MUIR: IODINE DIOXIDE.

LXXIX—Iodine Dioxide.

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MILLON, in 1844 (Ann. Chim. Phys., [iii], **12**, 333), described the preparation of an oxide of iodine, to which he gave the formula I_2O_4 , by the interaction of nitric acid and iodine, and also by the interaction of hot concentrated sulphuric acid and iodic acid. I shall embody the results of my examination of Millon's second method for preparing the oxide in directions for the preparation of the compound.

Preparation of Iodine Dioxide.-To about 60 grams of powdered iodic acid, in a platinum dish, about 200 grams of concentrated sulphuric acid are added, and the mixture is heated and stirred. When oxygen has been evolved freely for a few minutes, and the liquid is dark brownish-yellow, the flame is lowered, and as soon as the vapours show a slight violet tint, the heating is stopped. This part of the process occupies ten or fifteen minutes. After cooling, the dish is kept for five or six days over sulphuric acid. The liquid is then poured off from the yellow, crystalline crust which has formed, the solid is powdered, and the powder is washed by the help of a little of the liquid before poured off into a funnel stopped with glass-wool, and drained by the aid of the pump. The solid is now transferred to a dry, porous tile, and kept in a desiccator for about a week, the solid being occasionally removed, rubbed to a fine powder, and replaced on the tile. When it is found, by making a trial with a little of the solid, that shaking for a minute or so with a very little cold water does not cause the separation of more than a minute quantity of iodine, the yellow solid is transferred to a funnel stopped with glass-wool, washed quickly with successive small quantities of cold water by the aid of the pump until the washings are free from sulphate (five or six washings generally suffice), and then with small quantities of absolute alcohol until the washings are quite colourless. The solid is then washed twice or thrice with dry ether, the washing liquid is removed as completely as possible by suction, the solid is placed on a porous tile which is kept over dry lime for a few days, and is then dried at 100° .

Taking the reaction of preparation to be $2HIO_3 - H_2O - O = I_2O_4$, about 30 per cent. of the theoretical yield of the dioxide can be obtained by working with moderate care.

Analysis of Iodine Dioxide.—For the analysis of this compound, I used a modification of the process described by Chretien, in 1898 (Ann. Chim. Phys., [vii], 15, 364), based on the fact that iodic anhydride reacts with an aqueous solution of oxalic acid in the presence of sulphuric acid at 100° to give carbon dioxide, water, and iodine.

A flask of about 250 c.c. capacity was employed, into the neck of which was ground a glass stopper, carrying an entrance tube leading nearly to the bottom of the flask, and an exit tube; the exit tube was connected with two glass-stoppered bottles containing an aqueous solution of potassium iodide, and surrounded by cold water. A weighed quantity of the compound was placed in the flask, dilute sulphuric acid and a measured volume of normal oxalic acid solution were added, a stream of washed carbon dioxide was kept passing through the apparatus, and the contents of the flask were boiled until iodine had ceased to pass over with the steam and the liquid in the flask was colourless. The iodine was estimated by standard thiosulphate, and the residual oxalic acid by standard permanganate solution.

The following are the percentages of iodine and oxygen found by this method. The specimens of iodine dioxide were prepared at different times; two of them were dried at 100°, the other two at 115°:

As the calculation assumes that the whole of the iodine of the compound is set free in the reaction, and that the oxygen which oxidises oxalic acid comes only from the compound, the results of the analyses demonstrate the accuracy of the equation:

 $I_2O_4 + 4H_2C_2O_4 = I_2 + 4H_2O + 8CO_2.$

Iodine dioxide reacts slowly with cold water, and quickly with hot water, to produce iodine and iodic acid. This reaction suggested another method for analysing the compound. A weighed quantity was boiled with water in a stream of washed hydrogen, the iodine was led into potassium iodide solution, and the iodic acid was estimated in the colourless liquid left in the flask by titration with standard sodium hydroxide solution, phenolphthalein being used as indicator. Assuming the reaction to be represented by the equation:

$$5I_2O_4 + 4H_2O = 8HIO_3 + I_2$$
,

the percentage of iodine dioxide can be calculated (1) from the quantity of iodine set free, and (2) from the quantity of iodic acid produced. The following results were obtained:

(1) From iodine: 98.88, 100.50 per cent. I_2O_4 . (2) From iodic acid: 99.83, 100.19, 100.50 per cent. I_2O_4 .

