

OXIDATION BY CHLORAMINE-T

Part I. Reaction between Hydrogen Sulphide and Chloramine-T

BY A. R. VASUDEVA MURTHY* AND B. SANJIVA RAO, F.A.Sc.

(*Indian Institute of Science, Bangalore*)

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INTRODUCTION

As early as 1905 Chattaway¹ observed that sulphonchloro amides take part in certain characteristic reactions, which show the presence of nitrogen-halogen linkages in their molecule. In such reactions, the halogen is replaced by hydrogen, and sulphonamide is regenerated. Chattaway also showed that sulphur was set free when hydrogen sulphide was treated with chloramine-T.

Coull, Hope and Gouguell² investigated the kinetics of the reaction between hydrogen peroxide and chloramine-T, in presence of hydrochloric acid. They suggested the existence of opposing reactions and developed a differential equation expressing the over-all rate of reaction between chloramine-T and hydrogen peroxide.

Afans'ev³ studied the mechanism of the oxidation of chloramine-T and concluded that in neutral solutions, the oxidising action was due to the hypochlorite ion while in acid solutions, free hypochlorous acid itself, functioned as the oxidant.

Bendall, Mann and Purdie⁴ found that, when an excess of hydrogen sulphide was passed into an aqueous solution of chloramine-T, sulphuric acid (with a trace of sulphur) was formed. They also observed that sulphuric acid was the main product, when a dilute solution of chloramine-T was titrated with aqueous hydrogen sulphide. On the other hand, when the titration was carried out with sodium sulphide, the principal product of oxidation was sulphur and the solution was markedly alkaline. Even when an excess of chloramine-T was used in the latter reaction, sulphur continued to be the main product, indicating thereby, that the freshly deposited sulphur was not oxidised by the reagent. From these results, they came to the conclusion that the oxidation of hydrogen sulphide was distinct from that of the sulphide ion and that elemental sulphur could not be an intermediate stage in the oxidation of hydrogen sulphide to sulphuric acid.

* This paper is a revised form of a part of the thesis of A. R. V. Murthy, accepted for the M.Sc. degree of the Mysore University. The investigation was conducted at the Central College, Bangalore.

Choppin and Faulkenberry⁵ carried out a systematic investigation of the oxidation of aqueous sulphide solutions by hypochlorites and found that the pH of the system affected the nature of the product of oxidation.

In the present study, it was observed that the nature of the products of the reaction between hydrogen sulphide and chloramine-T largely depended on the pH of the solution and that only sulphur and sulphuric acid were produced. Investigations were conducted to elucidate the nature of the phenomenon.

EXPERIMENTAL

Hydrogen sulphide.—Hydrogen sulphide was prepared by the action of water on aluminium sulphide. The gas was frozen by liquid air, the impurities pumped off, and the solid allowed to evaporate. The gas was collected and stored in glass globes.

Chloramine-T.—Chloramine-T was recrystallised from hot water. The crystals, on analysis, were found to be pure trihydrate. The aqueous solution of chloramine-T was standardised iodometrically before use.

Buffers.—For the lower pH values, hydrochloric acid—sodium acetate buffers were used while for higher pH values, phosphate-borax and borax-alkali buffers were employed.⁶

A solution of chloramine-T was quite clear in alkaline buffers but was turbid at pH 5.8. On further lowering of pH, the turbidity increased.

The apparatus shown in Fig. 1 was employed.

