STUDIES IN THE CHEMICAL BEHAVIOUR OF SOME COMPOUNDS OF SULPHUR

Part VI. The Reaction Between Hydrogen Iodide and Some Compounds of Sulphur

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It has been shown that hydrogen iodide is a valuable reagent in the study of the chemical behaviour of the oxides¹ and halides² of sulphur and of the esters of oxyacids³ of the element. This paper deals with the reactions between hydrogen iodide and the following compounds of sulphur:—

Sulphur nitride, Hexasulphamide, Tetrahydrosulphur nitride $(H_4S_4N_4)$, N-N tetraethyl-dithio-diamine, Tetra-ethyl-thio-diamine, Thionylaniline, Hydrogen disulphide and Hydrogen trisulphide.

(1) Hydrogen Iodide and Sulphur Nitrides

Sulphur Nitride.—Goehring⁴ studied the reaction between sulphur nitride and a solution of potassium iodide in anhydrous formic acid and found that on addition of water, three atoms of iodine were liberated, per atom of nitrogen.

MacDiarmid⁵ suggested that S_4N_3I was probably formed when hydrogen iodide reacted with sulphur nitride. The present author found that hydrogen sulphide was a significant product and the reaction was quantitatively studied by him.

EXPERIMENTAL

Sulphur nitride was prepared by passing dry ammonia into a chloroform solution of sulphur chloride as recommended by Arnold, Hugill and Hutson.⁶ On purification, orange yellow needles of the nitride melting at 177° C. were obtained. A stock solution of sulphur nitride in carbon tetrachloride was prepared and the purity of the compound determined. Nitrogen was estimated by a modified Kjeldhal method using boric acid solution as an absorbent for ammonia and a mixed indicator (Bromcresol green and methyl red) in the titration.⁷ Sulphur content was determined by hydrolysis of the nitride with alkali, followed by oxidation, and the estimation of the sulphate as its barium salt. The nitrogen content of the stock solution was $62 \cdot 82 \times 10^{-6}$ g. atoms of N per g. of solution while the sulphur value was $62 \cdot 88 \times 10^{-6}$ g. atoms, showing that the nitride was very pure.

Hexasulphamide.—This was obtained from the mother-liquor left on removal of sulphur nitride and purified by recrystallisation from alcohol, as suggested by Macbeth and Graham,⁸ and Arnold, *et al.*⁶ The crystals (square plates) of hexasulphamide melted at 108° C. The nitrogen content of the stock solution was 10.81×10^{-6} g. atoms of N per g. of solution and the sulphur value 65.18×10^{-6} g. atom. The ratio of S to N was thus 6.03, the theoretical value being 6.00.

Tetrakydro Sulphur Nitride.—Sulphur nitride solution in benzene was reduced by stannous chloride in alcoholic solution, as recommended by Meuwsen,⁹ to obtain tetrahydro sulphur nitride. The compound was purified by recrystallisation.

Reaction with Hydrogen Iodide.—Dilute solutions of the above three sulphur compounds were introduced into bulbs containing dry hydrogen iodide. The liberated iodine and hydrogen sulphide were estimated in the usual way. After titrating the iodine, the aqueous layer was employed for the determination of ammonia by the Kjeldahl method. The results are presented in the following table (Table I).