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$$5{\bf I}_2{\bf O}_4+4{\bf H}_2{\bf O}=8{\bf H}{\bf I}{\bf O}_3+{\bf I}_2.$$

Properties and Reactions of Iodine Dioxide.—Iodine dioxide is a lemon-yellow solid; when allowed to separate slowly from its solution in hot concentrated sulphuric acid, it appears under the microscope as a mass of minute, pale yellow, crystalline rosettes. The compound is not hygroscopic. Specific gravity 4.2 at 10° referred to water at the same temperature. As the molecular weight of the compound has not been determined, the formula may be written either IO₂ or I₂O₄. Decomposition begins at about 130° ; the products are iodine and oxygen.

Iodine dioxide is insoluble in, and is unacted on by, dry ether or glacial acetic acid; it dissolves very slowly and very slightly in monochloroacetic acid or acetone. When kept in contact with phenol, aniline, or pyridine, iodine is very gradually formed and dissolved, and a little iodine pentoxide is produced. Absolute alcohol reacts slowly with iodine dioxide; iodine passes into solution, and iodine pentoxide remains. The reaction is so slow that a gram of the compound is not wholly changed until it has been kept in contact with alcohol for about four months. The compound is changed to iodine and iodic acid by the action of cold nitric acid, whether concentrated or dilute. When shaken with cold concentrated hydrochloric acid, chlorine is given off, and a yellow solution is formed; when the liquid is heated, much chlorine is produced; there is no separation of iodine; the solution contains iodic acid and, probably, iodine chloride, but, after boiling with considerable excess of hydrochloric acid for some time, the iodic acid is entirely decomposed.

The action of cold dilute sulphuric acid is slow; the final products are iodine and iodic acid. Boiling dilute sulphuric acid reacts in the same way as boiling water; the equation given on p. 657 was verified quantitatively, excess of dilute sulphuric acid being used. When iodine dioxide is slightly moistened with concentrated sulphuric acid and left exposed to the air, iodine and iodic acid are gradually formed. Cold concentrated sulphuric acid (about 99 per cent. H_2SO_4) dissolves the compound slowly. I found that 100 c.c. of this acid dissolve 1.54 grams of iodine dioxide at 15—20°. Sulphuric acid of the concentration H_2SO_4 , H_2O dissolves iodine dioxide more freely than 99 per cent. acid; a little iodine is produced and dissolved, and the solution contains some iodic acid. When the oxide is heated with con centrated sulphuric acid, a little iodine is given off.

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Fuming sulphuric acid dissolves iodine dioxide. When heated, the liquid becomes green, and then gradually yellow; no iodine is given off. On cooling, a yellow solid is deposited, which, after washing with alcohol and drying at 100°, was found to contain 93 per cent. iodine dioxide mixed with a little iodine pentoxide. Therefore, fuming sulphuric acid dissolves iodine dioxide and oxidises some of it to pentoxide. No distinct evidence was obtained of the formation of compounds of iodine dioxide and sulphuric acid.

Aqueous potassium hydroxide reacts with iodine dioxide to form potassium iodate and iodide in accordance with the equation:

$$3I_2O_4 + 6KOH = 5KIO_3 + KI + 3H_2O.$$

The accuracy of this presentation of the reaction was proved by shaking a weighed quantity of the oxide with a measured volume, being a considerable excess, of standard potassium hydroxide solution, and determining the amount of alkali unacted on by titration with standard acid; also by adding a slight excess of nitric acid to a solution of the oxide in potassium hydroxide, precipitating by silver nitrate solution, adding more nitric acid, boiling, and weighing the silver iodide. The results of applying these methods were very fairly satisfactory. For instance, 1.1275 grams of iodine dioxide were dissolved in 150 c.c. of N/5-potassium hydroxide solution; 112 c.c. of the potash solution remained unacted on; therefore, 38 c.c. of N/5-potash were used to react with the oxide, and this is equivalent to 1.2084 grams of I_2O_4 if the equation given above is correct. In another experiment, 0.1877 gram of the oxide was used, and 0.1846 gram was found. In another experiment, 0.0650 gram potassium iodide was found in the solution of 0.3754 gram iodine dioxide in potash, and the equation required that 0.0653 gram potassium iodide should have been produced.