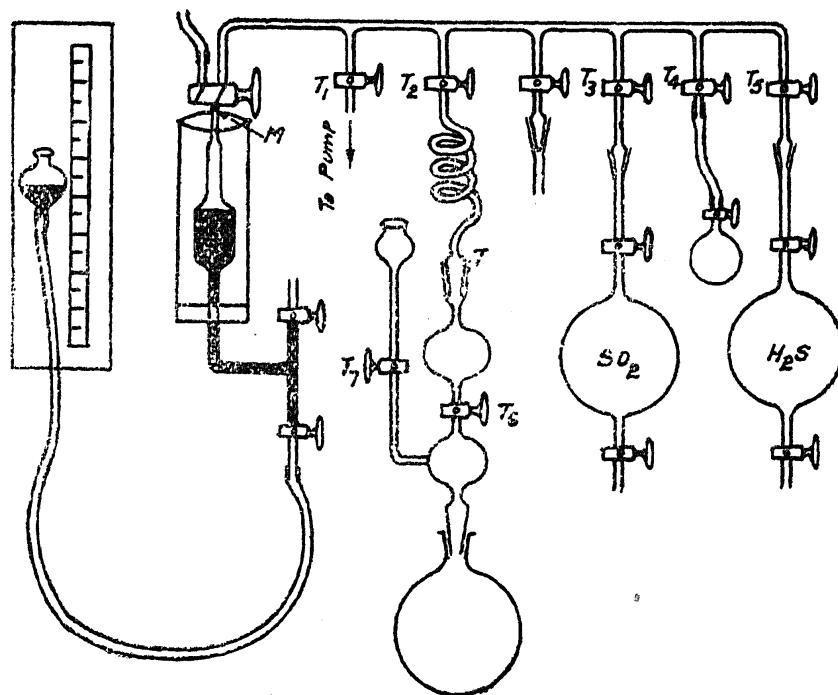


FIG. 1

The reaction vessel, along with the gas burette, was evacuated (T_1 , T_2 and T_6 being open and the rest of the stop cocks closed) and was tested for leakage. T_1 and T_2 were then closed and an appropriate volume of hydrogen sulphide from the globe was let into the graduated tube through the tap T_5 . The mercury level was adjusted to the mark and the reading on the graduated scale noted down. Then, tap T_2 was opened and the mercury level gradually raised, driving the gas slowly into the reaction vessel. When the mercury level came to the mark M , the tap T_2 was closed. The mercury level was once again brought to the original mark, and the reading noted, the difference between the two readings being the pressure of the gas employed for the reaction with chloramine-T.

Twenty ml. of 0.2 N chloramine-T was mixed with an equal volume of the selected buffer. The reagent was introduced into the flask through the tap T_7 . An appropriate correction was applied for the very small amount of hydrogen sulphide left over in the gas burette.

After about half an hour, taps T_2 and T_6 were closed, and the reaction vessel was taken out, and shaken well. A known volume of standard sodium arsenite solution was added and the arsenite left over after reaction with the residual chloramine-T was determined iodometrically in presence of sodium bicarbonate. It has already been stated that sulphur and sulphuric acid are the only products of oxidation of hydrogen sulphide by chloramine-T. On this basis, the extent of each of the two types of oxidation can be calculated from the volume of hydrogen sulphide employed, and the chloramine-T consumed, the equations being:—

$$a + b = y$$

$$a + 4b = 1.12x$$

where

y = ml. of H_2S (at N.T.P.) oxidised,

a = ml. of H_2S oxidised to sulphur,

b = ml. of H_2S oxidised to sulphuric acid,

x = ml. of 0.1 N chloramine-T consumed by the hydrogen sulphide

The following table gives the extent of each of the two reactions, at various pH values.

Reaction between Hydrogen Sulphide and Chloramine-T

Sl. No.	pH of solution	Buffer used	Value of 'a'	Value of 'b'	Ratio of b to a	Remarks
1	Soln. highly acid (2 N H_2SO_4)		0.08	7.48	Complete oxidation to sulphuric acid	
2	0.65	Acetate	0.46	7.65	16.6	
3	"	"	0.8	6.4	8.0	
4	2.64	"	0.67	7.28	10.9	
5	4.76	"	0.81	6.95	8.6	
6	4.76	,, +2 ml. of sodium molybdate	0.54	6.74	12.5	
7	4.76	,, +10 ml. of sodium molybdate	0.61	7.06	11.6	
8	4.76	,, +0.5 ml. of sodium molybdate	0.55	6.6	12.0	
9	7.0	Phosphate	2.8	4.53	1.6	
10	7.0	,, +brucine	3.66	3.69	1.0	
11	7.0	,, +osmic acid	3.52	3.56	1.0	
12	7.0	,, +2 ml. of sodium molybdate	1.9	5.37	2.8	
13	7.0	,, +2 ml. of sodium molybdate	2.04	4.98	2.4	
14	7.0	,, +10 ml. of sodium molybdate	2.07	4.98	2.4	
15	7.0	,, +0.5 ml of sodium molybdate	2.11	2.99	2.4	
16	7.0	,, +5 g. of sodium chloride	2.69	4.59	1.7	
17	7.0	,, +5 g. of sodium chloride + 2 ml. of sodium molybdate	1.97	5.41	2.9	
18	7.0	Borate	2.38	4.79	2.0	
19	7.0	,, +2 ml. of sodium molybdate	1.69	5.66	3.4	
20	7.0	,, +10 ml. of sodium molybdate	1.69	5.6	3.3	
21	7.0	Phosphate + 2 ml. of sodium tungstate*	4.59	2.55	0.55	
22	9.2	Borax	4.36	3.63	0.83	
23	9.2	"	4.30	3.6	0.85	
24	9.2	,, +10 ml. of sodium molybdate	4.31	3.62	0.66	
25	12	Borate	8.36	0.16	0.02	

* The sodium molybdate and the sodium tungstate solutions had 5% (by wt.) of the dihydrate of the salt.

