranate is filtered, and washed with 2% ammonium nitrate solution which contains a little ammonia but, of course, no hydroxylamine hydrochloride. The precipitate is ignited at dull red heat in an uncovered porcelain crucible to constant weight and weighed as  $U_3O_8$ .

The figures in the preceding table attest the accuracy of the method developed.

### Summary

The scanty literature dealing with the separation of beryllium from uranium has been critically reviewed, and a method for this separation has been developed.

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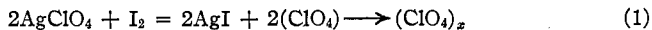
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

## THE REACTION BETWEEN SILVER PERCHLORATE AND IODINE. CHLORINE TETRA-OXIDE

BY M. GOMBERG

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Silver perchlorate is unique in that it is soluble in a variety of organic solvents<sup>1</sup> and may, therefore, undergo reactions which would not be feasible under ordinary conditions, such as in the presence of water. The reaction indicated in the title to this paper is one of this nature, and the investigation was undertaken in order to ascertain whether the compound radical  $(ClO_4)_x$  could be prepared.



Such a reaction would be analogous to that which Söderbäck recently employed with such eminent success in obtaining free thiocyanogen<sup>2</sup> from metal thiocyanates; it is also, in principle, a variation of the general method used in preparing triarylmethyl radicals, and in other syntheses.



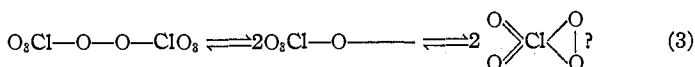
Would the prospective new oxide of chlorine prove more stable, or less so, than are the 3 known oxides of chlorine, namely, the  $Cl_2O$  of Balard, the  $ClO_2$  of Davy, and the  $Cl_2O_7$  of Michael and Conn?<sup>3</sup> Would it remain monomolecular and as a free radical, isomeric with the  $ClO_4'$  anion, or

<sup>1</sup> (a) Gomberg, *Ber.*, **40**, 1867 (1907); (b) *Ann.* **370**, 160 (1909). (c) Hill, *This Journal*, **43**, 254 (1921).

<sup>2</sup> Söderbäck, *Ann.*, **419**, 219 (1919).

<sup>3</sup> (a) Michael and Conn, *Am. Chem. J.*, **23**, 444 (1900); (b) Meyer and Kessler, *Ber.*, **54**, 566 (1921).

would it polymerize to  $O_3Cl-O-O-ClO_3$ , which might be properly termed perchloryl peroxide? Or would, perhaps, a phenomenon occur here similar to that encountered in the class of organic free radicals, the triarylmethyls, and we should be dealing with the sensitive system



These were some of the questions that were presented.

Numerous experiments have been carried out during the last year and a half, with chlorine, bromine and iodine, and with solvents chosen from a wide range of compounds, in the attempt to answer these questions. Iodine and ether have been found best suited for this reaction because of the formation of less by-products than was the case when the other halogens and any other solvent were employed. That the reaction proceeds with the formation of the substance,  $(ClO_4)_x$ , became evident early in the progress of the work. The isolation, however, of this compound in its pure state had to be abandoned, for the present mainly for these two reasons: first, side-reactions to the extent of 15% were found to ensue in addition to the main reaction, and the elimination of the by-products proved of considerable difficulty; second, the substance  $(ClO_4)_x$ , upon concentration of its solution, was found to react with the substances which served as solvents in the process of its preparation. An attempt was made to determine the molecular state of the new oxide of chlorine by an indirect method, and the result, although uncertain for various reasons, indicates that the radical probably is dimolecular in ether. The margin of accuracy in that determination does not, however, furnish sufficient evidence either in favor of or against the assumption of a state of partial dissociation into the monomolecular phase. For that matter, silver perchlorate itself has also been found to be dimolecular. Until further experimental evidence of more positive character shall have been obtained, the new oxide will be designated simply as  $(ClO_4)_x$ , and will be spoken of in this paper as chlorine tetra-oxide, following the precedent of Mellor<sup>4</sup> in the naming of the substance of the formula,  $(IO_2)_x$ . Should the molecular formula prove to be  $(ClO_4)_2$ , the name would naturally be changed to chlorine octoxide.

The experimental evidence concerning the existence of chlorine tetra-oxide is of 2-fold nature: first, the specific chemical reactions of the individual substance itself; second, the behavior of the substance, which is unlike that of absolute perchloric acid and of ethyl perchlorate under the same circumstances—two substances which might conceivably be formed under the conditions of our reaction.

<sup>4</sup> Mellor, "Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., III, 291 (1922)

### Silver Perchlorate and Iodine in Ether

**The Principal Materials.**—**SILVER PERCHLORATE.** Three hundred g. of freshly precipitated and most thoroughly washed silver oxide was suspended in about 3 liters of hot water and to this was added, in portions of about 15 cc. each, perchloric acid of 60% strength, which was entirely free from hydrochloric acid. Only about 80% of the calculated amount of perchloric acid was added and the mixture was digested on the water-bath for 10 days. The filtered solution was then diluted to 12 liters and allowed to stand for several days, in order to permit the settling of any silver chloride that might have been dissolved in the conc. silver perchlorate solution. The perfectly clear solution was then concentrated on the water-bath to a very thick sirup; this was further heated in an electric oven at 110°, at 120°, and finally at 135° to 140°. The solid mass was rapidly broken up in a pre-heated mortar, sifted through a pre-heated, 40-mesh sieve, and again dried at 140° to a constant weight. The material was then uniform in composition, white in appearance and free from water. As the salt is extremely hygroscopic, it was kept over phosphorus pentoxide.

**IODINE.**—The iodine, bought as guaranteed to be 99.9% pure, was distilled in a current of steam from a solution of the halogen in pure potassium iodide. It was then dried over sulfuric acid for weeks, and finally was sublimed in a current of dry air. Fortunately, iodine is not hygroscopic.

**ETHER.**—The commercially available ether marked, "distilled over sodium," which is claimed to be suitable for the Grignard reaction, was allowed to stand for several days over an abundance of fresh, bright, metallic sodium. It was then distilled with very gentle heat, the vapors passing through a 12.5cm. column filled with metallic sodium, and the condensate was carefully protected against the moisture in the air. The commercial ether marked "distilled over sodium," however free it may be from alcohol and water, contains some volatile substance that acts slowly upon sodium without evolution of hydrogen, and the metal becomes coated with a yellow layer of spongy material. The impurity, perhaps, is acetaldehyde, or it may be some other volatile substance susceptible to resinification by alkalies. Ether free from such extraneous material was obtained by shaking several times the purified or the ordinary ether with dil. sulfuric acid (1:1), filtering through a column of solid potassium carbonate, and then distilling from potassium carbonate. Ether treated in this manner failed to impart yellow coloration to sodium, even after it had remained for several days in contact with the metal; the sodium after a while became coated with a thin layer of white, transparent gelatinous material, which peeled off readily on shaking the mixture, leaving the metal perfectly bright. The ether was finally redistilled through a column of metallic sodium, and the first fraction rejected. If the contention of Durand<sup>5</sup> be true, that ether gradually reacts with metallic sodium, producing sodium ethylate and butane, then our ether may have contained, in spite of all precautions, a minute amount of butane.

**Procedure in the Preparation and Handling of Chlorine Tetra-oxide.**—About 20 g. of silver perchlorate, in a small weighing bottle, was kept for several hours in the drying oven at 135° to 145°; of this salt, while hot, a portion of 3 to 10 g. was quickly transferred into a pre-heated test-tube, the latter stoppered, and cooled in a desiccator. After it had been weighed, this material was poured into the reaction flask, and a measured amount of purified, freshly distilled ether added. The reaction flasks were Pyrex Florence flasks of 150, 200, or 300cc. capacity.