Interaction of Iodine Dioxide and Sulphur Trioxide.—A quantity of iodine dioxide, weighing 1.02 grams, was placed in a weighed \land -shaped tube; sulphur trioxide, prepared by heating fuming sulphuric acid, was passed into the tube, which was sealed off and weighed; the weight of sulphur trioxide added was 1.25 grams. The ratio of the two oxides was nearly I_2O_4 : 5SO₃. The tube was heated to 80° for eight hours; excess of sulphur trioxide was then distilled off into the other limb of the tube; the tube was cut; that part of it which contained the solid matter was kept in a desiccator over lime for some days, and then weighed. The contents of the tube were washed out, and the tube was weighed. The weight of the solid matter in the tube was 1.789 grams; hence the weight of sulphur trioxide which had combined with 1.02 grams of iodine dioxide was 1.789 - 1.02 = 0.769 gram. The ratio 1.02: 0.769 is the same as 318: 239.7; that is to say, the results of this experiment point to the formation of the compound $I_2O_4,3SO_3$ (ratio=318: 240).

The following method was adopted as the result of many attempts to discover the most suitable conditions for the preparation of a compound of iodine dioxide and sulphur trioxide. About 20 grams of sulphur trioxide are distilled into a tube of good glass, about 300 mm. long, sealed at one end and narrowed near the other end; from 5 to 8 grams of iodine dioxide are shaken into the tube, which is then sealed. The tube is almost wholly immersed in water, in an upright position, and heated to 85-90° for about twenty-four hours until an apparently homogeneous, pale yellow solid is obtained, covered by a yellowish-green liquid. While still hot, the tube is reversed and allowed to drain for some time; the tube is now cut, and the portion which contains the yellow solid is at once placed in a wide tube and heated to 90° in a slow stream of dried carbon dioxide until fumes of sulphur trioxide have almost ceased to appear, usually for about six hours. The solid in the tube is quickly powdered, and heated in dried carbon dioxide at 95-100° until sulphur trioxide has entirely ceased to be evolved. The solid is then quickly transferred to a weighing tube and kept in a desiccator.

Analysis of the Compound of Iodine Dioxide and Sulphur Trioxide.—By dissolving the compound in dilute potassium hydroxide solution, reducing iodate to iodide by sulphur dioxide, removing excess of the latter by boiling, and precipitating silver iodide, after acidifying by nitric acid, the percentage of iodine found was 47.15. The formation of a compound, $I_2O_4,3SO_3$, was indicated by the experiment described in the last section; this formula requires I=45.52 per cent. The most concordant results were obtained by using Chrétien's method (described on p. 657), namely, boiling with sulphuric acid and a measured volume of standard oxalic acid, leading the iodine into a solution of potassium iodide, and determining the amount of oxalic acid oxidised by the oxygen combined with iodine in the compound.

The sulphur trioxide of the compound was determined by dissolving in hydrochloric acid, adding iron wire, warming for some time, and then precipitating by a solution of barium chloride (compare Kämmerer, J. pr. Chem., 1861, 83, 73). Complete analyses were made of two specimens of the compound, and partial analyses of four other specimens. The following percentage quantities of the components were found:

= 44.25 47.2241.55 41.05 Mean = 43.51Ι 10.94 9.96 11.20 = 10.610 = 10.04,, $SO_3 = 45.20$ 41.2740.98 43.12 42.64 ,, $\begin{array}{cccccccc} I_2O_4, 3SO_3 \mbox{ requires } I=45\cdot52\ ; \ O=11\cdot47\ ; \ SO_3=43\cdot01\ \mbox{ per cent.} \\ I_2O_4, 7SO_3 \ , & I=42\cdot47\ ; \ O=10\cdot70\ ; \ SO_3=46\cdot83 \ ,, \end{array}$ $2I_{9}O_{4}, 7SO_{3}''$

