

298. *Lower Oxides and Sulphates of Iodine.*

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*Iodine Dioxide.*

MILLON (*Ann. Chim. Phys.*, 1844, **12**, 330, 345, 353; *J. pr. Chem.*, 1845, **34**, 321) described the preparation of iodine dioxide (1) by the action of very concentrated nitric acid on iodine and (2) by the action of hot concentrated sulphuric acid on iodic acid. Kammerer (*J. pr. Chem.*, 1861, **83**, 65, 72) claims to have repeated the preparation by Millon's first method and to have obtained an oxide,  $I_6O_{13}$ , by passing sulphur dioxide over iodic acid at  $100^\circ$  and washing the product with water and alcohol. Kappeler (*Ber.*, 1911, **44**, 3496) prepared iodine dioxide by Millon's second method and showed that  $I_6O_{13}$  is identical with iodine dioxide. We find that the product of reaction of iodine and cold nitric acid of *d* 1.5 is almost exclusively iodine pentoxide, a result which agrees with that of Guichard (*Compt. rend.*, 1909, **148**, 923; *Bull. Soc. chim.*, 1909, **5**, 86), who obtained a better yield by using nitric anhydride. His observation that the partially decomposed iodine pentoxide turns brown and that the brown colour is not removed by an organic solvent, has also been confirmed.

Iodine dioxide is, however, obtained by Millon's second method, as stated by Muir (*J.*, 1909, **95**, 656) and by Kappeler (*loc. cit.*).

*Experimental.*

1. *The Action of Nitric Acid on Iodine.*—Iodine dissolves in cold nitric acid (*d* 1.40), giving a brown coloration, but no solid product is obtained after a fortnight. On heating, the solution obtained is deep brown and unusual needle-like crystals of iodine are deposited on cooling; these were found in three specimens to contain 99.85, 99.93, and 99.15% of iodine.

When fuming nitric acid (*d* 1.5) and powdered iodine are triturated for about 10 minutes, a voluminous yellow powder is obtained, which on drying becomes brown and retains its colour on washing with carbon tetrachloride. The solid readily absorbs moisture, and the brown colour deepens. When washed alternately with water and alcohol, the solid disappears without residue, although Millon states that iodine dioxide is left behind on such treatment.

Iodine was determined by reduction with sulphur dioxide and precipitation of silver iodide in the presence of nitric acid.

Sample.	Mode of drying the sample.	Time, hours.	Iodine % (experimental).
A	Over solid KOH and CaCl	36	75.99
B	"	72	75.61
C	"	72	76.12
D	Over solid KOH and CaCl <sub>2</sub> in vacuum desiccator	16	75.29
E	"	24	75.68
F	Dried at 85°	—	75.54

Oxygen values were determined as described (*J.*, 1934, 1088). Found in samples A—F, 23.38, 23.40, 23.84, 23.72, 23.58, 23.82.

These results show that the product is mainly iodine pentoxide (Calc.: I, 76.04; O, 23.96%), a small amount of iodic acid being probably also present.

2. *The Action of Hot Concentrated Sulphuric Acid on Iodic Acid.*—Iodine dioxide was obtained by the process described by Muir (*loc. cit.*), one-tenth of the quantities he specifies being used.

The final drying was carried out on a porous plate over lime at room temperature, and not at 100° as Muir recommends, since some decomposition occurred at this temperature.

Percentages of iodine in four samples were 79.11, 78.87, 79.32, 79.04 (Calc. for  $I_2O_4$ , 79.87). Oxygen values were 20.12, 19.96, 20.17 (Calc. for  $I_2O_4$ , 20.13). The formula was confirmed by determining the amount of iodine as iodate produced on dissolving the oxide in hot water, boiling off the free iodine, reducing with sulphur dioxide, and determining iodide as silver iodide in presence of nitric acid. Free iodine was found by difference. Oxygen values calculated from the iodate results were in agreement with those obtained by direct experiment.

