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# XXVIII.—Formation of Dithionic Acid by the Oxidation of Sulphurous Acid with Potassium Permanganate.

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It is usually stated that sulphurous acid is oxidised by potassium permanganate to sulphuric acid. Sulphuric acid is undoubtedly the principal product of the action, but if an acidified solution of sulphurous acid of known strength is titrated with a standardised solution of potas sium permanganate, the permanganate ceases to be decolorised when the quantity used is about nine-tenths of that necessary to completely oxidise the sulphurous acid to sulphuric acid. Lunge and Smith (J. Soc. Chem. Ind., 1883, p. 460) ascribe this discrepancy to loss of sulphur dioxide by volatilisation. As the constancy of the results under different conditions of dilution gave us reason to believe that this was not the true explanation, we determined to carry out the experiment under conditions in which loss by volatilisation and also atmospheric oxidation were impossible.

The apparatus employed was that suggested by one of us, in conjunction with Professor Dunstan, for the estimation of nitrites (*Pharm.* J., 1889, [III.], 19, 741). A round-bottomed flask is fitted with an india-rubber cork and wide glass tube, and to this is connected a burette, by a piece of pressure tubing, which can be closed by a screw clip. Water is boiled in the flask until the apparatus is free from air, and then the clip is screwed up and the flask cooled. A liquid can now be drawn into the partially vacuous flask from the burette, and titrations are carried out by filling the burette with the standardised solution. Before using the apparatus for the purpose of these experiments, it was ascertained that the india-rubber connections had no appreciable action on the solutions used.

The sodium sulphite employed in the experiments was crystallised from the commercial salt until free from sulphate and carbonate. When estimated by means of iodine, the purified salt gave results corresponding exactly with the formula  $Na_2SO_3 + 7H_2O$ . 0.4 grams of the pure salt, dissolved in recently boiled water, was run into the flask from the burette, and dilute sulphuric acid, also recently boiled, was added. The burette was washed out with the standardised solution of permanganate and then filled with it. The permanganate solution was now run in little by little, the flask meantime being constantly shaken, to prevent the permanganate from remaining unattacked in the glass tube. The permanganate required in a series of eight concordant determinations was 18.74 c.c. (1 c.c. = 0.001206 gram available)oxygen), equal to 0.0226 gram of oxygen absorbed. The oxygen required to oxidise 0.4 gram of  $Na_3SO_3 + 7H_2O$  to sulphate is 0.0254 gram.

These experiments, made under conditions in which volatilisation or atmospheric oxidation of sulphurous acid was impossible, show that only 89 per cent. of the oxygen necessary to oxidise the sulphurous to sulphuric acid was absorbed, and this can only be explained by supposing that a part of the sulphurous acid was oxidised to an intermediate compound incapable of further oxidation by the permanganate solution. It occurred to us as most probable that the compound was dithionic acid, first prepared by Welter and Gay Lussac in 1819, by passing sulphur dioxide into water containing manganese dioxide in suspension. That this was the substance was rendered more probable by the observation of Berthier in 1843 (Ann. Chim. Phys., [iii.], 7,

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p. 77),\* that when sulphur dioxide is passed into solutions of potassium chromate or dichromate, dithionic acid is formed in addition to sulphuric acid.

In order to test this supposition, the experiment was repeated on a large scale. The gas spontaneously volatilising from liquid sulphur dioxide was passed into cold water, and potassium permanganate solution was run in at the same time, care being taken to keep the sulphurous acid in excess until the end of the operation, when the exact additional quantity of permanganate required was added. The sulphuric acid and manganese were precipitated by baryta, and the excess of baryta precipitated by subsequently passing carbon dioxide through the mixture; the filtered liquid, when evaporated on the water bath, yielded crystals which had the properties of potassium dithionate. When heated alone or with hydrochloric acid, sulphur dioxide was evolved and sulphate of potassium left, but no sulphur set free; moreover, when heated with nitric acid, sulphate of potassium was the only product, all these reactions being characteristic of a dithionate.

Before obtaining the crystals pure enough for analysis, a tedious process of recrystallisation was necessary in order to get rid of the potassium carbonate left in the residue when this process of isolation is employed. This, however, provided an opportunity of searching for products of the oxidation of sulphurous acid other than dithionic and sulphuric acids, but no fractions were obtained which gave evidence of the existence of a third substance, and it was concluded that dithionic and sulphuric acids were the only products. The potassium dithionate finally obtained had a neutral reaction, was free from carbonate and sulphate, and gave the same figures on analysis when recrystallised.

For identification, several methods of analysis were employed. (A.) The aqueous solution of the salt was heated with hydrochloric acid in the air-free flask (closed), until decomposed into sulphurous and sulphuric acid, and the sulphurous acid estimated by solution of iodine run in from the burette. (B.) The aqueous solution of the salt was boiled with hydrochloric acid in the air-free flask (open), until free from sulphurous acid, and the remaining sulphuric acid estimated as barium sulphate. (C.) The solution of the salt was boiled with hydrochloric acid, the sulphuric acid produced precipitated with baryta water, the excess of baryta removed by carbon dioxide, and the potassium estimated in the solution as platinochloride. The results of the analyses were as follows.

