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XXXII. *On the Decomposition of Oxides and Salts by Chlorine.* By ALEXANDER W. WILLIAMSON, Esq.*

THE compounds formed by the action of chlorine on the hydrates of the alkalies and earths have long since attracted the attention of chemists by their powerful bleaching properties. As they were produced by simply bringing together chlorine with the base in presence of water, they were at first considered as direct and simple combinations of chlorine with the oxide, and were therefore called oxychlorides.

Berzelius first showed this view to be untenable. He considered these compounds as containing a chloride and an oxygen salt of chlorine, the acid of which he assumed identical with that of Stadion, namely, 1 equivalent of chlorine to 3 of oxygen.

Serullas obtained by the evaporation of a solution of soda, which had been treated with chlorine, crystals of chloride of sodium, while the mother-liquid retained its bleaching properties unaltered. This experiment shows that a chloride and an oxygen salt of chlorine, which possesses the bleaching properties, are contained in these compounds.

By acting on the oxide of mercury with chlorine, Balard succeeded in obtaining a combination of oxygen with chlorine, which in its bleaching properties, as well as its salts, showed much resemblance to the oxygen acid supposed to be contained in the oxychlorides. He determined the composition of this acid at 1 equivalent chlorine to 1 of oxygen.

Millon has endeavoured to recall the ancient view with some modification. He considers these compounds as analogous to peroxides, so that the atoms of oxygen which the peroxide of a metal contains beyond its oxide are here replaced by chlorine.

This view was but imperfectly refuted, and indeed the subject remained in considerable doubt until Gay-Lussac made known his interesting researches on the combinations of chlorine with bases.

I will here recall some of the principal facts, but must refer for further particulars to the original treatise of this great master.

If a mixture of a chloride with a corresponding salt of hypochlorous acid in their equivalent parts be treated with sulphuric acid in excess, chlorine is given off. If, on the contrary, the acid be added in a dilute state, and prevented by continual agitation from acting unduly on any particular part, and only so much acid be added as is sufficient to decompose the oxygen salt, then hypochlorous acid is alone set free, and can be di-

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stilled over unchanged. The so-called oxychlorides, when similarly treated, behave in the same manner.

The process in these instances is extremely simple, if we only recollect that hypochlorous acid with hydrochloric sets chlorine free by forming water; or, which is the same thing, the metal of the chloride deoxidates the hypochlorous acid in order to be able to combine as oxide with sulphuric acid, while from both the chlorine is set free.

In the second instance the salt of hypochlorous acid is alone decomposed, while no excess of sulphuric acid is present to cause a decomposition of the chloride.

Now if these oxychlorides were simple combinations of chlorine with oxide, the first drop of sulphuric acid would set free chlorine.

Founded on the correctness of this view, this great chemist has given us a method of preparing hypochlorous acid, far more practical than that formerly used. He distils the so-called chloride of lime with dilute nitric acid, which must be very carefully added in the manner above described, and distils off the hypochlorous acid. He confirms Balard's statement of its composition. Hypochlorous acid possesses, according to Gay-Lussac, the following properties:—It is a feeble acid, weaker perhaps than carbonic, although they mutually expel one another from their salts. Its salts have a great inclination to decompose into chlorides and chlorates. These salts, as such, possess no bleaching properties. In order to give a bleaching reaction, they must be decomposed by a stronger acid. They are partly decomposed by chlorine. Hypochlorous acid can be distilled over from any of these salts after treating it with chlorine.

I will now communicate some experiments which I have made on the action of chlorine on bases, and the products of this action. My principal object during these experiments was to become better acquainted with the manner of the formation, with the properties and decompositions of this most interesting compound, hypochlorous acid.

The experiments were performed in the laboratory at Giesen, and I had, during the course of them, the advantage of the presence and counsel of Professor Liebig.

