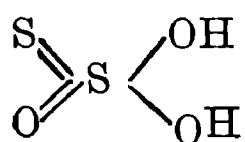


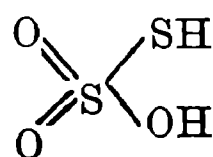
A Note on the Constitution and Isomerism of Thiosulphuric Acid.

BY PRIYADARANJAN RÂY.

It is well known that the constitution of thiosulphuric acid may be represented in two different ways as given by formulae I and II:—



I



II

The formula I accounts for the formation of its salts from sulphites and sulphur and for the decomposition of the acid into sulphurous acid and sulphur. On the other hand, the decomposition of heavy metal thiosulphates in presence of water by heat into sulphide and sulphuric acid, the formation of sodium alkylthiosulphate and its decomposition by acids into mercaptan and sulphate as well as its oxidation by nitric acid to alkylsulphonic acid and sulphuric acid speak strongly in favour of the second formula.

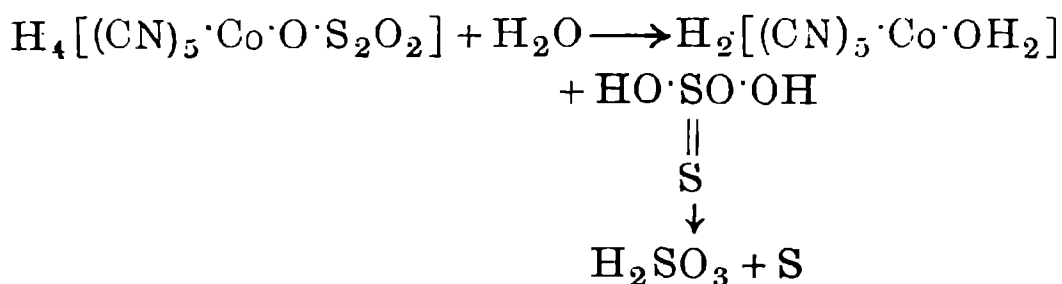
That the thiosulphates are decomposed by acids under certain circumstances with liberation of hydrogen sulphide was already observed by Colson (*Bull. Soc. chim.*, 1880, [2], 34, 66), Vaubel (*Ber.*, 1889, 22, 1686) and Vortmann (*Ber.*, 1889, 22, 2307); (cf. Bassett and Durrant, *J. Chem. Soc.*, 1927, p. 1401; Foerster, *Z. anorg. Chem.*, 1928, 177, 61).

Further Piccard and Thomas (*Helv. Chim. Acta*, 1923, 6, 1032), have shown that sulphur trioxide and hydrogen sulphide dissolved in liquid carbon dioxide at -50° , when cooled to liquid air temperature, combine with each other. The authors concluded from this that they succeeded in synthesising the veritable thiosulphuric acid $\text{SO}_3 \cdot \text{SH}_2$, corresponding to the formula II.

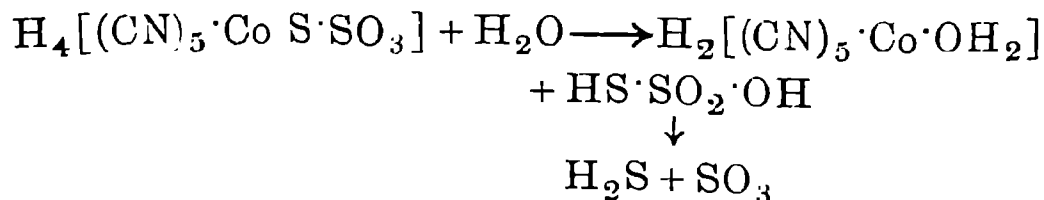
Very convincing evidence regarding the existence of two isomeric forms has been obtained in this laboratory and the two modifications

as constituents of a complex acid have actually been isolated. When preparing the complex thiosulphate-pentacyanocobaltic acid $\text{H}_4[(\text{CN})_5 \cdot \text{Co} \cdot \text{S}_2\text{O}_3]$, whose potassium salt was described in this Journal (Rây, *J. Indian Chem. Soc.*, 1927, 4, 325), from its basic lead salt by decomposition with hydrogen sulphide, it was observed that the solution of the complex acid thus obtained differed in its behaviour from that of the solid acid prepared by evaporating the above solution in *vacuo* over sulphuric acid.

The solution of the complex acid freshly prepared from the lead salt was *yellow to orange in colour* according to concentration. It hydrolysed on heating and the thiosulphuric acid liberated thereby decomposed into sulphurous acid and sulphur.



