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I.—*The Action of Hydrogen Sulphide on a Neutral Solution of Potassium Permanganate.*

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WHEN a slow current of hydrogen sulphide is passed through a 1% solution of potassium permanganate, the purple solution becomes brown and a white deposit of sulphur appears round the delivery tube. After a short time, a greyish-brown solid separates without appreciable rise in temperature; this slowly changes first to a yellow mixture of hydrated manganese dioxide, manganese sulphide, and sulphur and finally to a pink precipitate of manganese sulphide containing much sulphur, the temperature rising rather more than 10°.

The course of the reaction was investigated in stages.

When a solution of potassium permanganate was shaken with hydrogen sulphide solution, a brownish-black precipitate of hydrated manganese dioxide and sulphur formed immediately; the faintly alkaline filtrate contained unchanged permanganate. The precipitate was well washed by decantation with air-free water, and the manganese dioxide in it was estimated by determining the amount of chlorine it liberated from hydrochloric acid. The liquid left over from this estimation was treated with sodium carbonate, and the total manganese weighed as Mn_3O_4. Three estimations gave values of 1 : 3·8, 1 : 3·1, and 1 : 2·7 for the molecular ratio $MnO : MnO_2$, showing that the manganese is only partly precipitated as hydrated dioxide.

Through solutions of potassium permanganate of various concentrations hydrogen sulphide was passed until the whole of the manganese was converted into sulphide. The precipitate was filtered off, and the manganese present in it as sulphide was estimated by two methods : (1) The sulphide was extracted with dilute hydrochloric acid, the solution filtered, and the manganese precipitated as carbonate and weighed as Mn_3O_4. Recovery = 99·8% of theory. (2) The sulphide containing free sulphur was ignited and so converted into Mn_3O_4. Recovery = 99·9% of theory.

The yellow filtrate, which contained colloidal sulphur and was faintly alkaline to phenolphthalein, was freed from hydrogen sulphide by shaking under reduced pressure, and kept in a vacuum desiccator. The sulphur deposited was filtered off and the liquor, now colourless, was left in a vacuum desiccator over a dehydrating agent for some days. Needle-shaped crystals of potassium thiosulphate and rhombic crystals of potassium sulphate grew in it as it became concentrated. The filtrate did not contain polythionates, sulphide, or sulphite. To test for polythionates, the filtrate was examined qualitatively by the tests given by Takamatsu and Smith (J., 1880, **37**, 592), Bassett and Durrant (J., 1923, **123**, 1279), Gutmann (*Ber.*, 1905, **38**, 3277; 1907, **40**, 3614), Sander (*Z. angew. Chem.*, 1915, **28**, 9; 1916, **29**, 11, 16), and Riesenfeld and Feld (*Z. anorg. Chem.*, 1921, **119**, 225) in comparison with control thionate solutions of known concentrations.

It was shown that hydrogen sulphide has no action on thiosulphates by passing the gas through standard solutions of sodium thiosulphate at various temperatures; the excess was removed under diminished pressure, and the solutions were titrated against iodine solution. The absence of colloidal sulphur was demonstrated by negative results on the addition of electrolytes and with the cataphoresis test.

Estimation of the Compounds produced at Various Stages in the Action of Hydrogen Sulphide on Potassium Permanganate.

In all cases, the excess of hydrogen sulphide was removed by means of a suction pump or by the addition of lead carbonate.

(1) *Estimation of the Products of the Complete Reaction.*—The manganese is quantitatively precipitated as sulphide (see above).

The sulphate in the filtrate was estimated as barium sulphate, the precautions advised by Taylor (*J. Soc. Chem. Ind.*, 1923, **42**, 294T) being taken but acetic acid being used instead of hydrochloric acid as suggested by Müller (*Bull. Soc. chim.*, 1916, **19**, 8) when sulphates are being estimated in presence of thiosulphates. The thiosulphate in the filtrate was estimated iodometrically, the solution being first acidified with acetic acid (Müller, *loc. cit.*). The mean of several results gave 61·86% of potassium recovered as potassium sulphate and 38·16% as potassium thiosulphate. The sum of these values, 100·02, shows that the whole of the potassium is eventually recovered in these two forms. Practically the same values were obtained from experiments at temperatures ranging from −3° to

+76°. The values approximate to three molecules of potassium sulphate to two of potassium thiosulphate, and the result, when the reaction is complete, can be summed up in the equation

$$10KMnO_4+22H_2S=3K_2SO_4+2K_2S_2O_3+10MnS+22H_2O+5S.$$

At the end of the reaction the solution is alkaline and, if it is not acidified before the titration with iodine, the values for the thiosulphate are always high. Control experiments showed that the lead carbonate used to remove the excess of hydrogen sulphide from the solution has no action on the thiosulphate. The thiosulphate found in a solution (4·170 g. per litre) which had been treated with hydrogen sulphide, shaken with lead carbonate, filtered, and then titrated against iodine was 4·164; 4·167; 4·170; and 4·165 g. per litre.