<sup>5</sup> Durand, *Compt. rend.*, 172, 70 (1921).

according to the experiment, and were fitted with excellently ground glass stoppers of Pyrex glass, the grinding surfaces in mutual contact extending down for 35 to 45 mm. When the progress of the reaction was being studied in its successive stages, the requisite amount of iodine was added by opening at intervals the flask and quickly dropping in weighed amounts of iodine, until finally all had been so transferred. Such procedure, of course, exposed the reaction mixture for brief intervals to the air, but the moisture absorbed from that source could not have been more than the merest trace, owing to the volatility of ether and the consequent outward pressure. When the progress of the reaction was not being followed, all the iodine was added at once—but not directly to the ether, although this may be done provided the mixture be kept in ice water until the halogen has all gone into solution. Usually, the entire weighed amount of iodine was placed in a small glass basket supported on a stem long enough to keep the capillary opening at the bottom of the basket sufficiently above the surface of the ether. The basket consisted of a test-tube 1.5 cm. wide and 3 cm. long, to the bottom of which was sealed the supporting stem. Attached to the bottom of the basket was also a short capillary tube, 0.5 cm. long, of bore so narrow that crystals of the solid iodine could not drop through. By inclining the flask at intervals until the capillary opening just touched the surface of the ether, an amount of iodine could be leached out each time sufficient to keep up the progress of the reaction. During the intervals between the successive additions of iodine the flask was kept rotating on an inclined revolving table. As silver perchlorate is soluble in ether only to a limited extent, the amount of solvent was seldom, if ever, enough to dissolve from the start all the perchlorate in the flask. A few sharp-edged pieces of glass rod were, therefore, placed in the flask, in order to comminute the salt, and thus make it dissolve more rapidly in the ether as the reaction progressed. This also served to prevent the crystals of the perchlorate from becoming completely coated with a dense crust of silver iodide.

In the earlier experiments, the amount of iodine added was strictly equivalent to the quantity of silver perchlorate taken. It became evident, however, that to add so much was inadvisable, because an appreciable amount of iodine was usually left unacted upon. The procedure was then so changed that towards the end of the reaction the iodine was added to the colorless solution a little at a time, the supposed end-point being indicated by the permanency of the iodine color in the reaction mixture; but this procedure also proved to be unsatisfactory, and there was reason to believe that the true end-point was reached some time prior to the apparent end-point. Finally, the method adopted was as follows. Enough silver perchlorate was taken to make a 0.1 *N* to 0.12 *N* solution, and a little less than the theoretical amount of iodine was added in the

basket. After all of the iodine had been taken up—after 10 to 24 hours on a shaking machine—the clear solution was siphoned into another flask, leaving behind the insoluble silver salts. The slight amount of silver perchlorate still present in the ether was carefully determined using a small sample of the latter, and then exactly the calculated amount of iodine was added to the solution. At the end of the reaction the solution usually contained no silver perchlorate and was colorless or only faintly yellow. The reaction mixture was protected from exposure to light throughout the whole of the experiment.

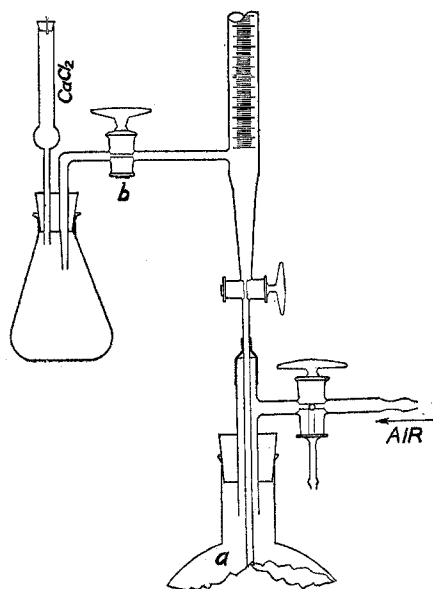


Fig. 1.

with a buret arranged as illustrated in Fig. 1. The ether solution was forced into the buret by means of carefully dried air, any accidental suspension of silver iodide was allowed to settle, and the clear liquid was drawn off through Stopcock *b* in portions of 20 to 30 cc., into small Erlenmeyer flasks which were provided with finely ground glass stoppers.

**Manner of Stating the Results.**—As it proved impossible to isolate chlorine tetra-oxide from its dilute ether solution, it became imperative to find out what other products were formed through side-reactions, and to what extent they were produced. Consequently, the experiments were carried out on a strictly quantitative basis. For purposes of ready comparison, all reactions are interpreted in terms of normality factors, the unit being 0.1 *N*. It may be added, that as the molar weight of chlorine tetra-oxide is 99.8, a 0.1 *N* solution is almost exactly a 1% solution. Similarly, a 0.1 *N* solution of silver perchlorate contains 2.07% of the silver salt.

Solutions thus obtained which, presumably, should have contained nothing but chlorine tetra-oxide were, however, found to contain extraneous material that interfered in the study of the properties of the new oxide of chlorine. After the nature of this by-product had been determined further changes in the procedure of preparing chlorine tetra-oxide were introduced, designed to remove the impurity. These supplemental changes are described under "Elimination of the By-products."

The following simple arrangement was used for sampling the ether solution for studying the reactions of chlorine tetra-oxide, qualitatively or quantitatively. The flask *a*, containing the reaction product, was connected, as rapidly as possible,

The system of designating all reactions and products in 0.1 *N* factors has been applied, not merely to those products which are actually in solution, but as if they were all in solution. For instance, if 7.25 g. of silver perchlorate and 150 cc. of ether are taken in an experiment, the "total silver perchlorate" present is  $2.331 \times 0.1 N$ , and the "soluble S. P." is, according to the temperature, from 0.75 to  $0.85 \times 0.1 N$ . Suppose now, that 30% of the calculated amount of iodine has been added and after the disappearance of the iodine color, 5 cc. of the solution has been removed for a test and found to take up 1.6 cc. of 0.1 *N* potassium thiocyanate, then the new ether system is: "Sol. S. P.,"  $0.320 \times 0.1 N$ ; "total S. P.,"  $\frac{(2.331 \times 150) - (0.320 \times 5)}{145} = 2.400 \times 0.1 N$ ; chlorine tetra-oxide and silver iodide should each be  $0.699 \times 0.1 N$ , provided there were no side-reactions. With every removal of a portion of the solution, and with every addition of solvent or of reactants, appropriate corrections must be made for each component of the newly established system. In this way one can tell what concentration of chlorine tetra-oxide should finally result. A comparison of the calculated amount with that actually obtained in the experiment, reveals at once the fact whether, and to what extent, by-products have been formed.

In view of the exacting nature of the operations required in preparing chlorine tetra-oxide, the effort was made to utilize each such preparation for various experiments, which did not necessarily have direct relation to each other. Hence, the same serial experiment number appears in different tables in which the experimental results are summarized. The number refers in each table to the particular preparation of chlorine tetra-oxide; about 50 such preparations were made for purposes of quantitative work.

**Decrease in Solubility of Silver Perchlorate with Increase of Amount of Chlorine Tetra-oxide.**—Silver perchlorate was found to be soluble in absolute ether to the extent of about  $0.75$  to  $0.90 \times 0.1 N$ , at ordinary room temperature. These wide variations can be accounted for in several ways. First, the influence of temperature is quite appreciable. In boiling ether, silver perchlorate is only about 40% as soluble as it is in the same solvent at  $27^\circ$ , and yet the difference in temperature is only  $7^\circ$ . The perchlorate forms with ether a very loose, easily dissociable compound; it is not unlikely that this etherate, fairly soluble at lower temperature, loses ether at higher temperatures and the salt is less soluble than the etherate.<sup>6</sup> A second cause for the variation in the solubility of silver

<sup>6</sup> In one experiment, a solution of silver perchlorate was evaporated to dryness under reduced pressure at room temperature. The residue consisted of well-formed, long, needle-like crystals. While this residue was being weighed, pressure suddenly developed within the flask, ether vapors were given off, and the crystals spontaneously broke up into an opaque powder. The loss in weight occasioned by this phenomenon was about 0.070 g. per g. of the salt.

perchlorate is the fact that perchlorates have a pronounced tendency to form supersaturated solutions in organic solvents, and these come to an equilibrium with extreme slowness.