The first point which I endeavoured to ascertain was the quantity of chlorine with which a base is capable of combining. Barytes was first subjected to this examination. A concentrated solution of this earth was saturated with chlorine by conducting a stream of the gas, which had been washed by water, slowly into it. This process was not considered complete until the liquid had assumed a strong colouring of chlo-

rine. It was then agitated with a repeatedly renewed quantity of atmospheric air until no free chlorine could be perceived in it. This solution had the peculiar astringent taste of hypochlorous acid, and its powerful bleaching properties. It was oversaturated with ammonia and heated to the boiling-point, and having added an excess of nitric acid, it was precipitated by nitrate of silver. After separating it from this precipitate, the barytes was thrown down by sulphuric acid. Three determinations, conducted in this manner, gave the following results. For each determination a fresh liquid was prepared.

I. 0.550 chloride of silver = 0.136 chlorine.

0.243 sulphate of barytes = 0.159 barytes.

This gives 818 chlorine to 957 barytes.

II. 1.468 chloride of silver = 0.361 chlorine.

0.654 sulphate of barytes = 0.429 barytes.

This gives 805 chlorine to 957 barytes.

III. 1.836 chloride of silver = 0.453 chlorine.

0.781 sulphate of barytes = 0.513 barytes.

This gives 843 chlorine to 957 barytes.

The average of these three gives 822 chlorine to 957 barytes, or nearly 2 equivalents.

The question which now naturally presents itself is, in what manner can the chlorine be contained in this liquid, and in what combinations? The following experiments were instituted in order to ascertain this:—

To part of the original liquid a solution of nitrate of silver was added, by which a *pure white* precipitate of chloride of silver was formed, which increased by standing. Another portion was treated with barytes water until the smell and bleaching reaction of hypochlorous acid had disappeared. Nitrate of silver now formed a black precipitate, which gradually decomposed, giving off oxygen.

The cause of this striking difference in the two reactions is evidently that in the first instance all the base was combined with chlorine in the form of chloride, while hypochlorous acid remaining free in the liquid, gradually increased the precipitate by its own decomposition. In the second case, the hypochlorous acid being combined with barytes gave the black precipitate, consisting of a mixture of chloride with peroxide of silver.

To test the correctness of this explanation the following experiments were made:—

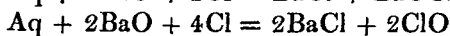
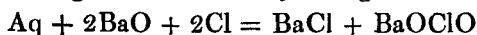
Aqueous hypochlorous acid was neutralized with barytes. This salt possessed no bleaching properties. Carbonic acid precipitated carbonate of barytes. The liquid, after separa-

tion from the precipitate, was boiled until all free hypochlorous acid had disappeared. It now contained no traces of a hypochlorous acid salt, as proved by the fact that tincture of litmus was not bleached by it, though an excess of sulphuric acid was added, proving that the barytes salt was completely decomposed by carbonic acid.

A solution of barytes was saturated with chlorine in the manner above described, and being freed from superfluous chlorine, was now treated in a similar manner with carbonic acid. No precipitate whatever was formed, which must have been the case had any hypochlorous acid been combined with barytes. The hypochlorous acid salt, formed by the action of the first equivalent of chlorine with the base, had thus been entirely decomposed by the second equivalent.

When I further state, that on this liquid being subjected to distillation, hypochlorous acid passed over, while the residue consisted of chloride of barium with a small quantity of chlorate of barytes, then I think it will be beyond a doubt, that of the two equivalents of chlorine which the barytes took up, one combined with the barium, the other with its oxygen.