(2) *Investigation of the Mechanism of the Reaction by a Study of Two Intermediate Stages.*—Hydrogen sulphide was passed through the solution until the hydrated manganese dioxide was converted into a dirty yellow, granular mass. The values then found for potassium recovered as sulphate and as thiosulphate were 59·61, 58·54% and 34·32, 32·45%, respectively, of the total potassium. Since the sum of these values (93·93, 90·99) does not account for all the potassium present, it appears that some other sulphur compound of potassium is first formed which is subsequently decomposed by hydrogen sulphide into potassium sulphate and thiosulphate; the average final values for potassium recovered as sulphate and as thiosulphate were 61·66% and 38·27%, respectively (sum, 99·93). This compound may be one (or more) of the polythionates, for penta-, tetra-, and tri-thionates are known to be thus decomposed by hydrogen sulphide (Debus, J., 1888, **53**, 328) and the authors have shown that dithionates slowly undergo a similar change in presence of this gas.

Identification of the Compounds formed in Solution when the Manganese is precipitated as Hydrated Manganese Dioxide.

A solution of potassium permanganate was shaken with successive small quantities of half-saturated aqueous hydrogen sulphide until the brown colour just disappeared. (When this was done carefully with standard solutions, it was not possible to obtain a definite end-point.) The filtered liquid, which was faintly alkaline, contained sulphate, thiosulphate, and dithionate, but no sulphide, sulphite, penta-, tetra-, tri-thionate, colloidal sulphur or manganese. In view of the difficulty of testing for thionates in presence of one another, the tests given (p. 2) were performed both on the filtrate and on control solutions of thionates of known concentrations.

The distinction between thiosulphate, dithionate, and trithionate was made as follows : The solution decolorised iodine solution and gave a black precipitate with silver nitrate. (The solution gave no precipitate when warmed with hydrochloric acid. This was due to the low concentration of the thiosulphate.) Dilute aqueous potassium permanganate added to the solution was first bleached (thiosulphate), then a blood-red coloration developed, and brown hydrated manganese dioxide was slowly precipitated. This suggested the presence of tri- or di-thionate. The filtrate from the precipitation of the sulphate by barium chloride was warmed with dilute hydrochloric acid; sulphur dioxide was detected, but sulphur was not deposited. Sulphate was detected in the solution (distinction from thiosulphate). Trithionates give sulphur dioxide, sulphate, and sulphur. Dithionates give sulphur dioxide and sulphate only. In dilute solutions the sulphur may not be precipitated. Mercuric chloride gives a yellow precipitate with trithionates, but does not react with dithionates. With this reagent, the filtrate gave a white turbidity. This is given by thiosulphates in very dilute solution. This suggests the absence of trithionates and the presence of thiosulphate. Ammoniacal silver nitrate had no action on the filtrate. A trithionate would have given a brown coloration.

Action of Hydrogen Sulphide on Hydrated Manganese Dioxide.

The blackish-brown precipitate of hydrated manganese dioxide obtained by the action of dilute aqueous sodium hypochlorite on a solution of manganous chloride, after being thoroughly washed with water, was free from alkali, chloride, and hypochlorite. It was suspended in water, through which scrubbed hydrogen sulphide was then bubbled for some time. A large proportion of the dioxide was converted into manganese sulphide contaminated with sulphur, and the solution, which was neutral to phenolphthalein, contained manganese as sulphate and thiosulphate. Ordinary dry A.R. manganese dioxide, when suspended in water and treated with hydrogen sulphide, gave the same results, and so also did hydrated manganese dioxide formed by the action of hydrogen sulphide on potassium permanganate and washed free from sulphate and thiosulphate and until the washings gave no indication of alkalinity with phenolphthalein. The presence of dithionate was not definitely proved, but independent experiments showed that manganese dithionate is decomposed by hydrogen sulphide into the sulphate and thiosulphate.

If neutral potassium sulphate was added to the water in which the hydrated manganese dioxide was suspended, the solution, in which manganese could not be detected, became alkaline to phenolphthalein and, when hydrogen sulphide was passed into it, the manganese was completely converted into manganous sulphide. The alkalinity was probably due to the adsorption of sulphate ions of the potassium sulphate. This would also account for the alkalinity of the solution in the reaction under investigation.

Quantitative Estimation of Intermediate Products in the Filtrate.