It was found that the speed of the reaction between silver perchlorate and iodine commenced to slow down appreciably after an amount of iodine had been added to produce about  $0.5 \times 0.1 N$  of chlorine tetra-oxide. We have obtained  $2.5 \times 0.1 N$  and  $3 \times 0.1 N$  solutions, but it required in such cases several days of continuous shaking to complete the reaction. As an illustration, in one experiment (No. 15) with 145 cc. of ether and silver perchlorate to make a solution  $1.77 \times 0.1 N$ , the first addition of iodine, equivalent to  $0.5 \times 0.1 N$ , was used up in 1 hour; the next portion, additional  $0.32 \times 0.1 N$ , disappeared in 2 hours; the third addition,  $0.60 \times 0.1 N$ , required almost a day. This progressive decrease in the speed of the reaction found its explanation in the proportionate decrease in the solubility of silver perchlorate with the increase in the concentration of chlorine tetra-oxide in the ether. This peculiar influence upon the solubility of the salt has been verified repeatedly, using various mechanical devices to induce thorough agitation in the intervals between the additions of iodine, and continuing the agitation for as long as 3 to 6 hours each time. In the following table are collected some of the results obtained. During the course of each experiment, at intervals, samples of 5 cc. of the ether solution were taken out for the determination of the amount of silver perchlorate dissolved therein; to the remaining solution was added a definite additional amount of iodine, and in some instances a slight additional amount of ether.

In the third column in the table is given the total amount of silver perchlorate taken for the experiment; in the fourth column, the concentration of chlorine tetra-oxide, calculated as if equivalent to the amount of iodine that was added. The actual amount of chlorine tetra-oxide is, as will be shown later, about 85 to 90% of that so calculated. In the fifth column will be found the amount of silver perchlorate still remaining as such, the figures being obtained by subtracting the figures in Col. 4 from the corresponding figures in Col. 3. The figures in Col. 6 were obtained directly by titration.

It is apparent that silver perchlorate becomes so very slightly soluble in ether when the concentration of chlorine tetra-oxide reaches a little over  $0.1 N$ , that it is not practicable to carry the reaction further than that concentration. We are, however, at a loss to explain this remarkably depressing influence on the solubility of the silver salt. It cannot be that the latter forms an insoluble double compound with chlorine tetra-oxide. Were that the case, then the amount of chlorine tetra-oxide left in the ether should be much less than that calculated from the quantity of iodine, but this is not the case. The phenomenon is the more puzzling, since,

when the ether solution is decanted upon fresh solid silver perchlorate, the depressing influence is wanting, and the solubility of the salt reaches normal values of  $0.75$  to  $0.90 \times 0.1 N$ . The cause, consequently, must be sought in some kind of mechanical change in the perchlorate salt it-

TABLE I  
INFLUENCE OF CHLORINE TETRA-OXIDE UPON THE SOLUBILITY OF SILVER PERCHLORATE

Expt.	Vol. of solution Cc.	Total AgClO <sub>4</sub> taken $\times 0.1 N$	Iodine taken and (ClO <sub>4</sub> ) <sub>2</sub> produced $\times 0.1 N$	AgClO <sub>4</sub> unreacted $\times 0.1 N$	AgClO <sub>4</sub> in solution in the ether $\times 0.1 N$
24	75	1.994	0.000	1.994	0.795
	70	2.079	0.222	1.857	0.930
	65	2.167	0.547	1.620	1.020 (?)
	65	2.088	0.771	1.317	0.680
	65	2.036	1.000	1.036	0.140
	55	2.393	1.279	1.114	0.000
25	150	1.569	0.000	1.569	0.730
	145	1.598	0.264	1.334	0.962
	140	1.621	0.547	1.074	0.670
	140	1.597	0.813	0.784	0.230
	140	1.589	1.064	0.525	0.035
	140	1.587	1.299	0.288	0.012
26	275	1.203	0.000	1.203	0.870
	270	1.209	1.063	0.146	0.030
38	160	1.747	0.000	1.747	0.870
	210	1.317	1.201	0.116	0.060
	205	1.341	1.248	0.093	0.030
	205	1.340	1.237	0.103	0.000
39	206	1.667	1.296	0.371	0.023
40	220	1.529	1.235	0.294	0.042
	214	1.312	1.177	0.135	0.040
	204	1.312	1.212	0.100	0.000
41	213	1.610	1.326	0.284	0.040
45	260	1.418	0.000	1.418	0.810
	255	1.430	1.178	0.252	0.044

self, effected during the course of the reaction, and one that militates against the solubility of the salt in ether. We have observed, not infrequently, that the silver iodide came down, not in the usual amorphous form, but in white, perfectly transparent crystalline grains, plainly visible as such to the naked eye. If these crystals do not represent a metastable modification of silver iodide, then perhaps they constitute mixed crystals of the iodide and the perchlorate which are insoluble in ether and which resist mechanical disintegration by the beads in the flask. Upon exposure to air, or upon the addition of water, the crystalline appearance is lost and the usual, amorphous, yellow silver iodide is produced. This matter deserves further investigation.

**Silver Chloride as a By-product in the Reaction.**—The circumstance that silver perchlorate, even when used in the practicable amounts of



0.1 *N* concentrations, invariably took up somewhat less than the calculated amount of iodine, is explained by the fact that, in addition to silver iodide, some silver chloride was also produced in the reaction. That the chloride did not result from photochemical decomposition of a portion of the silver perchlorate into silver chloride and oxygen, was proved by blank experiments: a solution of the salt in ether, with no iodine added, gave no silver chloride after a week's exposure to diffused daylight. Nor did it seem probable that chlorine tetra-oxide itself was undergoing appreciable decomposition into chlorine and oxygen, whereupon the liberated chlorine, if so produced, would react with some silver perchlorate. A solution of the tetra-oxide, decanted upon fresh silver perchlorate, was allowed to stand for several days, but only a trace of silver chloride was formed. The conclusion that the silver chloride must be formed in the course of the reaction between the perchlorate and iodine, was confirmed by experiment. It was found that the formation of silver chloride commences actually with the first addition of iodine, and that the amount of the chloride increases as more iodine is added.

**Secondary Precipitation of Silver Iodide.**—The following phenomenon was not infrequently encountered. When the dilute ether solution of chlorine tetra-oxide was being siphoned from the mixture of the silver iodide and the undissolved silver perchlorate, the perfectly clear solution would suddenly begin to grow opaque and a fine suspension of silver iodide would appear. This secondary precipitation of silver iodide, as well as occasionally also a similar tertiary precipitation, were especially pronounced in those instances when the reaction mixture, prior to being siphoned off, was throughout carefully protected from light. Is some colloidal silver iodide held in solution, and is it coagulated on exposure to light or air, or by merest traces of moisture? This possible explanation had to be abandoned soon.

**The Presence of a Colorless, Unstable Iodo Compound.**—After the occurrence of the secondary precipitation, the ethereal solution was, as a rule, free from dissolved silver salts; but, although colorless previously to the formation of the secondary precipitate, the solution then frequently showed the presence of some free iodine. The amount of the latter varied in different experiments, but was seldom more than  $0.05 \times 0.1 N$ , or about 0.0006 g. in 1 cc. of the solution. Upon the addition of water to the ether solution, a slight additional quantity of iodine was set free. Manifestly, a small amount of a colorless, very sensitive iodo compound was present which, through photochemical or some other influence, readily liberated iodine. If the ether happens to contain at the same time some silver perchlorate in solution, then secondary precipitation of silver iodide will ensue; if no silver perchlorate be present, or if the amount of iodine liberated should happen to be in excess of that equivalent to the silver

in solution, then the ether solution, after the secondary precipitation of silver iodide, will contain some free iodine.

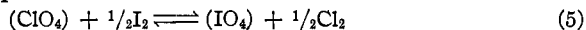
What is the nature of this unstable iodo compound? At first it was assumed that it is iodine perchlorate.



