CCXV.—*Autoreduction of Sulphurous Acid.*

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The decomposition of sulphurous acid in aqueous solution has been repeatedly observed, but the reaction is usually a slow one unless fairly high temperatures are used. Thus dilute solutions of sulphur dioxide, exposed to sunlight for two months, yield sulphur and sulphuric acid (*Jahresber.*, 1873, 164). The reaction represented by the equation $3H_2SO_3 = 2H_2SO_4 + S + H_2O$ occurs when dilute solutions of sulphur dioxide are heated for several hours under high pressure in sealed tubes at 150—180° (Berthelot, *Ann. chim. phys.*, 1898, [vii], **14**, 289)

The sulphites, bisulphites, and metabisulphites also undergo autoreduction when heated at 150—200°, with production of sulphur and a sulphate and sometimes the thiosulphate (Geuther, *Annalen*, 1884, **224**, 218; Divers, T., 1885, **47**, 205). It is explicitly stated by Barbaglia and Giucci (*Ber.*, 1880, **13**, 2325) that the interaction of sulphur dioxide and a sulphite could not be detected during eight hours' heating at 140°.

The slow decomposition of sulphurous acid, which gives as ultimate products sulphur and sulphuric acid, was studied in greater detail by Jungfleisch and Brunel (*Compt. rend.*, 1913, **156**, 1719). By sealing the solid hydrate in tubes, they attained concentrations of sulphur dioxide much higher than those in Berthelot's experiments. By this means the reaction was observed in the course of several days' heating at 100° or during longer periods at lower temperatures. Evidence was quoted to show that the yellow solution first produced in these experiments contained hyposulphurous acid, $H_2S_2O_4$, which then decomposed to give sulphuric acid and sulphur.

It has now been found that sulphurous acid, liberated in solution from its salts at temperatures of 100—120° or lower, may undergo instantaneous autoreduction with production of hydrogen sulphide. The reaction is best seen by dropping powdered sodium sulphite or metabisulphite, or saturated solutions of these salts, into hot aqueous sulphuric acid of 60—70 per cent. concentration, to which a small quantity of antimonious oxide has previously been added. The orange sulphide appears immediately or on further heating. The antimony salt is not a catalyst necessary to the reaction, for it may be added afterwards or used to show the presence of hydrogen sulphide in the evolved gases by passing them over the moist oxide. Traces of the sulphides of mercury, lead, and copper are also obtained by sudden dilution of hot sulphuric or phosphoric acid solutions to which the oxide of the metal in question has been added and then solid sodium sulphite or metabisulphite.

This reaction may be assumed to follow the equation $4H_2SO_3 = H_2S + 3H_2SO_4$, corresponding to the change occurring when solid sodium sulphite is heated above 150°, namely, $4Na_2SO_3 = Na_2S + 3Na_2SO_4$.

It represents a possible intermediate stage in the liberation of free sulphur; this further reaction may, in fact, sometimes be observed in the above cases.

It appears, moreover, that this rapid autoreduction occurs only with sulphurous acid liberated from its salts, for all attempts to obtain it by using gaseous sulphur dioxide, saturated solutions, or the solid hydrate in place of the sulphites gave negative results. It seems possible that the high reducing power of the sulphurous acid under these conditions may be due to the momentary existence of the acid of the unsymmetrical formula, $H\cdot SO_2\cdot OH$, produced from a corresponding metallic salt such as was postulated by Divers and Shimidzu (T., 1886, **49**, 577).

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