<sup>\*</sup> We are indebted to Mr. W. J. Sell for this reference. The fact is mentioned in both Gmelin's *Handbook* and Watt's *Dictionary* (original edition), but the reference given in both is wrong.

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	Found.	Calculated for H	$X_2S_2O_6$
<ul> <li>A. Sulphur, liberated by hydrolysis as SO<sub>2</sub></li> <li>B. Sulphur, liberated by hydro-</li> </ul>	13.47 per cent.	13·44 per c	e <b>n</b> t.
lysis as SO <sub>3</sub>	13.60 ,,	13.44 ,,	
C. Potassium	32.53 ,,	32.77 ,,	

These results fully identify the substance as potassium dithionate not only by the percentage of potassium and total sulphur, but also by the characteristic hydrolysis of dithionic acid into equivalent proportions of sulphurous and sulphuric acids.

Having demonstrated that dithionic acid, as well as sulphuric acid, is a product of the oxidation of sulphurous acid by permanganate of potassium, we next endeavoured to obtain a further knowledge of the reaction by determining the influence of dilution, temperature, and acidity on the relative proportions of the products. For these experiments, the apparatus previously described and a solution of permanganate of the same strength were employed.

I.—Influence of Dilution (Temperature and Acidity Constant).

Ν	$a_2SO_3 +$	$7H_2O$ taken	Water.	Permanganate required.
1.	0.4	gram.	21 c.c.	18 9 c.c.
2.	0.4	,,	61 ,,	18.7 ,,
3.	0.4	,,	161 ,,	18·7 "

II.—Influence of Temperature (Dilution and Acidity Constant).

N	$a_{2}SO_{3} + 7$	H <sub>2</sub> O.	Temperature.	Permanganate, required.
1.	0·4 g	gram.	_80°	18·8 c.c.
2.	0.4	,,	- 2°	18.8 ,,

III.—Influence of Acidity (Dilution and Temperature Constant).

N	$a_2SO_3 +$	-7H <sub>2</sub> O.	Dilute $H_2SO_4$ , 5%	Permanganate required.
1.	0.4	gram.	5 c.c.	18 <sup>.</sup> 8 c.c.
2.	0.4	·,	60 ,,	18·6 "
3.	0·4	,,	150 "	18·6 ,,

These experiments show that a variation in the amount of water or of acid, or in the temperature, does not produce any appreciable variation in the proportion of sulphurous and sulphuric acids. This remarkable result indicates that the dithionic acid is not a chance product, but that its formation is an essential part of the reaction. Dithionic acid is intermediate between sulphurous and sulphuric acids, its hypothetical anhydride being  $S_2O_5$ , and it might be supposed to be formed as a first stage in the oxidation of sulphurous to sulphuric acid. That this is not the case is, we think, made clear by the foregoing experiments, for varia-

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tion in the conditions of temperature and dilution would certainly affect the quantity of dithionic acid left unoxidised.

It seems much more probable that the formation of dithionic as well as of sulphuric acid is due to the different oxidising effects of the oxides of manganese during the various stages of reduction. It is to be supposed that, in reducing the  $Mn_2O_7$  of the permangate to  $MnO_2$ , the sulphurous acid is oxidised to sulphuric acid completely, for when a solution of sulphurous acid is poured into excess of permanganate solution, sulphuric acid is the only product. If manganese dioxide, even in a very fine state of division and diffused in water, is added to excess of sulphurous acid solution, both dithionic and sulphuric acids are produced, but the proportion of the former appears to be larger than when potassium permanganate is used. It appears, therefore, that the formation of dithionic acid is due to a stage in the reduction of  $MnO_2$ to MnO.

The relative proportion of the two acids produced almost exactly corresponds with the equation

 $17H_{2}SO_{4} + 6KMnO_{4} = 2K_{2}S_{2}O_{6} + K_{2}SO_{4} + 6MnSO_{4} + 6H_{2}SO_{4} + 11H_{2}O_{4}$ According to this equation, 88.2 per cent. of the oxygen required to oxidise sulphurous to sulphuric acid is used ; in our experiments, 88.9 per cent. of that required was used. As the proportion of dithionate represented by the above equation is that which would be produced were it formed during a stage of the reduction of the permanganate corresponding with the conversion of  $Mn_3O_4$  into 3MnO, it might be expected that the oxide Mn<sub>3</sub>O<sub>4</sub> would itself oxidise sulphurous to dithionic acid. If, however, this oxide, prepared by heating the dioxide to fusion, be finely powdered and diffused in water, and the mixture added to the solution of sulphurous acid, sulphuric acid is the only product of oxidation. This fact, however, does not preclude the possibility of there being a corresponding stage in the reduction of the dissolved manganese compounds in which dithionic acid is produced. At any rate, its formation must be due to the weak oxidising action of the permanganate in one of the later stages of its reduction.

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