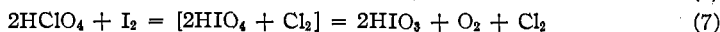
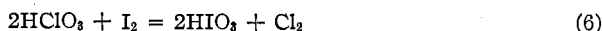
A reaction of this nature would be not unlike that which is known to occur with some other silver salts: silver pyrazole gives with iodine iodo-pyrazole instead of di-pyrazyl,<sup>7</sup> and silver indazole in ether gives, upon treatment with iodine, iodo-indazole<sup>8</sup> instead of the anticipated di-indazyl.

The presence of a compound so unstable, as the hypothetical iodine perchlorate might presumably be, would indeed account for the ready photochemical liberation of iodine, but it would not explain the formation of silver chloride. Consequently, this view concerning the constitution of the sensitive iodo compound was abandoned for what seemed to be a more plausible explanation.

**Probable Formation of Iodine Tetra-oxide.**—The occurrence of all the various disturbing phenomena and by-products that have been mentioned in the preceding paragraphs appeared readily explained on the hypothesis that an equilibrium in the sense,



was being set up as soon as an appreciable concentration of chlorine tetra-oxide had been reached. The chlorine which is being liberated would merely set free from silver perchlorate an additional slight amount of chlorine tetra-oxide, and thus the formation of silver chloride would be fully accounted for. The iodine tetra-oxide, presumably unstable, would satisfactorily account for the photochemical liberation of iodine and the consequent reaction following in the train, namely, the secondary precipitation of silver iodide. Moreover, the presence of a residual slight amount of this unstable colorless iodo compound in the ether would account for the fact that the solution, after the secondary precipitation of silver iodide, liberates a still further quantity of iodine when it comes into contact with water or with metals. Such a reaction between chlorine tetra-oxide and iodine would, after all, only be analogous to similar reactions that are known to occur between chloric acid and iodine,<sup>9</sup> and between perchloric acid and iodine.<sup>10</sup>



<sup>7</sup> Buchner and Fritsch, *Ann.*, **273**, 264 (1893).

<sup>8</sup> Auwers, *Ber.*, **55**, 1143 (1922).

<sup>9</sup> Kammerer, *Pogg. Ann.*, **138**, 227 (1871). Lamb, Bray and Geldard, *This Journal*, **42**, 1636 (1920).

<sup>10</sup> Kammerer, *J. prakt. Chem.*, [1] **90**, 190 (1863); *Pogg. Ann.*, **138**, 390 (1869). Friend, "Textbook of Inorganic Chemistry," Griffith and Co., London, **8**, 248 (1915). Michael and Conn, *Am. Chem. J.*, **25**, 89 (1901).

It is of no consequence for our present discussion that the reactions between chloric or perchloric acid and iodine are not metathetical, but rather oxidation reactions.<sup>11</sup> It is sufficient that these reactions do occur with the chlorate ion and the perchlorate ion. Consequently, we may well assume that a reaction of this nature between the chlorine tetra-oxide and iodine (Equation 5) is also quite probable.

On the basis of the above hypothesis it is obvious that silver chloride on the one hand and iodine tetra-oxide on the other should be produced in equivalent amounts. The former product can be readily estimated directly as such; but the latter, only indirectly, through the summation of its decomposition effects, namely, (a) the quantity of the silver iodide in the secondary precipitation, (b) the residual free iodine present thereafter in the ether, and (c) the still further quantity of iodine, or iodides, producible on the addition of water to the ether solution.

Experiments designed to test the quantitative relation between silver chloride and iodine tetra-oxide gave most satisfactory evidence in support of the above hypothesis. The ether solution was protected from light throughout the period of the reaction between silver perchlorate and iodine. The clear solution was quickly siphoned from the insoluble silver salts into a fresh flask and was exposed to sunlight or strong electric light, and then carefully dried air was passed through the solution for a few minutes. After the newly formed silver iodide had settled, the solution was again siphoned over into a fresh flask, leaving behind for estimation, the secondarily precipitated silver iodide, designated in Table II as  $\text{AgI}_{\text{sp}}$ . To the decanted ether solution was added about 0.5 g. of finely divided, so-called molecular, silver and the mixture was shaken until the color of iodine disappeared; the amount also of this new silver iodide,  $\text{AgI}_{\text{ms}}$ , was determined. An aliquot portion of the now colorless ether solution was allowed to stand for a day over a measured amount of 0.1 *N* aqueous silver nitrate solution, and the quantity of silver iodide thus formed,  $\text{AgI}_{\text{et}}$ , determined. These 3 precipitates of silver iodide contain together all of the iodine that originally existed as iodine tetra-oxide. The assumption is made that no appreciable decomposition of iodine tetra-oxide had occurred during the period when the ether solution was being protected from light.

Below is given a table covering some of the experiments. On the whole the agreement in the amounts of silver chloride and the iodine tetra-oxide is quite satisfactory, considering the unavoidable errors in the estimation of the latter, especially those errors which are likely to occur in siphoning the solution from one flask into another. The order of magnitude of the two products is always the same: when the silver chloride is comparatively high, the iodine tetra-oxide is also similarly high, and *vice versa*. Ordinarily, this side reaction amounts to 10 to 12% of the main reaction, the

<sup>11</sup> See the discussion on p. 385 of Ref. 4.

amount of silver chloride increasing with increase in the concentration of the chlorine tetra-oxide. Expts. 42, 43 and 45 were made particularly to test the effect of light on the extent to which the side-reaction had taken place. In Expt. 42, the reaction mixture was illuminated throughout the whole operation; in the other two, it was carefully protected from light up to the period of induction of the secondary precipitation of silver iodide. The evidence is obviously not sufficient to warrant definite deductions therefrom.

TABLE II  
QUANTITATIVE RELATION BETWEEN SILVER CHLORIDE AND IODINE TETRA-OXIDE

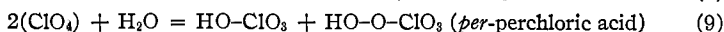
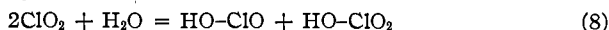
Expt.	Volume of solution Cc.	Total I added $\times 0.1 N$	$AgI_{sp}$ $\times 0.1 N$	$AgI_{ms}$ $\times 0.1 N$	$AgI_{et}$ $\times 0.1 N$	$(IO_4)_x$ calc. $\times 0.1 N$	$AgCl$ found $\times 0.1 N$
21	250	....	....	....	0.105	0.105	0.143
23	75	....	0.084	0.028	....	0.052	0.136
25	140	1.255	....	....	0.072	0.100	0.081
26	223	1.082	0.021	0.010	0.036	0.067	0.068
27	325	0.641	0.000	0.024	0.011	0.035	0.045
28	160	1.063	0.042	0.030	0.053	0.125	0.094
30	147	1.259	0.082	0.043	0.050	0.175	0.139
37	215	0.776	0.025	....	0.018	0.043	0.083
38	205	1.237	0.026	0.038	0.061	0.125	0.163
39	215	1.074	0.057	....	0.070	0.127	0.127
40	209	1.212	0.041	0.027	0.072	0.140	0.162
41	205	1.249	0.041	0.051	0.050	0.142	0.164
42	106	1.069	0.079	0.000	0.058	0.137	0.118
43	185	1.527	0.070	0.023	0.120	0.213	0.198
45	240	1.178	0.044	0.080	0.039	0.163	0.118

**Elimination of the By-products.**—With the recognition of the nature of the side-reaction, the process of preparing chlorine tetra-oxide was so modified as to eliminate as much as possible of the unstable iodo compound. The new procedure consisted in taking invariably an excess of silver perchlorate, and adding in the basket enough iodine to make about 0.1 *N* solution in the ether. After all the iodine had disappeared, the solution was siphoned into another flask and exposed to light for about  $\frac{1}{2}$  hour. Five cc. of the perfectly clear solution was forced into the pipet and the amount of silver perchlorate in the sample estimated. Just the exact amount of iodine to react with the silver perchlorate was then added to the rest of the solution. After the mixture had stood, perfectly dry air was passed into the solution, in order to break up as much more of the iodine tetra-oxide as possible. In case the solution then showed more than a faintly pink color, molecular silver was added and the mixture shaken until practically all of the iodine had disappeared. The solution was then made up to a definite volume and, if not used at once, was siphoned from the mixture of the silver iodide and the metallic silver into another flask. In that way, about  $\frac{2}{3}$  of all the iodine tetra-oxide was eliminated,

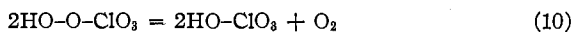
leaving still in the solution enough of the iodo compound to be equivalent to 0.02 to 0.05  $\times$  0.1 *N*, that is, 0.0002 to 0.0005 g. of iodine in 1 cc. of the ether solution. We know of no means of eliminating this last fraction, and in all our quantitative experiments with the chlorine tetra-oxide solutions a corresponding correction was introduced. The solution can be kept several days without apparent deterioration.