## Analysis.

	I.	II.
Total iodine .....	79.08	79.08
Iodine as iodate .....	63.64	63.54
Free iodine .....	15.44	15.54
Oxygen value calculated from iodate result .....	20.04	20.01
Oxygen value observed .....	20.20	19.96
Ratio of free iodine : iodine as iodate .....	1 : 4.12	1 : 4.08
Calc. ratio for $I_2O_4$ .....	1 : 4	

Iodine dioxide is a yellow granular powder which does not absorb moisture, is only very slightly soluble in cold water, but dissolves in hot water, forming iodic acid and iodine. With hydrochloric acid it evolves chlorine and gives a yellow solution owing to the formation of iodine monochloride:  $I_2O_4 + 8HCl = 2ICl + 3Cl_2 + 4H_2O$ .

With concentrated aqueous ammonia, the solid reacts with effervescence and becomes black from the formation of nitrogen iodide. This behaviour is regarded as characteristic of iodine in a state of oxidation lower than quinquivalent. The black solid, like nitrogen iodide, dissolves in excess of aqueous ammonia, on warming, to a practically colourless solution.

3. *Action of Heat on Iodine Dioxide.*—Iodine dioxide decomposes slowly at 85° but more rapidly at about 130°. Known amounts (0.13—0.33 g.) were heated at 110°, 125°, and 130° respectively in an open weighing bottle. When the weight became constant (after about 4 hours), the percentage loss found with three specimens was 16.40, 16.03, and 15.93. The residue was light brown and absorbed moisture with darkening in colour, was soluble in water, and analysis showed that it was largely iodine pentoxide. Iodine in four samples was 75.75, 75.86, 76.03, 75.59% (Calc. for  $I_2O_5$ , 76.04). Oxygen values in three specimens were 22.80, 21.68, and 22.76% (Calc. for  $I_2O_5$ , 23.96).

These results indicate that decomposition occurs according to the equation:  $5I_2O_4 = 4I_2O_5 + I_2$ , and not into iodine and oxygen as stated by Muir. The percentage loss of iodine according to the equation is 15.97, which agrees with that found.

*Sulphates of Iodine.*

Millon (*loc. cit.*) claims to have prepared as intermediate products in the action of hot concentrated sulphuric acid on iodic acid the compounds (a)  $4I_2O_5, I_2O_4, SO_3, H_2O$ ; (b)  $2I_2O_5, I_2O_4, SO_3, H_2O$  and (c)  $I_2O_4, 2(SO_3, H_2O)$ . Oxygen and sulphate values were determined. Chrétien (*Compt. rend.*, 1896, 123, 814) describes a sulphate, ( $\alpha$ )  $I_2O_3, SO_3, \frac{1}{2}H_2O$ , or  $(IO)_2SO_4, \frac{1}{2}H_2O$ , obtained by dissolving iodine in a hot solution of iodic acid in concentrated sulphuric acid, and also by heating a mixture of iodic acid and concentrated sulphuric acid until abundant vapours of iodine are evolved for some time. He states that when this solution is kept over concentrated sulphuric acid, it begins to crystallise after some days, and the crystals continue to deposit for some months. Besides this sulphate, Chrétien (*Ann. Chim. Phys.*, 1898, 15, 367) describes: ( $\beta$ )  $2SO_3, 2H_2O, 3I_2O_4$ ; and ( $\gamma$ )  $2SO_3, 2H_2O, 2I_2O_4, I_2O_5$ . From the ratio of free iodine to iodine as iodate, the oxide of iodine in combination with sulphuric acid was deduced. Kappeler (*Ber.*, 1911, 44, 3501) made no analyses, but considered that Chrétien's sulphate ( $\alpha$ ) was the intermediate product in the formation of  $I_2O_4$ , the latter being produced from it by reaction with iodic acid:  $(IO)_2SO_4 + 2HIO_3 = 2(IO)IO_3 + H_2SO_4$ . We have further studied the intermediate sulphate produced in Muir's method and find that its composition can be represented as that of a mixture of approximately equimolecular quantities of the compounds  $I_2O_3, H_2SO_4$  and  $I_2O_4, H_2SO_4$ . We have been unable to prepare Chrétien's compound ( $\alpha$ ) by his method. Our analysis showed that the product was probably  $I_2O_3, H_2SO_4$  containing some  $I_2O_4, H_2SO_4$ .