DISCUSSION

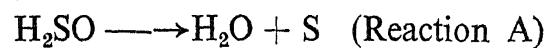
The experimental results recorded in this paper can be explained on the basis of the formation of dihydrogen sulphoxide (H_2SO) as the primary product of oxidation of hydrogen sulphide. Bendall and coworkers⁴ also considered the sulphoxide to be a possible intermediate product in the oxidation of hydrogen sulphide by chloramine-T. They attempted to isolate

the sulphoxide but were unsuccessful. They attributed their failure, to further oxidation of the intermediate product, at a very rapid rate.

Dihydrogen sulphoxide, it may be pointed out, would resemble hydrogen peroxide and hydrogen persulphide in its properties and would therefore be highly unstable. The inability of Bendall *et al.* to isolate the sulphoxide is, in our opinion, due to the high instability of the sulphoxide, rather than to its rapid oxidation to sulphate.

It is well known that the peroxide and the persulphide of hydrogen are catalytically decomposed by a variety of substances. Hydrogen ion has a stabilising influence on the two compounds while hydroxyl ion brings about their rapid decomposition. The sulphoxide would presumably behave in a similar way towards catalysts.

Dihydrogen sulphoxide can undergo two simultaneous reactions—a decomposition (Reaction A) and an oxidation (Reaction B):—



At low pH, owing to the greater stability of the sulphoxide, Reaction A would take place to a much smaller extent than Reaction B. As the pH increases however, the stability of the sulphoxide decreases and at high pH values, it decomposes so readily as not to admit of any appreciable oxidation. Therefore, as the pH increases, there is a progressive increase in the value of "a" and a corresponding decrease in the value of "b".

It has to be pointed out, that only the unionised hydrogen sulphide is likely to form the sulphoxide on oxidation. In the case of sulphide ions, the oxidation would consist of loss of electrons by the ions to give rise to elemental sulphur. In solutions in which the hydrogen sulphide was partly ionised, sulphur liberation would be due to two causes:—(i) oxidation of sulphide ion and (ii) decomposition of dihydrogen sulphoxide.

The liberated sulphur is not appreciably oxidised by chloramine-T even when the oxidant is in large excess, as noticed by Bendall *et al.*⁴ Oxidation of elemental sulphur would however, take place in highly alkaline solutions of hypochlorite. The sulphur would first react with the alkali to form sulphide and thiosulphate, and these products would then be oxidised by the hypochlorite, as pointed out by Choppin and Faulkenberry.⁵ Willard and Cake⁷ noticed that for the quantitative oxidation of sulphide to sulphate the hypochlorite was to be in large excess and that the solution should be about 4 N in regard to the alkali.

From the experimental data obtained by Choppin and Faulkenberry⁵ it is clear that the oxidation of sulphur to sulphate by the hypochlorite, is noticeable only at a pH higher than 10. As has been pointed out earlier in the paper, the active principle of chloramine-T as an oxidant, is probably hypochlorous acid or its anion (Afans'ev³). A close agreement between the results of the present investigation (wherein chloramine-T has been used) and those obtained by Choppin and Faulkenberry with hypochlorite is therefore to be expected. Such agreement is indeed quite noticeable. With the exception of borate buffer of pH 12, the solutions employed by us were all of a pH lower than 10 and the chances of oxidation of primarily formed sulphur to sulphate could therefore be ruled out.

It has already been indicated that catalysts would influence the stability of dihydrogen sulphoxide. Such catalysts would consequently affect the relative magnitude of the two reactions A and B. This is clearly noticeable in the case of solutions of pH 7.0. The sulphate and sulphur produced in these experiments, varied with the composition of the solution. The presence of molybdate considerably raised sulphate formation, while sodium tungstate markedly reduced the oxidation of sulphate or possibly hastened the decomposition of hydrogen sulphoxide. Brucine and osmic acid seemed to have the same effect as the tungstate, though to a smaller extent. It is significant that in presence of platinised asbestos, relatively more sulphur is produced. Finely divided platinum is known to decompose hydrogen peroxide and can be expected to have a similar effect on dihydrogen sulphoxide.

SUMMARY

When hydrogen sulphide is oxidised by chloramine-T, the sulphide may yield sulphur, or sulphate, or both the products. The relative proportion of the two products of oxidation depends on the pH, of the solution and on the presence of certain catalysts. At low pH, sulphate is produced in relatively high amounts, while at higher pH values, sulphur formation is greater. Presence of molybdate increases sulphate yield, while tungstate on the other hand, diminishes it. It is suggested that the primary product of oxidation of hydrogen sulphide is dihydrogen sulphoxide (H_2SO) which, being analogous to hydrogen peroxide and hydrogen persulphide, is likely to be more stable at low pH values. The sulphoxide undergoes two simultaneous reactions, (a) decomposition into water and sulphur and (b) oxidation to sulphate. This accounts for the greater production of sulphate at low pH values, and of elemental sulphur in alkaline solutions,

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