The product of the reaction between the two oxides is very hygroscopic, and it is possible that more than one compound is formed in the reaction; these considerations account, in my opinion, for the discrepancies in the analytical data. The analyses prove, I think, that the formula I_2O_4 , $3SO_3$ expresses the composition of the main, if not the only, product of the interaction which occurs when iodine dioxide and sulphur trioxide are heated together to $85-90^{\circ}$, and the solid which is formed is heated to $95-100^{\circ}$ in a stream of dried carbon dioxide until sulphur trioxide ceases to be evolved. This conclusion is strengthened by the results of weighing the quantities of the two oxides and the quantity of the compound formed by their union (see p. 660), and also by the estimation of iodine in the compound by precipitation as silver iodide (see p. 660).

Properties and Reactions of the Compound I204,3803.-The compound is a pale yellow solid; a specimen of it was unchanged after keeping in a corked tube in a desiccator for three months. When heated, iodine, oxygen, and sulphur trioxide begin to be evolved at about 120°; after heating to 190° for a few minutes, the residue contains a considerable quantity of sulphur trioxide. The compound is very hygroscopic; when exposed to the air for a short time, iodine separates, and after a day or two a white, crystalline solid is formed, which was proved to be iodic acid; a few yellow specks remained after exposure to the air of about half a gram of the compound for three months. When shaken with cold water, in very small quantities at a time, sulphur trioxide is removed, along with a little iodine, and iodine dioxide remains mixed with traces of iodic acid. The compound dissolves in a large quantity of cold water, the water becoming coloured by dissolved iodine; the solution contains iodic and sulphuric acids. When the compound is added slowly, in very small quantities at a time, to about twenty times its weight of absolute alcohol, cooled continuously by running water, almost the whole of it dissolves, forming a slightly yellow liquid, which becomes gradually more deeply coloured on standing; iodine and sulphur trioxide were found in the solution; after a few days a very small quantity of a yellow solid remained, which was proved to be iodine dioxide. Crystals of iodic acid were obtained by allowing the solution in alcohol to evaporate at the ordinary temperature. Ether very slowly dissolves sulphur troxide from the compound, and, finally, leaves iodine dioxide.

Compound of Iodine Pentoxide and Sulphur Trioxide.-As Kämmerer (J. pr. Chem., 1861, 83, 73) stated that a compound of iodine pentoxide and sulphur trioxide, to which he gave the formula 51205,SO3, is formed by passing dried sulphur dioxide over iodine pentoxide at 100°, and as Weber (Ber., 1887, 20, 87) described a compound of the composition I₂O₅,3SO₃, I thought it advisable to determine whether iodine pentoxide and sulphur trioxide combine when heated to 100°. About 5 grams of iodine pentoxide (I_2O_5) were heated in a sealed tube with about four times its weight of sulphur trioxide in the manner described on p. 660 for about twenty-four hours. When most of the excess of sulphur trioxide had been poured off, the residual solid was heated to 90° in a slow stream of dried carbon dioxide until sulphur trioxide ceased to be given off; it was then quickly powdered, and again heated to 100° in carbon dioxide so long as any traces of sulphur trioxide were evolved. A pale yellow, hygroscopic solid, closely resembling the compound I_2O_4 , $3SO_3$, was thus obtained. The substance was analysed by the method described on p. 660.

The following results were obtained:

Found :	I	=	51.67	51.87	$\mathbf{M}\mathbf{e}\mathbf{a}\mathbf{n}$		51.77
	0	=	17.18	15.69	,,	=	16.43
	SO_3	=	32.16	33.89	,,	=	33.02
$[_{2}O_{5}, 2SO_{5}]$, req	uire	I = 51.42;	0 = 16.19;	$SO_{3} = 32$	39	per cent.

These results prove, I think, that a compound of iodine pentoxide and sulphur trioxide is formed by heating these compounds to about 100°, and make it very probable that the compound formed in my experiments had the composition $I_2O_5,2SO_3$. The formation and fair stability towards heat of the compounds $I_2O_4,3SO_8$ and $I_2O_5,2SO_3$ show that both of the oxides of iodine have slightly basic properties, and emphasise the connexion between iodine and manganese, elements which the periodic system of classification places in the same group.

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