### Reactions of Chlorine Tetra-oxide

**Hydrolysis.**—When the ethereal solution of chlorine tetra-oxide is shaken with water, the tetra-oxide is at once hydrolyzed and a corresponding amount of perchloric acid appears in the aqueous layer. It might be expected that the primary course of hydrolysis in this case would be similar to the hydrolysis of chlorine dioxide.

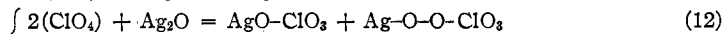
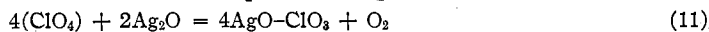


While, however, the dioxide hydrolysis is, as Bray<sup>12</sup> found, exceedingly slow unless alkali be present, with the tetra-oxide the hydrolysis is rapid and complete in pure water. The hypothetical *per*-acid of perchloric acid is not likely to prove to be very stable. It should gradually suffer decomposition as follows.



The aqueous solution of chlorine tetra-oxide indeed possesses oxidizing power and liberates iodine from hydriodic acid. Perhaps the difficulties encountered in obtaining a sharp end-point when titrating the products of hydrolysis of chlorine tetra-oxide with alkali may have been due to the oxidizing effect of the *per*-perchloric acid on the indicators. Additional evidence concerning the probable formation of this acid is given under the reaction of chlorine tetra-oxide on silver oxide.

**Reaction with Silver Oxide.**—Chlorine tetra-oxide reacts quantitatively with silver oxide and gives rise to salts soluble in ether. As with water, so in the reaction with silver oxide, there are two possibilities: the formation of silver perchlorate may take place either in one step, as in Equation 11, or in two steps, as in Equations 12 and 13.



Ethereal solutions of chlorine tetra-oxide were added to a suspension of dry silver oxide in a known amount of ether, the combined 2 volumes of the ether, in each of the experiments, 30, 39, 40 and 45, of Table III, being more than ample to hold in solution all of the silver perchlorate that could possibly be formed. After 24 to 40 hours' standing, with frequent shaking, the ether solution was removed by filtration with suction,

<sup>12</sup> Bray, *Z. anorg. Chem.*, **48**, 221 (1906).

and the insoluble residue was washed first with ether, then with water. The amount of silver salts dissolved in each of the two solvents was determined separately. In Table III are given some of the results, indicating, first, the concentration of the chlorine tetra-oxide in contact with the silver oxide, and second, the relative distribution of the resulting silver salts, that is, the amount dissolved in the ether and that quantity which remained undissolved in the volume of ether used, but dissolved in water, allowance having been made for the slight solubility of the oxide itself. Obviously, such relative distribution is bound to vary somewhat in different experiments, for the results depend upon the concentration of the salts and upon the quantity of ether employed in washing the undissolved residue.

TABLE III  
FORMATION OF SILVER SALTS FROM CHLORINE TETRA-OXIDE

Expt.	Volume of sample Cc.	Conc. of (ClO <sub>4</sub> ) <sub>2</sub> × 0.1 N	Distribution of silver salts	
			Dissolved in ether %	Dissolved in water %
30	30	0.587	87	13
39	45	0.458	78	22
40	45	0.593	84	16
45	55	0.468	84	16
			× 0.1 N	
38	20	1.177	0.835	
41	30	1.135	0.903	
43	20	1.220	0.900	

Expts. 38, 41 and 43 show clearly that in the other four experiments, 30, 39, 40 and 45, there was more than sufficient ether present in each case to keep in solution amounts of silver perchlorate equivalent to the chlorine tetra-oxide in these 4 samples. Consequently, unless we attribute the apparent insolubility in these instances to partial adsorption of silver perchlorate on the solid silver oxide, we must conclude that some other salt than the perchlorate is present in the ether, and one which is less soluble in ether. Whether this is really silver *per*-perchlorate, must remain merely a plausible working hypothesis until the time when the salt shall be actually isolated and its composition determined by analysis.

**Liberation of Iodine from Iodides.**—An ethereal solution of chlorine tetra-oxide added to an aqueous solution of potassium iodide sets free iodine at once; the amount of the latter increases on standing, reaching a maximum in a few hours. The oxidizing effect, however, is not at all what is to be expected from the reaction as in Equation 14.



Instead of one equivalent of iodine being set free for each ClO<sub>4</sub>, only about 1/4 to 1/3 of that amount is found; nor were the results different when, instead of an aqueous potassium iodide solution, a suspension of finely

divided cadmium iodide in ether was employed, in which the cadmium salt is slightly soluble. With ethyl iodide in ether no iodine is set free.

Whether the low results for iodine are due to the partial decomposition of the *per*-perchloric acid with liberation of free oxygen as such, or whether the oxidation proceeds partially to form iodic acid, as Bray<sup>13</sup> found to be the case with chlorine dioxide,  $\text{ClO}_2$ , under certain conditions, must remain undecided for the present.

**Reaction with Metals.**—Chlorine tetra-oxide combines directly with many metals, and the corresponding perchlorates result. The velocity and the completeness of the reaction must depend, among other factors, upon the solubility in ether of the respective perchlorates. With metals of constant valence the reaction may readily serve as a method of estimating the chlorine tetra-oxide quantitatively.

*Zinc.*—With zinc, the reaction manifests itself as soon as the metal is introduced into the ether solution. The solution becomes pink, because of the reduction to free iodine of the residual small amount of iodine tetra-oxide, and the metal becomes coated with a yellow, sirupy layer of zinc perchlorate, but this soon dissolves completely. There is also an appearance of some gas production during the first few minutes. Whether hydrogen was really being produced in this case, or whether the minute bubbles result from local overheating of the ether in consequence of the chemical reaction between the metal and chlorine tetra-oxide, was difficult to determine with certainty. When the metal was allowed to remain long in contact with the ether solution, zinc chloride was produced, in addition to the perchlorate and a small quantity of the iodide, in proportion to the time the zinc remained in the ether. The amount formed, however, was never large, and even after 8 days' standing it never constituted more than 7 to 10% of the quantity of the perchlorate. It appears quite likely that the chloride results not from the direct reduction of the chlorine tetra-oxide, but rather from the reduction of zinc perchlorate by the metal. Bray<sup>14</sup> came to the same conclusion in his work on the reaction between chlorine dioxide and metals, in presence of water.

For quantitative purposes, 20 to 30 cc. of the tetra-oxide solution was drawn into a small flask, a weighed bar of zinc about 5 mm. in diameter and 4 cm. long was quickly introduced and the flask set aside for 24 to 48 hours. The loss in weight of the metal was determined; the ether solution was then allowed to evaporate over an aqueous standard solution of silver nitrate, and the amounts of the chloride ion and iodide ion determined. The total loss in weight of the zinc, minus the loss equivalent to the formation of zinc iodide, was taken as due to the formation of zinc perchlorate. No correction was made for the formation of zinc chlor-

<sup>13</sup> (a) Bray, *Z. physik. Chem.*, **54**, 731 (1905); (b) Ref. 12, p. 217.

<sup>14</sup> Ref. 13a, p. 592.

ide, for it was assumed that the chloride represented what initially was zinc perchlorate.