The following is the formula explaining the decomposition :



In endeavouring to purify this mixture, of chloride of barium and hypochlorous acid, from all free chlorine contained in it, I noticed a remarkable circumstance, which I will relate. By agitating the solution with repeatedly renewed portions of atmospheric air, I was able to obtain a colourless liquid, which possessed but a very slight smell of chlorine. But when this was allowed to stand for a few minutes, especially in a strong light, the colour and smell of chlorine re-appeared. Now, as no chlorine had access to it from without, this must have been caused by a decomposition of the hypochlorous acid. This decomposition takes place in common daylight, more rapidly in direct sunshine, and most rapidly when the liquid is heated in a water-bath. The solution, after decomposition had ceased, and no more chlorine was given off, contained a considerable quantity of chlorate of barytes. The liquid now contained no hypochlorous acid, either free or combined. The following analysis was made in order to determine the proportion of chlorine remaining in it. The barytes was first precipitated by sulphate of soda. The chloric acid was then deoxidized by means of sulphurous acid, and after separation from the sulphate of barytes, the whole of the chlorine was determined by means of nitrate of silver, thus :—

Sulphate of barytes $1.597 = 0.940$ barytes.

Chloride of silver $1.998 = 0.493$ chlorine.

This is rather more than 1 eq. of chlorine.

I next endeavoured to ascertain the proportion of chloric acid in this amount. For this purpose a portion of the same liquid was precipitated by nitrate of silver, which gave the quantity of chlorine combined as chloride. After separating it from this precipitate the liquid was treated with phosphorous acid, which naturally precipitated metallic silver and a barytes salt, but also reduced the chloric acid. After heating for some time, the precipitates were dissolved in nitric acid, and the chloride of silver which formed, determined.

First precipitate of chloride of silver $4.992 = 1.182$ chlorine.

Second precipitate $0.787 = 0.154$...

This gives to 6 parts of chlorine as chloride, nearly 1 as chlorate. The theory requires to 5 of chloride 1 of chlorate; but part of the oxygen had probably escaped either free or as hypochlorous acid.

Having thus found that on treating barytes with chlorine the decomposition takes place in so simple a manner, I next endeavoured to find out whether the same laws would not hold good in the case of the alkalies. Of these I first chose potash, which was prepared by decomposing a solution of pure sulphate of potash by barytes water.

I. 4.051 of this solution gave 0.272 sulphate of potash = 0.107 potash, or 3.628 per cent. 18.819 were saturated with chlorine, in the same manner as the barytes had been, and gave, after reduction by ammonia and sulphurous acid, a precipitate of 3.314 chloride of silver = 0.818 chlorine.

Calculated to the amount of potash, this gives to 590 potash 706.5 chlorine, instead of 443 , which is 1 equivalent.

II. 17.397 of the solution which was used for this determination gave 1.337 nitrate of potash = 0.6225 potash.

19.027 gave 3.031 chloride of silver = 0.748 chlorine, or in 590 potash 647 chlorine, instead of 443 . The average of these two gives to 590 potash 677 chlorine, or to 2 eqs. of potash 3 of chlorine.

This liquid possessed the smell of hypochlorous acid as well as its bleaching properties. It contained no salt of hypochlorous acid, that is to say, that all this acid contained in it was in a free state, as was proved by the above-described reaction with silver.

A considerable quantity of chloric acid was contained in this liquid, but was not determined, as it depended only on the time allowed to elapse between the preparation of the liquid and its being made use of for analysis.

What now can be the cause of potash combining with a less quantity of chlorine than is the case with barytes? This arises probably from the stronger affinity of potash for chloric acid, which causes a decomposition of hypochlorous acid, by which chloric acid is formed and chlorine set free. Hence it is evident that by the formation of a small quantity of chloric acid the total quantity of chlorine in the liquid must be much diminished.

I now treated carbonate of potash in a similar manner with chlorine, and obtained the well-known liquid, possessing, from the first action of the chlorine, the smell and other properties of free hypochlorous acid, a considerable quantity of which was carried away by the escaping carbonic acid. Now, if this liquid be heated for some time in a water-bath, the hypochlorous acid is completely destroyed, chlorine is disengaged, and the liquid now contains a mixture of chloride of potassium with chlorate of potash. As the hypochlorous acid was from its first formation uncombined, the chloric acid must have, in all probability, been formed by a different process from that which took place in the preceding instance, where, by the action of chlorine on a hypochlorous acid salt, chloric acid formed, partly by taking the oxygen directly from the base, partly, perhaps, by a decomposition of hypochlorous acid. We here have a mixture of hypochlorous acid with chloride of potassium; after heating which we find part of the chloride of potassium is changed into chlorate of potash.