*Experimental.*

The intermediate product obtained in Muir's method from 6 g. of iodic acid and 20 g. of sulphuric acid was kept on a porous plate over sulphuric acid in a desiccator. It was a yellow crystalline powder or crust.

Iodine was estimated by dissolving the compound in warm water containing sulphurous acid, and precipitating silver iodide in presence of nitric acid. Found in four samples A to D : 61.13, 60.46, 60.98, 61.79%.

Sulphate radical was determined by dissolving the powder in hot water and treating the solution, containing iodine, iodic acid, and sulphuric acid, with zinc dust and a small amount of hydrochloric acid so as to reduce iodine and iodic acid to iodide. The sulphate in the filtrate was precipitated as barium sulphate. Found in the samples A to D, 24.09, 25.71, 22.52, 24.32%.

The oxygen value was determined as before (J., 1934, 1088) and found to be : A, 13.30, 13.30; B, 14.27; C, 14.35; D, 14.13.

The values for iodine and sulphate radical agree fairly closely with the formula  $I_2O_4, H_2SO_4$  (Calc. : I, 61.06;  $SO_4$ , 23.07%), but the oxygen value calculated according to the decomposition :  $2I_2O_4, H_2SO_4 = 2H_2SO_4 + 2I_2 + 4O_2$  is 15.38, whilst the experimental values are lower. This indicates that some lower oxide of iodine is also present. The ratio of free iodine to iodine as iodate was determined as in the case of iodine dioxide. The oxygen value determined was in agreement with that calculated from the iodate value.

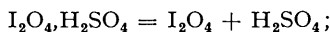
	C.	D.
Total iodine .....	60.98	61.79
Iodine as iodate .....	44.76	45.96
Free iodine (by difference).....	16.22	15.83
Oxygen value calculated from iodate .....	14.13	14.47
Oxygen value found .....	14.35	14.13
Ratio of free iodine : iodine as iodate .....	1 : 2.75	1 : 2.77

The calculated ratios for  $I_2O_4$  and  $I_2O_3$  are 1 : 4 and 1 : 1.5, respectively, so that the observed value corresponds with  $I_2O_3 + I_2O_4$ , viz., 1 : 2.75.

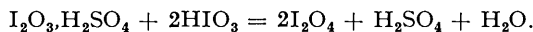
The results can be explained if the intermediate product is a mixture of *approximately* equimolecular quantities of  $I_2O_3, H_2SO_4$  and  $I_2O_4, H_2SO_4$ .

The empirical formula calculated from the mean percentages of iodine, sulphuric acid, and available oxygen (I, 61.09;  $H_2SO_4$ , 24.65; O, 14.01) is  $I_4O_7, 2H_2SO_4$ , viz.,  $I_2O_3, I_2O_4, 2H_2SO_4$ .

We suppose that the two sulphates,  $I_2O_3, H_2SO_4$  and  $I_2O_4, H_2SO_4$ , in the mixture behave differently on washing with water. With  $I_2O_4, H_2SO_4$ , sulphuric acid is washed away, leaving  $I_2O_4$  :



whilst in the case of  $I_2O_3, H_2SO_4$ , reaction occurs with some iodic acid produced by reaction with water, as suggested by Kappeler (*loc. cit.*) for the compound  $(IO)_2SO_4$  :



We have attempted without success to prepare Chrétien's sulphate  $I_2O_3, SO_3, \frac{1}{2}H_2O$ . Sample A was prepared by heating together iodic acid and concentrated sulphuric acid, and samples B and C by dissolving iodine in a hot solution of iodic acid in concentrated sulphuric acid, in all cases till abundant iodine vapours were given out for some time. The products were dried and analysed as before.