*Magnesium.*—The reaction with magnesium is similar to that with zinc. The gas production, following for a brief interval the introduction of the metal, is more noticeable than in the case of zinc, but in this instance also it subsides at once when the liquid is cooled. Here again, some residual iodine tetra-oxide in the ether is reduced to free iodine as soon as the metal is introduced but, unlike the case with zinc, the iodine is not taken up by the magnesium. Presumably, the failure of our magnesium to combine with the iodine must be ascribed to the fact that the metal we used, square bars 5 mm. in diameter with polished smooth surfaces, offered less favorable conditions for combination than those which prevail in a Grignard reaction. The total loss in weight of the metal was taken as that which had combined with the chlorine tetra-oxide, the reduction to the chloride being less than in the case of zinc.

*Copper.*—When a spiral of bright copper wire is dropped into the ethereal solution of chlorine tetra-oxide in a test-tube, the metal rapidly becomes coated with a white layer of cuprous perchlorate, which readily peels off and settles at the bottom of the tube as a crystalline white powder. Later the cuprous salt in its turn begins to unite with more chlorine tetra-oxide and gives rise to cupric perchlorate, which is soluble in ether and colors the solution green. Söderbäck found that the reaction between copper and thiocyanogen proceeds also in this manner—initially the cuprous salt alone is produced and ultimately that and the cupric salt are formed. The overlapping in the formation of the two copper salts precluded the use of copper as an agent in the quantitative estimation of chlorine tetra-oxide. The loss in weight of the metal has been found to fall somewhere between the losses calculated for cuprous and cupric perchlorate.

Cuprous perchlorate has never, to our knowledge, been described. The white crystalline salt was washed with ether and dried.

Subs., 0.0910: CuO, 0.0450. Calc. for  $\text{CuClO}_4$ : Cu, 38.99; calc. for  $\text{Cu}(\text{ClO}_4)_2$ : Cu, 24.22. Found: 39.51.

With *tin* and with *iron* the reaction proceeds quite readily. Just as with copper, two series of salts are finally produced; stannous and stannic, and ferrous and ferric perchlorates, respectively.

With *cadmium*, the reaction is much slower than with zinc. With *bismuth*, it proceeds only to the extent of about 20% in 24 hours, and with *lead* it is even slower, the metal becoming coated with a brown-yellow deposit.

With metallic *silver*, chlorine tetra-oxide reacts only to the extent of 10% even after the solution has been shaken with molecular silver for several days on the shaking machine. This is surprising in view of the fact that the resulting perchlorate is soluble in ether.



**Quantitative Estimation of Chlorine Tetra-oxide.**—The amount of chlorine tetra-oxide which may be formed in a given experiment may be calculated: (a) from the silver perchlorate, or (b) from the iodine. The amount of silver perchlorate that has been converted into chlorine tetra-oxide is obtained by subtracting from the initial total amount of the salt taken, first, that quantity of it which has not entered into reaction at all and which, consequently, can be dissolved by water from its admixture with the silver halides, and second, that amount which has been converted into silver chloride. Having kept account of the exact amount of ether used in each stage of the operation, one can now calculate the final concentration of the chlorine tetra-oxide that must result.

In calculating, with iodine as the starting point, the anticipated yield of chlorine tetra-oxide, it is necessary to bear in mind that only a portion of the iodine existing as iodine tetra-oxide regenerates, through the secondary precipitation of silver iodide, an equivalent amount of chlorine tetra-oxide; that portion, however, which appears in Table II as  $\text{AgI}_{\text{ms}}$  and  $\text{AgI}_{\text{et}}$ , is lost as far as production of chlorine tetra-oxide is concerned. Hence, the sum of these latter 2 iodine fractions only is to be subtracted from the total iodine taken, in arriving at the equivalent quantity of the anticipated chlorine tetra-oxide.

In Table IV are summarized some of the results obtained, including the total amounts of the reactants, the calculated yields of chlorine tetra-

TABLE IV  
QUANTITATIVE ESTIMATION OF CHLORINE TETRA-OXIDE

Expt.	Total reactants		(ClO <sub>2</sub> ) <sub>2</sub> calc. from		(ClO <sub>2</sub> ) <sub>2</sub> found through reaction with			Ag <sub>2</sub> O × 0.1 N
	AgClO <sub>4</sub> × 0.1 N	Iodine × 0.1 N	AgClO <sub>4</sub> × 0.1 N	Iodine × 0.1 N	H <sub>2</sub> O × 0.1 N	Zn × 0.1 N	Mg × 0.1 N	
26	1.088	1.082	1.020	1.036	1.129	0.898	1.039	...
27	0.638	0.641	0.593	0.606	0.660	0.526	0.617	0.600
28	1.055	1.063	0.961	1.010	...	1.079	1.079	0.985
30	1.298	1.259	1.159	1.166	1.302	1.238	1.307	1.173
37	0.813	0.776	0.730	0.758	0.800	0.756	0.691	0.695
38	1.340	1.237	1.177	1.138	1.187	1.140	1.155	0.835
39	1.169	1.074	1.042	1.004	1.045	1.093	1.051	1.030
40	1.311	1.212	1.149	1.113	1.162	1.128	1.135	1.068
41	1.306	1.249	1.142	1.148	1.143	1.169	1.096	1.135
42	1.125	1.069	1.007	1.011	1.004	1.023	1.003	...
43	1.486	1.484	1.294	1.341	1.337	1.256	1.308	1.222
45	1.165	1.178	1.047	1.059	1.035	1.033	1.039	1.030

oxide on the basis of the corrections discussed above, and finally the actual amounts of chlorine tetra-oxide, as obtained from its four principal reactions: with water, zinc, magnesium and silver oxide.

It will be noticed that the theoretical yields calculated by the two independent methods agree among themselves quite well; that the agree-

ment in the quantities of chlorine tetra-oxide, as determined by the four different methods, is also quite satisfactory; and that the concentrations, as determined experimentally, are very close to those calculated, usually within 5%. The conclusion, therefore, is justified that, except for the slight formation of iodine tetra-oxide, practically no side reactions occur in this method for the preparation of chlorine tetra-oxide.

**Molecular Weight.**—The indirect method was employed, a method which has given dependable results with organic free radicals<sup>15</sup> and with thiocyanogen.<sup>16</sup> The plan was to determine the elevation in the boiling point of ether with silver perchlorate as the solute, then add the requisite amount of iodine to the same solution and redetermine the boiling point after the reaction had taken place. Obviously, no change in the boiling temperature of the solution should occur in case silver perchlorate and chlorine tetra-oxide are both monomolecular, since the resulting silver iodide, being insoluble in ether, would exert no influence.

We used the elegant method recently described by Menzies and Wright,<sup>17</sup> employing their differential thermometer and the boiling-point tube, the latter, however, supplied at the upper end with a stopper and a calcium chloride tube so as to protect the solution from moisture in the air.<sup>18</sup> The boiling point of a sample of freshly distilled ether was determined in terms of the differential thermometer. The flask was then emptied and refilled with a solution of silver perchlorate in ether of the same origin; but no sooner was heat applied, then precipitation of the crystalline salt commenced, and in order to keep the salt in solution, it was found necessary to add an amount of ether that reduced the concentration of the perchlorate from 0.667 to  $0.381 \times 0.1 N$ . Unfortunately, with that low concentration of the boiling solution the reading on the differential thermometer differed by only 2 mm. from that when the pure solvent was used, which was equivalent to an elevation of the boiling point of  $0.06^\circ$ . The addition of iodine to the perchlorate solution did not alter materially the boiling temperature, the reading on the thermometer being almost exactly the same for the colorless chlorine tetra-oxide solution as for the silver perchlorate solution.

<sup>15</sup> Gomberg and Cone, *Ber.*, **37**, 2037 (1904).

<sup>16</sup> Lecher and Goebel, *ibid.*, **54**, 2223 (1921).

<sup>17</sup> Menzies and Wright, *THIS JOURNAL*, **43**, 2314 (1921).

