CCLXIX.—The Reaction between Ferrous Phosphate and Sulphur Dioxide in Phosphoric Acid Solution; the Nature of the Decomposition Products.

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It has been shown (preceding paper) that the main characteristics of the oxidation of ferrous phosphate by sulphur dioxide can be explained by the assumption that the reaction consists of a primary reversible reaction in which ferrous phosphate is oxidised to ferric phosphate by sulphur dioxide, the latter being reduced to an active intermediate product which decomposes irreversibly in a secondary reaction with the formation of sulphur.

The object of the experiments here described was to obtain some information as to the nature of the intermediate product and if possible to identify it.

In the first place, the intermediate product postulated must have the power of reducing ferric phosphate in phosphoric acid solu-It has been shown in an earlier paper (Wardlaw, Carter, and tion. Clews, T., 1920, 117, 124) that neither sulphur dioxide nor ordinary sulphur effects this to an appreciable extent. Secondly, it must decompose under the conditions of the experiments by an irreversible reaction giving rise to sulphur and products that have no further influence on the course of the reaction. No sulphate is formed in the reaction, consequently substances which would give rise to sulphate in their decomposition are excluded. Since sulphur appears at a very early stage of the reaction, the decomposition of the substance in question must be very rapid and the quantity present in the solution at any instant correspondingly small. follows that it must be a very active reducing agent.

The possible intervention of the following substances has been suggested in the earlier papers: 1. Hyposulphurous acid $H_2S_2O_4$, 2. Thiosulphuric acid $H_2S_2O_3$, 3. An active or nascent sulphur, 4. Hydrogen sulphide. All these substances would give rise to sulphur under the experimental conditions—the first three by spontaneous irreversible reactions, the fourth by reaction with the sulphur dioxide present.

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Experiments were instituted to determine their action on ferric phosphate in concentrated phosphoric acid solution. Solid sodium hyposulphite and sodium thiosulphate added to the warm solution in an inert atmosphere caused considerable reduction. No appreciable reduction occurred when hydrogen sulphide was passed through a warm solution. A mixture of hydrogen sulphide and sulphur dioxide was also tried, but here again no reduction was observed.

The reduction of sulphurous acid and sulphites to hyposulphites is a well-known reversible reaction that has been extensively studied in alkaline solution by Jellinek (Z. Elektrochem., 1911, 17, 157). On the other hand, the direct reduction of sulphites or sulphur dioxide to thiosulphates has not been observed, although under certain conditions thiosulphates are formed as a stage in the decomposition of hyposulphites (Jellinek, Z. anorg. Chem., 1911, 70, 93). It therefore seemed more probable that the active product was hyposulphurous acid, and the earlier experiments were designed to test this view.

Attempts were made to test directly for hyposulphite in the reaction mixture, but all the reactions for this acid that are applicable under the conditions of the experiment depend on its powerful reducing properties, and in phosphoric acid ferrous phosphate itself is a powerful reducing agent and can effect all these reductions. No distinctive test could be found.

The influence of additions of sodium hyposulphite on the course of the reaction was studied in the apparatus employed for following the course of the reaction. The hyposulphite was dissolved in dilute alkali (free from air) in an inert atmosphere in a tap funnel inserted through the bung of the reaction flask, and introduced into the flask at a suitable time. The course of the reaction was followed before and after the addition in the way already described. The results of two experiments are given in Fig. 1. It will be seen that the effect of the addition of a quantity of hyposulphite probably large in comparison with that which might be expected to exist in the solution, is hardly appreciable.

A more direct test of the formation of hyposulphite during the reaction was based on the following considerations. Whilst a solution of sodium hyposulphite decomposes on being acidified without forming any sulphate in the absence of air, in the presence of air partial oxidation occurs at the same time and sulphate is formed (Meyer, Z. anorg. Chem., 1903, **34**, 43).

It was first shown that the same occurs in phosphoric acid. Some solid sodium hyposulphite was added to phosphoric acid and shaken with air while the decomposition was in progress. A marked formation of sulphate was observed. Sulphur dioxide and

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air were now passed together through a solution of ferrous phosphate in phosphoric acid at 100°. Sulphur was formed, showing that reduction of sulphur dioxide had occurred, but no sulphate could be detected in the solution. If hyposulphurous acid were formed in the reduction of sulphur dioxide, it might be expected to be partially oxidised to sulphate by the air; the non-formation of sulphate, therefore, is evidence against the formation of hyposulphurous acid in the reaction.

A more conclusive method of distinguishing between the various possibilities would consist in a determination of the rates of decomposition under the experimental conditions and comparison with the course of the reaction.