	A.	B.	C.
Total iodine .....	62.74	62.04	62.04
Iodine as iodate.....	39.01	38.79	38.50
Free iodine .....	23.73	23.25	23.54
Oxygen value calculated from iodate .....	12.30	12.21	12.13
Oxygen value found .....	12.30	12.33	—
$H_2SO_4$ .....	24.91	26.77	—
Ratio of free iodine : iodine as iodate .....	1 : 1.64	1 : 1.65	1 : 1.635

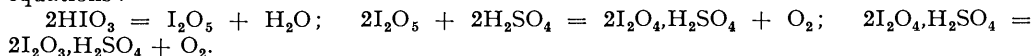
The calculated ratios for  $I_2O_3$  and  $I_2O_4$  are 1 : 1.5 and 1 : 4, hence the sulphate produced appears to consist mainly of  $I_2O_3, H_2SO_4$  containing a small amount of  $I_2O_4, H_2SO_4$ .

Sample B appears to contain some free sulphuric acid. The complete analyses of A and B are : total I, 62.74 (A), 62.04 (B);  $H_2SO_4$ , 24.91 (A), 26.77 (B); O value, 12.30 (A), 12.13 (B); total, 99.95 (A), 100.94 (B).

The empirical formula for A corresponds with  $I_{1.94}O_3, H_2SO_4$ , i.e., approximately with

$I_2O_3 \cdot H_2SO_4$  (Calc. : I, 63.50;  $H_2SO_4$ , 24.50; O, 12.00%). The composition of sample B also agrees with the formula  $I_2O_3 \cdot H_2SO_4$ , but it contained a little free sulphuric acid.

These results indicate that the sulphate is  $I_2O_3 \cdot H_2SO_4$  and not, as found by Chrétien,  $I_2O_3 \cdot SO_3 \cdot \frac{1}{2}H_2O$ . It has been shown above that the intermediate product of the action of hot concentrated sulphuric acid on iodic acid consists of a mixture of  $I_2O_4 \cdot H_2SO_4$  and  $I_2O_3 \cdot H_2SO_4$ , and the assumption that  $I_2O_3 \cdot SO_3 \cdot \frac{1}{2}H_2O$  is the only intermediate product is erroneous. The action of hot concentrated sulphuric acid on iodic acid may be represented by the following equations :



On further heating, the oxide of iodine decomposes to give iodine vapour and oxygen.

The sulphates of iodine are yellow hygroscopic solids which turn dark in colour on absorbing moisture. They are insoluble in cold water, but dissolve in hot water, giving iodic acid, iodine and sulphuric acid.

#### *The Action of Ozonised Oxygen on Iodine.*

Andrews and Tait (*Proc. Roy. Soc.*, 1859, **9**, 606; *Phil. Trans.*, 1860, **150**, 113) found that ozonised oxygen reacts with iodine at room temperature to give a greyish-yellow powder, the ozone being destroyed without change in volume of the gas. According to Ogier (*Compt. rend.*, 1877, **85**, 957) the substance formed by passing ozonised oxygen over iodine at 40—50° is  $I_2O_3$  (ratio of oxygen to iodine in three samples was 5.27, 5.52, 5.25; calc. for  $I_2O_3$ , 5.29). Ogier (*Compt. rend.*, 1878, **86**, 722) passed an electric silent discharge continuously through a tube containing a mixture of oxygen and iodine vapour. He states that in the lowest part of the tube the oxide  $I_2O_3$  was deposited, followed in succession by iodine dioxide,  $I_2O_4$ , iodic anhydride,  $I_2O_5$ , and periodic anhydride,  $I_2O_7$ . Only the last supposed compound, described as a white powder, was analysed, the ratio of oxygen to iodine being given as 2.20, 2.30, and 2.21 in three samples (calc. for  $I_2O_7$ , 2.26). Fichter and Rohner (*Ber.*, 1909, **42**, 4093), by bubbling oxygen containing 8% of ozone through a saturated solution of iodine in chloroform, and also by treating dry iodine with ozonised oxygen at 40—50°, obtained a product the analyses of which agreed with the formula  $I_4O_9$ , which they regarded as an iodate of tervalent iodine,  $I(IO_3)_3$ . This began to lose iodine at 75° and decomposed rapidly at 120—130°. Beger (*Chem. Ztg.*, 1909, **33**, 1232) prepared the compound by the action of ozonised oxygen on iodine at 40—60°, and his analyses agree with the formula  $I_4O_9$  (Found : I, 78.0, 77.9, 77.8. Calc. for  $I_4O_9$  : I, 77.9%).