<sup>18</sup> We have found it desirable to modify the manner of hanging the lift pump on the lower end of the thermometer. The fragile three-legged prong was removed altogether; a loosely fitting glass tube about 2cm. long and notched, oppositely, at each end, was slipped over the lower end of the thermometer, and into the upper end of this tube was inserted the ejecting end of the pump. This arrangement shielded the longer arm of the thermometer from the spray of the hot solution. This is, we believe, an important precaution when, as in our case, the difference in the level in the two arms of the thermometer happens to be comparatively slight.

*Data.*—Volume of ether at b. p., 55.5 cc. Boiling temp., 34.4°. Conversion factor, 1 mm. = 0.03222°.  $K_2$ , for one mole of solute in 100 cc. of ether, 31.1. Solute, silver perchlorate, 207.3.

Diff. therm. reading (zero), 11 mm. Silver perchlorate, 0.4428 g. Diff. therm. reading (above zero), 12.9 mm. After 0.1770 g. iodine added, 13.0 mm. After 0.0690 g. iodine added, 13.0 mm.

$$\text{Mol. wt. of silver perchlorate} = \frac{31.1 \times 0.4428}{0.03222 \times 1.9 \times 55.5} = 407.5.$$

An elevation in boiling point of 0.06° by the ebullioscopic method, does not furnish a reliable basis for deduction. Nevertheless, in view of the fact that silver perchlorate is, according to Hill,<sup>19</sup> associated in benzene at the freezing point of the latter, it may be concluded from our results that in ether also the salt exists largely as the bimolecular compound, (AgClO<sub>4</sub>)<sub>2</sub>. Since the addition of 90% of the calculated amount of iodine did not materially affect the boiling point of the solution, it must be further inferred that chlorine tetra-oxide is presumably of the same order of association, and that its formula is (ClO<sub>4</sub>)<sub>2</sub>. Obviously, the limited data permit at present only a tentative conclusion, and nothing can be said concerning possible dissociation into free radicals.

#### Silver Perchlorate and Iodine in Various Solvents

Although silver perchlorate is practically insoluble in heptane, yet in this solvent it does slowly react with iodine. The solution acquires a dark gray color before the reaction proceeds far, and it fumes on exposure to air, suggesting that heptane is being attacked by chlorine tetra-oxide.

In benzene, silver perchlorate is soluble, and the reaction with iodine proceeds fairly rapidly; but here also the solution becomes quite dark after only a portion of the iodine has been added, and fumes on exposure to air.

In nitrobenzene, 2.1 g. of iodine was added to 3.6 g. of silver perchlorate. Even after 7 days the solution remained strongly colored, and only a small amount of silver iodide was produced.

Bromoform, ethylene bromide and ethylene chloride proved unsuitable as solvents, because silver perchlorate was found to react with them, giving silver bromide and chloride, respectively. The reaction is especially rapid with bromoform, the solution becoming quite warm from the heat of the reaction.

In cyclohexane solution there was apparently no reaction whatever.

Several attempts were made to use chlorobenzene as a medium, as it is a fair solvent for silver perchlorate. Iodine was taken up by the silver salt quite rapidly, the reaction being apparently complete on 1/4 to 1/2 hour's shaking. It was found, however, that more than the equivalent amount of iodine was required before all the silver salt was converted into

<sup>19</sup> Ref. 1c, p. 257.

the iodide. The excess over the calculated was from 10 to 20%. This was finally accounted for by the fact that a small amount of *p*-iodo-chlorobenzene was being produced. The chlorine tetra-oxide serves apparently as a catalyst in the direct iodation of chlorobenzene by iodine. As a by-product, hydrogen iodide, and consequently perchloric acid, must be formed. Because of this effect, and because of the darkening of the solution, the use of chlorobenzene as a solvent for chlorine tetra-oxide was abandoned.

### Silver Perchlorate and Bromine in Various Solvents

The action of bromine on silver perchlorate in organic solvents proceeds ever so much faster than that of iodine. Unfortunately, we have not yet found a solvent which meets the essential requirements of being unaffected by the perchlorate salt or by bromine and remains unaffected by the latter even after some chlorine tetra-oxide had been produced.

When bromine was added to silver perchlorate in ether, the bromine also being dissolved in ether, carbon tetrachloride or carbon disulfide, or added as vapors of bromine diluted with air, the precipitation of silver bromide was quite rapid. More bromine, however, was used up than was theoretically necessary for the amount of silver salt present, and apparently some bromine substitution derivatives of ethyl ether were being produced. Under these circumstances, hydrobromic acid, the unavoidable by-product, would set free some perchloric acid. Moreover, the phenomenon of secondary precipitation, described in the preceding part of this paper, was even more marked here than when working with iodine. Clouds of fine precipitate form near or at the surface of the liquid; on shaking the mixture these disappeared, only to re-appear soon when the solution was allowed to stand.

Chlorobenzene and nitrobenzene were substituted for ether as solvents. Again, it was found that while the formation of chlorine tetra-oxide ensued, the latter solvent seemed to facilitate, catalytically, substitution of bromine in the nucleus accompanied by the deleterious formation of hydrogen bromide. Thus, in one experiment 2.37 g. of silver perchlorate, 70 cc. of chlorobenzene and the theoretical amount of bromine were used, but there was still left 15% of the silver salt unacted upon. In another experiment, to 3.77 g. of the salt in 65 cc. of chlorobenzene, 30% of bromine in excess of the theoretical was added, and there still was 16% of the silver perchlorate left unchanged.

Carbon tetrachloride as a solvent is excluded, on account of its reaction with silver perchlorate. In one experiment, 2.65 g. of the silver salt and 1.02 g. of bromine in 70 cc. of the solvent were allowed to stand, with occasional shaking, for several days. The solution still retained an intense color of bromine, and phosgene and silver chloride were produced.

Carbon disulfide is unsuited as a medium for the reaction, for it is apparently oxidized by chlorine tetra-oxide to phosgene and sulfur dioxide.

The preparation of chlorine tetra-oxide would be greatly facilitated if a solvent were found which would meet the various requirements of volatility and inertness.

### Comparison of Chlorine Tetra-oxide with Perchloric Acid and with Ethyl Perchlorate in Ether

**Comparison with Perchloric Acid.**—Silver perchlorate in absolute ether was treated with carefully dried hydrogen chloride or its ethereal solution. In this way we obtained solutions of anhydrous perchloric acid of 1 to 3% concentration. Anhydrous perchloric acid is a powerful oxidizing agent, acting with explosive violence on wood, charcoal, paper, linen, rubber, benzene, etc.<sup>20</sup> As regards ether, Roscoe reported that on dropping the anhydrous acid into ether a violent explosion occurs, while, on the other hand, Michael and Conn found that in small amounts the acid may be mixed with well cooled dry ether. Prepared by our method, the ethereal solutions of the anhydrous acid showed no indication of decomposition, even after standing for several days.

There is no delay in the progressive ease of solution of the silver salt, and precipitation of silver chloride follows so quickly upon the addition of hydrogen chloride that this may serve as a moderately accurate indication of the end-reaction. The perchloric acid produced appears to exert at lower concentrations a favorable influence, and at higher, a depressing influence upon the degree of solubility of the silver salt in ether, but the depressing influence is much less than that of chlorine tetra-oxide. The following table shows this influence.

TABLE V  
INFLUENCE OF PERCHLORIC ACID UPON THE SOLUBILITY OF SILVER PERCHLORATE

Expt.	Vol. of solution Cc.	Total AgClO <sub>4</sub> taken × 0.1 N	HCl added or HClO <sub>4</sub> produced × 0.1 N	Solubility of AgClO <sub>4</sub> in ether × 0.1 N
31	95	2.616	1.495	0.850
	115	2.124	1.818	0.120
32	93	3.563	1.253	1.260
	119	2.732	1.874	0.480
	130	2.482	2.190	0.180
33	100	3.609	0.778	1.210
	125	2.839	1.338	1.070
	148	2.361	1.694	0.400
	163	2.136	1.998	0.000

Although the quantitative data concerning the influence exerted by chlorine tetra-oxide and by perchloric acid on the solubility of silver

<sup>20</sup> Roscoe, *J. Chem. Soc.*, 16, 85 (1863). Vorländer, *Ann.*, 310, 375 (1900). Ref. 3a, p. 445. Van Wyk, *Z. anorg. Chem.*, 48, 2 (1906).

perchlorate are not as concordant for either set as might be desired, nevertheless they bring out sufficiently clearly the contrast between these two factors.