A dilute solution of potassium permanganate was treated with half-saturated aqueous hydrogen sulphide in the way described on p. 3, the precipitate was well washed, and the washings and the filtrate were made up to a definite volume. Care was taken that the solution contained no free hydrogen sulphide. In aliquot portions, the sulphate and thiosulphate were estimated as described on p. 2, and the dithionate by Szentpaly-Peyfuss's method (*Z. anorg. Chem.*, 1924, **131**, 203).

TABLE I.

Estimation of Sulphate, Thiosulphate, and Dithionate in the Filtrate.

Percentage of the potassium recovered as sulphate	thiosulphate	dithionate.	Total recovered.
69·70 (79·72)	4·84 (19·98)	25·06	99·60
79·87 (83·67)	10·27 (15·98)	9·51	99·65
68·08 (78·82)	4·65 (20·76)	26·84	99·57

The potassium is quantitatively accounted for as sulphate, thiosulphate, and dithionate, but the results show variations in the proportions in which the components are present. If it is assumed that the dithionate decomposes quantitatively into sulphate and thiosulphate, the values given in brackets would be obtained for potassium as sulphate and thiosulphate.

The results can be reconciled with the average values of 61·66 and 38·27% found for the potassium recovered as sulphate and thiosulphate, respectively, in the completed reaction (p. 3) as follows. When a large excess of hydrogen sulphide is passed, air is practically excluded from the reaction. Possibly, also, any oxidising action of the hydrated manganese dioxide is confined to the hydrogen sulphide, because dithionates are not oxidised by manganese dioxide. It is suggested, therefore, that the first products of the reaction are potassium sulphate, potassium dithionate, hydrated manganese dioxide, and sulphur; all attempts to stop the action at this stage, however, have failed. The stoicheiometric proportions in which the potassium sulphate and thiosulphate are found at the end of the reaction preclude the possibility of potassium dithionate being the only potassium salt first formed. The second stage of the action may be represented by the equations

$$5K_2S_2O_6+13H_2S=3K_2S_2O_3+2K_2SO_4+13H_2O+15S \quad . \quad . \quad . \quad (1)$$

$$x\mathrm{MnO_2},y\mathrm{MnO},z\mathrm{H_2O}+(2x+y)\mathrm{H_2S}=(x+y)\mathrm{MnS}+(2x+y+z)\mathrm{H_2O}+x\mathrm{S},$$

and hence the final result is potassium sulphate and thiosulphate in solution and a precipitate of manganous sulphide and sulphur. When the dilute solution is shaken with hydrogen sulphide, air dissolves freely and a part of the dithionate is directly oxidised to sulphate at the expense of the thiosulphate which would otherwise have been formed from the dithionate in the presence of excess of hydrogen sulphide. Excess of hydrogen sulphide thus does the double duty of reducing the dithionate to sulphate and thiosulphate and protecting it from oxidation by dissolved air. In support of this argument, attention is directed to the results on p. 3. These represent a stage intermediate between those for the final values (K_2SO_4, 61·66%; $K_2S_2O_3$, 38·27%) and those given in Table I, *i.e.*, a stage in which the "protecting" action of the hydrogen sulphide has been fully exerted but in which its reducing action has been stopped before completing its work. Assuming the decomposition of the dithionate into sulphate and thiosulphate in the sense of equation (1), the values on p. 3, calculated for the final product, become $59{\cdot}61 + (0{\cdot}4 \times 6{\cdot}07) = 62{\cdot}04$ and $58{\cdot}54 + (0{\cdot}4 \times 9{\cdot}01) = 62{\cdot}14$ for the percentage of potassium present in solution as sulphate and $34{\cdot}32 + (0{\cdot}6 \times 6{\cdot}07) = 37{\cdot}96$ and $32{\cdot}45 + (0{\cdot}6 \times 9{\cdot}01) = 37{\cdot}86$ for the percentage of potassium present as thiosulphate.

These results support the argument that the hydrogen sulphide has a protecting and reducing action, since, in the completed reaction, it was used in excess of that required for the first stage and air could have taken little or no part in the reaction.

Summary.

The first products of the reaction between hydrogen sulphide and potassium permanganate in dilute solution appear to be colloidal hydrated manganese dioxide, which quickly coagulates to a gelatinous precipitate; sulphur; and potassium sulphate and potassium dithionate in solution.

When excess of hydrogen sulphide is passed through the solution, the hydrated manganese dioxide is converted into manganous sulphide with the separation of sulphur. The manganous sulphide is first formed as a colloid, which quickly coagulates to pink manganous sulphide. Excess of hydrogen sulphide decomposes the potassium dithionate into potassium sulphate and thiosulphate with the simultaneous formation of sulphur. A portion of the

sulphur is precipitated; the rest is in colloidal solution and is completely precipitated on standing.

The solution is alkaline throughout. This is probably due to the adsorption of the anions of the potassium salts by the hydrated manganese dioxide or manganous sulphide.

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