In view of the discrepancies in the literature, further experiments appeared to be desirable, and these have disclosed some new features of the reaction.

#### *Experimental.*

1. *Action of Ozonised Oxygen on Iodine.*—When ozonised oxygen containing about 10% of ozone is passed through a concentrated solution of iodine in carbon tetrachloride, reaction is apparent after about 2 hours. The action, however, does not occur in the solution itself, but at the surface, where iodine vapour reacts with ozone to give a yellow solid which slowly falls into the solution, so that it might be supposed that the solid was deposited from the solution.

This method of preparation, described by Fichter and Rohner, is neither convenient nor rapid.

The first method used by Ogier, when slightly modified, was found most suitable. Ozonised oxygen containing 8—10% by volume of ozone was passed through a U-tube with bulbs containing iodine which was warmed. The iodine vapour reacted with ozone with the production of yellowish vapours, which were passed through a tube packed with previously washed and dried glass wool. The yellow product collected on the glass wool was analysed. Iodine was found by dissolving the oxide in water, with which it reacts to give free iodine and iodic acid. The solution was reduced with sulphur dioxide, and the iodine weighed as silver iodide.

Sample.	Amount of product, g.	Silver iodide formed, g.	Iodine % (experimental).
A	0.0928	0.1350	78.60
B	0.0400	0.0584	77.77
C	0.0468	0.0684	78.07
D	0.0552	0.0798	78.12

Oxygen values were determined as previously described (J., 1934, 1088).

Sample.	Amount of product, g.	Oxygen evolved at S.T.P., c.c.	Wt. of oxygen, g.	Oxygen % (experimental).
A	0.0587	9.12	0.01303	22.19
B	0.0506	7.49	0.01070	21.14
C	0.0332	5.08	0.00726	21.85

These results show that the compound formed is  $I_4O_9$  (Calc. : I, 77.91 ; O, 22.09%).

In order to eliminate the possibility that traces of oxides of nitrogen present in the ozonised oxygen (produced from the small amount of nitrogen present in the cylinder oxygen) might play some part in the oxidation of iodine, an experiment was made with ozonised electrolytic oxygen (free from nitrogen). The same yellow product was obtained, containing 76.76% of iodine.

2. *Properties of  $I_4O_9$ .*— $I_4O_9$  is a light yellow, granular powder which (unlike  $I_2O_4$ ) is extremely hygroscopic. It turns brown on absorption of moisture with liberation of iodine, and with water gives a brown solution containing iodine and iodic acid. On treatment with hydrochloric acid, the oxide evolves chlorine and a yellow solution is obtained containing iodine chloride. On treatment with ammonia, nitrogen iodide is formed. The oxide begins to decompose at 75°, more rapidly at higher temperatures. Iodine vapours are evolved and the residue is brown. The oxide collected on glass wool was heated at 85° and 120°. The loss of weight was almost constant. The deep brown colour due to iodine in the residue was removed after prolonged heating.

Sample.	Time of heating, hrs.	Amount of sample, g.	Amount of residue, g.	Loss of wt., g.	Loss % (experimental).	
A	20	0.0644	0.0524	0.0120	18.63	(heated for a short time)
B	48	0.0719	0.0545	0.0174	24.20	
C	63	0.1044	0.0842	0.0202	19.46 (?)	
D	48	0.0358	0.0274	0.0084	23.49	
E	48	0.0606	0.0464	0.0142	23.43	
F	72	0.0606	0.0458	0.0148	24.32	

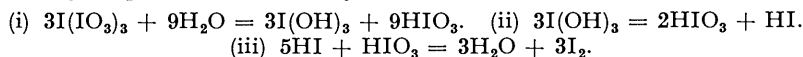
The percentages of iodine in the residue were 77.01, 76.45, 76.16, and 76.46, which correspond with iodine pentoxide (calc., 76.05). The higher value in the first sample is due to incomplete expulsion of iodine.