In the preparation of perchloric acid as described above, it was found that, unless a slight excess of hydrogen chloride be present, a small amount of silver salt remains in solution. With concentrations of perchloric acid about 0.1 *N*, the excess of hydrogen chloride required is insignificant, but with more concentrated solutions it may be as much as 0.004 to 0.008  $\times$  0.1 *N*. Whether silver chloride is slightly soluble in ethereal solutions of perchloric acid, or whether we have an equilibrium,  $\text{AgClO}_4 + \text{HCl} \rightleftharpoons \text{AgCl} + \text{HClO}_4$ , the result is the same. It is, however, essential that the solutions of the acid, intended for the study of its reactions with metals should contain no silver salts in solution. Otherwise, misleading results will be obtained because of the formation of a zinc-silver, or magnesium-silver couple, which exert a very distinctly accelerating effect on the reaction between the acid and metal.

Pure perchloric acid in ether, in concentrations comparable with those of chlorine tetra-oxide, dissolves silver oxide, does not oxidize hydriodic

TABLE VI  
ACTION OF PERCHLORIC ACID

Expt.	HClO <sub>4</sub> , calculated from		Ag <sub>2</sub> O $\times$ 0.1 <i>N</i> 1.504	HClO <sub>4</sub> found by							
	AgClO <sub>4</sub> used $\times$ 0.1 <i>N</i>	Titration of ether sol. $\times$ 0.1 <i>N</i>		Loss of Zn After days	Loss $\times$ 0.1 <i>N</i>	Loss of Mg After days	Loss $\times$ 0.1 <i>N</i>				
33		1.544		1	1.041	1	0.740				
						6	1.530				
34		1.370				1	0.718				
						10	1.398				
						13	0.329				
35	1.040	1.030	1.000	2	0.634	4	0.483				
						6	1.155				
										21	0.710
										29	0.984

acid, does not attack molecular silver and attacks copper hardly at all, acts upon zinc, and particularly upon magnesium, much more slowly than does chlorine tetra-oxide. Unlike its dilute aqueous solutions, ether solutions of the acid dissolve zinc with very little, if any, evolution of hydrogen, the latter being almost entirely used up in the reduction of some of the perchlorate to the chloride, and the latter therefore reaches nearly the amounts theoretically possible; that is, nearly  $\frac{1}{8}$  of the total quantity of zinc dissolved appears as the chloride. The acid dissolves magnesium much more slowly than chlorine tetra-oxide does, and this in itself constitutes an unmistakable means of differentiation between the two. Some of the results are tabulated above, Expt. 35 being carried out with particular care as to details.

**Comparison with Ethyl Perchlorate.**—This ester, first prepared by Hare and Boyle<sup>21</sup> from barium perchlorate and barium ethyl sulfate, was later investigated in detail by Roscoe.<sup>22</sup> It is described as possessing to a most unusual degree the tendency to explode spontaneously with great violence, but was found to be more stable when moist, and in presence of water it distilled at 74°. Roscoe found that the ester could not be prepared by the action of ethyl iodide upon silver perchlorate in alcohol, the resulting product being perchloric acid. In our experiments, using absolute ether and equivalent amounts of the silver salt and ethyl iodide we obtained quantitative yields of the ester, and the solutions seemed stable, showing no signs of decomposition after a week's standing. The formation of silver iodide commences at once and the reaction proceeds rapidly. It is advisable to have glass beads present, and the reaction mixture should be continually shaken, or the still undissolved silver perchlorate is likely to be converted into a hard cake. At the end of the reaction the ether was free from silver perchlorate and, in striking contrast to the ethereal solutions of chlorine tetra-oxide and of perchloric acid, the ether solution of the ester imparted but a slight acidity to water when shaken with it for 10 minutes. The hydrolysis of the ester is more rapid when the ether solution is allowed to stand in contact with dil. alkali. In one such experiment 5.312 g. of silver perchlorate, 4.0 g. of ethyl iodide and 213 cc. of ether were taken; the perchloric acid obtained after contact with water for 45 minutes was  $0.060 \times 0.1 N$ ; after contact with alkali for 2 days,  $1.030 \times 0.1 N$ ; for 3 days,  $1.070 \times 0.1 N$ ; for 5 days,  $1.175 \times 0.1 N$ ; ethyl perchlorate calculated was  $1.201 \times 0.1 N$ .

The solution of ethyl perchlorate did not dissolve silver oxide, and was practically without effect upon zinc, magnesium, copper, or silver, even on 20 days' contact with the metals.

The wholly negative behavior of ethyl perchlorate, in distinction from that of the substance assumed to be chlorine tetra-oxide, proves definitely that in the reaction between iodine and silver perchlorate no ethyl perchlorate is produced, either directly or through the subsequent effect of chlorine tetra-oxide on ether.

### Summary

1. A study of the action of iodine and of bromine on dry silver perchlorate in anhydrous solvents has been undertaken, with the aim of ascertaining whether the substance of the formula  $(ClO_4)_x$ , named for the present chlorine tetra-oxide, could be prepared. Aside from the general interest attached to the existence of an acid radical isomeric with the perchlorate anion, we asked this question: Would this new, and highest

<sup>21</sup> Hare and Boyle, *Phil. Mag.*, 19, 370 (1840).

<sup>22</sup> Roscoe, *J. Chem. Soc.*, 15, 213 (1862); *Ann.*, 124, 124 (1862).

oxide of chlorine prove correspondingly more stable than the oxide  $\text{Cl}_2\text{O}_7$ , just as the latter is more stable than the two lower oxides? The processes for purifying the principal materials and the procedure employed in studying the course of the reaction are described.

2. Absolute ether as the solvent and iodine as the halogen were found best suited for this reaction. Even with these, a small amount of a very labile iodo compound, surmised to be iodine tetra-oxide, was invariably produced. Evidence is advanced in favor of the following explanation:  $(\text{ClO}_4) + \text{I} \rightleftharpoons (\text{IO}_4) + \text{Cl}$ . Based upon the tendency of this iodo compound to decompose into iodine and oxygen, a method was worked out whereby this by-product could be almost entirely eliminated, leaving in the ether pure chlorine tetra-oxide.

3. It was found advisable, in preparing chlorine tetra-oxide, not to go much above concentrations of about 0.1 *N*. With solutions of this strength the following properties of the new oxide were ascertained. (a) The substance is colorless, is not volatile with vapors of ether, and remains undecomposed in that solvent. Its molecular state in ether is probably that of silver perchlorate itself, that is, dimolecular. Whether there is any measurable dissociation into the monomolecular phase of free radicals, as the chemical activity of the substance would lead one to infer, remains undetermined. (b) It is hydrolyzed with extreme readiness. Ultimately, perchloric acid is the only product, but reasons are given for assuming, tentatively, that the primary course of the reaction is,  $2(\text{ClO}_4) + \text{H}_2\text{O} = \text{HClO}_4 + \text{HOClO}_4$ . (c) With dry silver oxide the reaction is similar to that in the hydrolysis, and the corresponding silver salts are formed. (d) Chlorine tetra-oxide liberates iodine from iodides, but not in equivalent amounts. (e) It reacts quantitatively with zinc and with magnesium, forming perchlorates; with iron, tin and copper, forming salts of the metals of lower and of higher valence; it acts slowly and incompletely upon cadmium, bismuth and silver.

4. Ethereal solutions of anhydrous perchloric acid and of ethyl perchlorate were prepared. They were found to respond to the tests characteristic of chlorine tetra-oxide in a manner different from the latter. This difference in behavior disposes of the possible conjecture that the substance designated as chlorine tetra-oxide might conceivably be either perchloric acid or ethyl perchlorate.

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