(a) Addition of 0.094 gram of $Na_2S_2O_4$. (b) Addition of 0.435 gram of $Na_2S_2O_4$.

Unfortunately, hyposulphurous and thiosulphuric acids decompose so rapidly that this is not practicable. Some experiments were arranged in order to form an idea of the rate of decomposition of a hyposulphite in phosphoric acid at room temperature. A solution of sodium hyposulphite was made slightly alkaline to hinder its decomposition and added at room temperature to a considerable excess of phosphoric acid, air being rigorously excluded, when it was found that only about 20 per cent. remained undecomposed after three minutes. It is obviously impracticable to determine the velocity coefficient of the decomposition at the higher temperature, but a rough comparison may be made from the following considerations.

It was shown in the earlier paper that the reaction between sulphur dioxide and ferrous phosphate resolves itself into two stages, a rapid initial stage followed by a slower and almost uniform action.

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In the first stage, the intermediate product is being formed faster than it decomposes; it accumulates until its rate of decomposition is equal to its rate of formation. Thus the amount present reaches a maximum value which remains almost constant for a considerable period, giving rise to the second uniform stage. Here the rate at which the reaction proceeds is equal to and determined by the rate at which the intermediate product decomposes. Consider a typical case (this vol., p. 2375, Fig. 2, Curve I); in the uniform stage the rate of oxidation is about 1 per cent. in forty minutes, corresponding to the decomposition of about 2.4×10^{-5} equivalent of the intermediate product per minute. To form an estimate of the quantity of the intermediate product present during this stage, consider the first stage in which it is accumulating. An oxidation of 5 per cent. of the iron occurs in about fifteen minutes. The total amount of the intermediate product formed in this stage (as the net result of the direct and reverse reactions) corresponding to the oxidation of 0.25 gram of ferrous iron is 5×10^{-3} equivalent. Even if we assume that this quantity is present for the whole time, the total quantity decomposed during the interval is 2.4×10^{-5} equivalent per minute for fifteen minutes or 0.36×10^{-3} equivalent, and we arrive at an estimate of 4.6×10^{-3} equivalent of the intermediate product during the uniform stage. It appears, therefore, that the fraction of the intermediate product decomposing per minute is less than 1 per cent. under the experimental conditions, which is very much less than the fraction for hyposulphurous acid even at room temperature (80 per cent. in three minutes).

Summary.

The intermediate product resulting from the interaction of ferrous phosphate and sulphur dioxide in phosphoric acid has been further considered. It is probable that hydrogen sulphide is not a direct decomposition product of sulphur dioxide, although it may be a by-product in certain other cases.

Hyposulphurous acid $(H_2S_2O_4)$ and thiosulphuric acid $(H_2S_2O_3)$ possess the necessary reducing properties, but would not have a long enough life in the strong acid solution. They might, however, exist for a brief interval and decompose into another substance.

A nascent or active form of sulphur could quite conceivably possess the necessary reducing properties and decompose into the inactive sulphur at a rate required by the theory.

Colloidal sulphur has not been investigated beyond the experiments previously mentioned.

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Theoretical.

Since the conclusion of our experimental work the remarkable properties of the polythionates in acid solution and their surprising stability have been brought into prominence (Z. anorg. Chem., 1921, 119, 225; 1922, 125, 86). They are, moreover, capable of interacting with ferric salts and could conceivably possess the properties required for the intermediate product X. The only objection appears to be the well-recognised statement that a polythionic acid in acid solution decomposes on heating with the formation of sulphur dioxide, sulphur, and a sulphate. It is, however, conceivable that in reacting in the presence of a reducing agent like a ferrous salt, a polythionic acid would not give a sulphate but would simply break up into sulphur dioxide and sulphur. Further it is doubtful if the decomposition of the thionic acids by heat and acids under rigid exclusion of air has been studied.

In connexion with these views, it may be mentioned that Wardlaw and Sylvester (this vol., p. 968) quote strong evidence for the formation of a tetrathionate in a sulphuric acid solution of sulphur dioxide which has been reduced by tervalent molybdenum.

The recent studies on the nature of colloidal sulphur are also of special interest in this connexion. Colloidal sulphur can be produced by treating a solution of sodium thiosulphate with concentrated sulphuric acid and in this form can exist in very concentrated acids. It is thought that the sulphur sol exists as a micelle of μ -sulphur, a polythionic acid, and water, and Odén associates its stability with the presence of the thionic acids. If the sulphur sol has the power of interacting with a ferric salt it may be the active compound X we are seeking.

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