From the percentage of loss at 85° and 120°, it appears that decomposition occurs according to the equation :  $4I_4O_9 = 6I_2O_5 + 2I_2 + 3O_2$ , for which the calculated loss is 23.07%.

3. *Action of Water on  $I_4O_9$ .*—Fichter and Rohner (*loc. cit.*) found the ratio of free iodine to iodine as iodate in the aqueous solution of  $I_4O_9$  to be 1 : 11.5 in one case and 1 : 14 in the other ; the value expected according to the equation  $5I_4O_9 + 9H_2O = 18HIO_3 + I_2$  is 1 : 9. The high results are explained by the assumption that the oxide prepared by the action of ozonised oxygen on iodine dissolved in carbon tetrachloride contains free iodic acid produced by moisture which entered during the experiment. The ratio for the oxide prepared by the action of ozonised oxygen on iodine was 1 : 6.5 and this low value is explained as due to the presence of free iodine. In our experiments the iodine as iodate was found by dissolving the compound in water and then boiling off the free iodine produced. Iodic acid in the solution was reduced with sulphur dioxide, and the iodine estimated as silver iodide. Free iodine was found by difference.

	I.	II.	III.	IV.	V.	VI.	VII.
Total iodine.....	77.91	—	—	—	—	—	—
Iodine as iodate .....	67.59	67.77	69.71	68.77	68.23	68.14	69.52
Free iodine .....	10.32	10.14	8.20	9.14	9.68	9.77	8.39
Oxygen value calculated from iodate...	21.28	21.34	21.96	21.65	21.49	21.46	21.89
Oxygen value found	21.72	—	—	—	—	—	—
Ratio of free iodine : iodine as iodate .....	1 : 6.54	1 : 6.62	1 : 8.37	1 : 7.59	1 : 7.05	1 : 6.97	1 : 8.28

Although these values are better than those obtained by Fichter and Rohner, the experimental iodic iodine values are lower than that (70.12%) calculated from the equation  $5I_4O_9 + 9H_2O = 18HIO_3 + I_2$ . The reaction may be formulated in three stages :



The reaction equation was confirmed by determining the amount of free iodine produced, by extraction by carbon tetrachloride. To the solution in carbon tetrachloride, concentrated

potassium iodide solution was added, and the iodine titrated with thiosulphate. The percentages found in four samples were 9.10, 8.52, 8.40, 8.48 (calc., 7.79).

## SUMMARY.

Iodine pentoxide (not dioxide) is the product of reaction between concentrated nitric acid (*d* 1.50) and iodine. Iodine dioxide is produced by the action of hot concentrated sulphuric acid on iodic acid, as described by Muir, but the final drying of the compound is best effected at room temperature and at atmospheric pressure in a desiccator containing lime. The oxide  $I_2O_4$  is not hygroscopic. The decomposition at  $110^\circ$ ,  $125^\circ$ , and  $130^\circ$  takes place according to the equation:  $5I_2O_4 = 4I_2O_5 + I_2$ .

By heating iodic acid with concentrated sulphuric acid, a mixture of equimolecular quantities of  $I_2O_4, H_2SO_4$  and  $I_2O_3, H_2SO_4$  is obtained. On dissolving iodine in a hot solution of iodic acid in concentrated sulphuric acid, and also by heating a mixture of iodic acid and concentrated sulphuric acid till iodine is evolved, a sulphate of the composition  $I_2O_3, H_2SO_4$ , with a small amount of  $I_2O_4, H_2SO_4$ , is obtained. Chrétien's sulphate,  $I_2O_3, SO_3, \frac{1}{2}H_2O$ , could not be obtained.

By passing ozonised oxygen over gently heated iodine, reaction occurs in the vapour phase and a yellow product of the composition  $I_4O_9$  is obtained. This is very hygroscopic. It begins to decompose at  $75^\circ$ , and decomposition at  $85^\circ$  and  $120^\circ$  proceeds according to the equation:  $4I_4O_9 = 6I_2O_5 + 2I_2 + 3O_2$ .

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