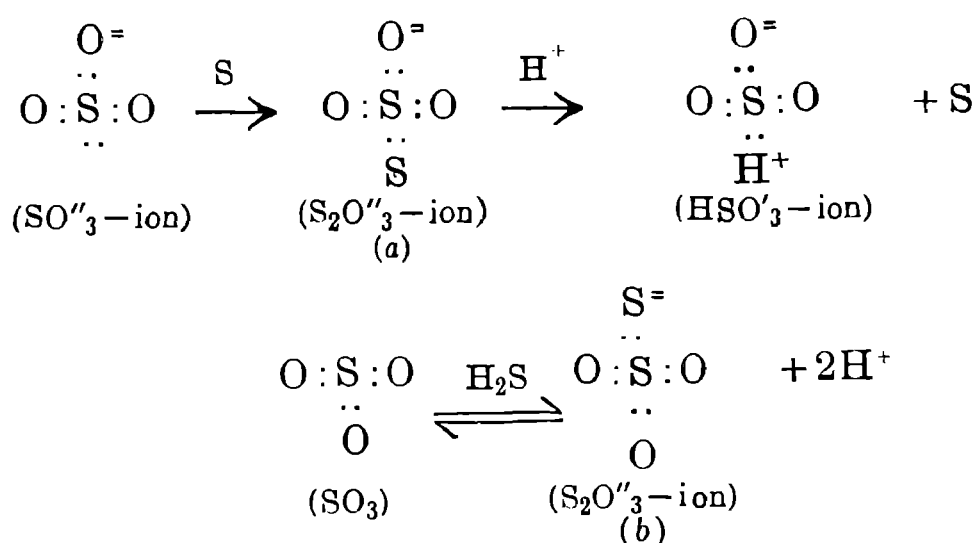
The potassium salt of this acid when heated with mineral acids in aqueous solution decomposed in a similar manner. Barium and calcium salts prepared by neutralisation of the aqueous solution of the acid, thus obtained, with their carbonates also underwent similar decomposition. On the other hand, the *orange red crystals* of the solid acid prepared from the above solution dissolved in water with *yellow to orange colour* with separation of a little sulphur and gave out hydrogen sulphide. On warming, the colour of the solution became *dark red* with increased evolution of H_2S gas. Sulphuric acid was formed in the solution. The solution did not yield any sulphur dioxide even on boiling. This evidently indicates a change in the structure of the complex acid during solidification whereby a change in the mode of linking of the thiosulphate S_2O_3 radical to the central cobalt atom occurs, and the thiosulphuric acid liberated from the latter (solid acid) by hydrolysis consequently presents a different structure.



The separation of a little sulphur that was observed when the solid acid dissolved in water was evidently due to the interaction between H_2S and SO_3 in the solid acid itself as the result of slight decomposition.

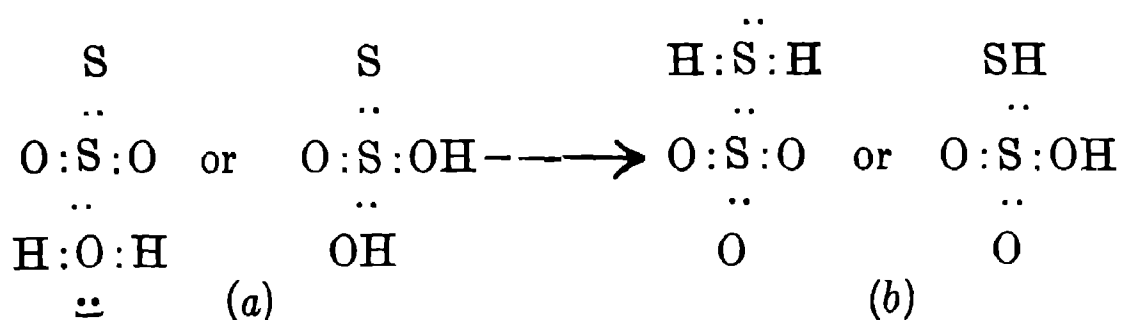
Further, the solution of the solid acid when neutralised with magnesium, calcium and ammonium carbonates gave *reddish brown salts*, which on treatment with mineral acids, evolved hydrogen sulphide and no sulphur dioxide. This proves beyond doubt that the complex acid exists in two isomeric modifications. The change is however an irreversible one, since the solid acid or its solution has not yet been found to change so as to give rise to the modification that exists in the original solution.

Judging by analogy, it may therefore be stated that the two varieties of thiosulphuric acid resulting from the hydrolysis of the two isomeric complex acids also present a case of irreversible change or true isomerism. In the light of the modern electronic theory of valency, the constitution and behaviour of the two modifications of thiosulphuric acid and the nature of the isomerism can be readily explained as shown below by forms (a) and (b).



The form (a) corresponds to the usual decomposition of thiosulphuric acid whereas (b) suggests that it can be formed by the condensation of hydrogen sulphide with sulphur trioxide just as the latter gives sulphuric acid with water. On decomposition, it should therefore give, on the assumption that no rearrangement occurs, hydrogen sulphide and sulphur trioxide or sulphuric acid. The course of decomposition in both cases is peculiarly alike consisting in the separation of a sulphur atom from the complex anion S_2O_3 , only with this difference that in the first case (a) it is dropped as elementary sulphur whereas in the second case (b) the sulphur leaves as a sulphide ion, which then combines with hydrogen ions to form hydrogen sulphide. In the ionic condition there is apparently little difference in the constitution of the two forms. It is only in the location of the charge in the complex $[\text{S}_2\text{O}_3]$ ion that a distinction could be detected. Conse-

quently the irreversible change of the first modification into the second consists in the transfer of charge from the co-ordinated oxygen to the co-ordinated sulphur atom by shifting of the electron pairs linking these atoms with the central sulphur atom. In the non-ionised form the change can be represented in a much clearer manner by the mobility of hydrogen atoms.



The two modifications of thiosulphuric acid corresponding to the forms (a) and (b) may be termed α - and β -thiosulphuric acids and the phenomenon as one of "electro-isomerism."

The conception of Werner that once an ion enters a co-ordination complex its hold upon the charge is weakened and the latter is distributed uniformly over the complex or is concentrated on the central atom seems however irreconcilable with the present knowledge. Presumably a neutral atom or an ion of the same cannot be held by the central atom with the same intensity of force. In some cases however a redistribution may indeed occur inside the complex after the combination has taken place.

Analytical results and other experimental details regarding the preparation and properties of the two isomeric complex thiosulphatopentacyanocobaltic acids as well as of their various salts will be published hereafter.