Now if this be the case, I must obtain the same result by treating a solution of chloride of potassium with hypochlorous acid. The experiment was made in the following manner:—In a concentrated aqueous solution of hypochlorous acid were dissolved crystals of chloride of potassium, and the mixture was heated in a water-bath until chlorine ceased to be disengaged. This liquid deposited, on cooling, scales of chlorate of potash, which was also easily detected in the mother-liquid.

This process must not be considered as a direct oxidation of the chloride, for peroxide of hydrogen produces no such effect.

It is well known that aqueous hypochlorous acid has a great tendency, especially when heated, to form chloric acid, setting free chlorine. Now when chloride of potassium is present, this chloric acid, in the moment of its formation, decomposes the chloride, setting free its chlorine, the metal oxidating itself at the expense of hypochlorous acid.

On treating carbonate of soda with chlorine I obtained similar results, with the difference, that chloric acid formed even more easily than was the case with potash, and consequently the total content of chlorine in the liquid was less.

The following is an experiment showing the nature of this decomposition:—Treat a concentrated solution of simple carbonate of soda with chlorine until a considerable quantity of bicarbonate is precipitated, but not until this precipitate commences to be decomposed. The liquid on being now left to itself in the light continues for several hours to give off carbonic acid with slight effervescence. We here have carbonate of soda mixed with chloride of sodium and free hypochlorous acid. These two latter, by gradually acting on each other, in the manner above described, set chlorine free, which decomposes the carbonate.

Now, as by treating carbonates with chlorine hypochlorous acid is obtained free, and can be distilled over quickly, it appeared to me that this might be an easy method of obtaining this acid for use. It is desirable for this purpose to choose a base which has not too powerful an affinity for chloric acid, and consequently from the chloride of which, hypochlorous acid can be quickly distilled off without decomposition. I chose, with this view, carbonate of lime.

This salt, prepared for the purpose by precipitation, was mixed up with about 40 parts of water, and dissolved in chlorine. When quickly heated to the boiling-point, this liquid gave off its hypochlorous acid, while the residue in the retort consisted of a solution of chloride of calcium with a small quantity of chlorate of lime.

This is a cheap and easy method of preparing this most interesting compound. It is well if a slight excess of carbonate of lime be left in the liquid when subjected to distillation; it speedily dissolves as the liquid becomes hot, and the acid is thus obtained free from chlorine, which is not the case without this precaution.

I was induced from this to try the action of chlorine upon other salts with stronger acids, and discovered a series of interesting decompositions, of which I will here state the outline; and hope, after further investigation, to be soon able to communicate the details.

A solution of tribasic phosphate of soda was treated with chlorine, which it absorbed with great avidity. This solution, after saturation, possessed a strong smell of hypochlorous acid, which I distilled over from it. The residue gave a strongly acid reaction, proving that the chlorine had taken 2 atoms of soda from the phosphate, forming with the metal chloride of sodium, and with the oxygen hypochlorous acid.

Common phosphate of soda gave a similar result. The residue after distillation consisted of the same phosphate as the preceding, with 1 atom chloride of sodium.

Two basic pyrophosphates behaved in exactly the same manner.

The next salt I subjected to this treatment was sulphate of soda. A solution of this perfectly neutral salt was saturated at the common temperature with chlorine, which was freely absorbed by it. The liquid remained colourless, which shows that the chlorine absorbed was not contained, as such, in solution. This neutral sulphate of soda was indeed decomposed. The liquid, after saturation with chlorine, consisted of a mixture of bisulphate of soda with chloride of sodium and free hypochlorous acid. Whether any neutral sulphate remained undecomposed I have yet to ascertain. On being subjected to distillation, hypochlorous acid passed over at the beginning of the operation. The liquid which first distils contains most of the acid. Each successive portion contains less of it than the preceding. This compound possesses such powerful oxidating properties, far exceeding, at the common temperature, those of nitric acid, that it might doubtless become a valuable aid to the chemist in many of his operations. It might even be made advantageously on a large scale in the above-described manner; the same sulphate of soda would of course serve for many operations. It is only necessary to boil down the residue of distillation and heat it until all the chlorine is driven out as hydrochloric acid, which also need not be lost. It is now reconverted into neutral sulphate of soda, which can be redissolved and treated with chlorine as before.

The aqueous solution of hypochlorous acid may easily be prepared so as to contain in a given weight more bleaching power than the well-known lime compound. It will keep for a considerable time, even when concentrated, with but very little decomposition if protected from light, and, of course, heat. I offer this as a hint for the consideration of manufacturers of bleaching powders. Should it prove a practical simplification of the method hitherto used for preparing the bleaching compounds, and thereby have any beneficial effect on the manufactures for which these are required, I shall feel myself amply rewarded.

The salts of sulphuric acid with the following bases are decomposed in like manner. Oxide of copper, peroxide of iron, oxide of zinc, protoxide of manganese, also the double salt of alumina and potash; even sulphate of lead, when suspended in water and treated in like manner, was slightly decomposed. Chromate of potash was also decomposed. Borax was entirely decomposed: the solution deposited after concentration crystals of boracic acid. Nitrate of potash slightly. Acetate of lead was decomposed, forming chloride and peroxide.

These decompositions only take place in the presence of water. Crystallized sulphate of soda is not acted upon in its dry state by chlorine, though the crystals contain water.

Concluding from analogy that similar decompositions might be produced by cyanogen, I treated a solution of tribasic and common phosphate of soda with this gas: both were decomposed. The solution assumed a yellow colour, which by the further action of cyanogen became much darker. Upon distilling this liquid hydrocyanic acid passed over, and part of the above-mentioned yellow brown acid was precipitated in the residue in the form of a brownish substance, which probably contains the oxygen of the soda, for no cyanic acid was formed; but, as I have stated already, I hope to be soon able to communicate further particulars regarding these interesting decompositions.

XXXIII. *On some of the Substances which reduce Oxide of Silver and precipitate it on Glass in the form of a Metallic Mirror.* By JOHN STENHOUSE, *Ph.D.**

IT has long been known that aldehyde, when heated in a tube with ammonio-nitrate of silver, reduces the oxide to the metallic state, and forms a brilliant coating on the inner surface of the tube. Three other substances, saccharic acid, salicylic acid and pyromeconic acid, were also known to possess the same property, though the coatings which they yield are much darker, and therefore less beautiful than those formed by aldehyde. This was the state of our knowledge previous to the announcement, about six months ago, of Mr. Drayton's process for silvering mirrors in the cold, by means of ammonio-nitrate of silver and an alcoholic solution of the oils of cloves and cassia. †

I find that the number of substances which, especially when assisted by heat, give more or less brilliant coatings of reduced silver, is much greater than has hitherto been supposed. Thus grape-sugar forms a pretty brilliant mirror even in the cold. When unassisted by heat the mirror is rather slowly formed, requiring from six to twelve hours; but when a slight heat is applied it forms very readily in the course of a few minutes; the coating is much darker than that produced either by aldehyde or by Drayton's process. Cane-sugar also yields a mirror when assisted by heat, but none in the cold. Gum-arabic and starch also yield dark-coloured mirrors, but more slowly, and require considerable boiling: so do phloridzine

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† See the preceding volume, p. 546.

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