Compounds of Sulphur							
Compound	Expt. No.	Nitride taken*	Hydrogen sulphide obtained	Iodine g. atom × 10 ⁴ per g. of solution	Ammonia as g, of N×10 ⁶ per g, of solution	Ratio I : H ₂ S	Ratio NH3:H2S
Sulphur Nitride (N ₄ S ₄)	1 2 3 4	4.83 7.28 10.54 15.65	4-80 7-16 10-48 15-54	24 · 12 35 · 96 52 · 64 78 · 58	4-87 7-18 10-52 15-58	5-01 5-02 5-02 5-02	1.01 1.00 1.00 1.00
	-	ĺ			Ave.	5.02	1.00
Hexasulphamide (S ₆ NH ₂)	1 2 3 4	6.84 8.98 12.24 15.66	6·78 8·86 12·15 15·56	14·98 19·65 26·92 34·05	1 • 12 1 • 45 2 • 02 2 • 58	2·21 2·22 2·21 2·18	0 • 165 0 • 164 0 • 166 0 • 166
					Ave.	2.20	0.165
Tetrahydro sulphur nitride (H ₄ N ₄ S ₆)	1 2 3 4	5.53 7.62 13.48 17.76	5.49 7.56 13.34 17.68	22-08 30-31 53-63 71-25	5.51 7.58 13.38 17.72	4.02 4.01 4.02 4.03	1.00 1.00 1.00 1.00
					Ave.	4.02	1.00

TABLE IReaction Between Hydrogen Iodide and Certain Nitrogen

* Quantities of sulphur and its compounds have been expressed in terms of g. atoms of S \times 10⁶ per g, of solution,

24

The experimental results indicate that the reduction of the nitrogen compounds of sulphur proceeds as follows:

$$N_4S_4 + 24 HI \rightarrow 4 H_2S + 4 NH_4I + 20 I$$
 (1)

$$S_{5}NH_{2} + 14 HI \rightarrow 6 H_{2}S + NH_{4}I + 13 I$$
 (2)

$$H_4S_4N_4 + 20 HI \rightarrow 4 H_2S + 4 NH_4I + 16 I$$
 (3)

It will be noticed from the above equations that a molecule of each of the nitrogen compounds reacts with a large number of molecules of hydrogen iodide. Undoubtedly the above reactions take place in several stages. Intermediate stages in the reduction of sulphur compounds by hydrogen iodide have been noticed in several cases.^{1, 2, 3} With the above nitrogen compounds, however, it was not practicable to prove experimentally the formation of intermediate compounds as the reduction with hydrogen iodide proceeded rapidly to the final stage of hydrogen sulphide.

The nature of the reaction between hydrogen iodide and sulphur nitride (and its tetrahydro derivative) has been interpreted by Goehring⁴ as evidence of the oxidising power of sulphoxylic acid (H_2SO_2), under certain conditions.¹⁰ To explain the results, it is however hardly necessary to ascribe oxidising power to sulphoxylic acid. It is well known that in non-aqueous media, hydrogen iodide is an energetic reducing agent. The observation of Goehring can be satisfactorily explained on the basis of this powerful reducing action of hydrogen iodide.

As has already been pointed out,¹ Goehring added water to the formic acid solution of potassium iodide on its reaction with the sulphur compounds studied. Thereby, the true nature of the reaction was masked as the hydrogen sulphide liberated was oxidised by iodine. If this oxidation of hydrogen sulphide is taken into account, we find that the experimental results of Goehring are in agreement with the findings of the present author. Goehring found that per atom of nitrogen in sulphur nitride, three atoms of iodine were liberated, while the present author found that 5 atoms of iodine and a molecule of hydrogen sulphide were set free for every atom of nitrogen, as indicated in equation (1).

(2) Hydrogen Iodide and Thioamines

Stamm and Goehring^{10, 11} reported the liberation of iodine when tetramethyl-dithio-diamine and tetraethyl-thio-diamine were treated with formic acid solutions of potassium iodide. The action of hydrogen iodide on the two thioamines and on thionyl aniline has been studied quantitatively by the present author, using the technique described in an earlier paper,

A. R. VASUDEVA MURTHY

Tetraethyl-dithio-diamine and tetra-ethyl-thio-diamine were prepared by treating diethyl amine with calculated amounts of disulphur dichloride and sulphur dichloride respectively, in petroleum-ether solution (Lengfeld and Stieglitz¹² and Michaelis and Luxembourg¹³). Thionyl aniline was prepared by treating aniline with a suitable quantity of thionyl chloride in benzene (Michaelis and Herz¹⁴). The three liquids were purified by distillation under reduced pressure. Stock solutions of the thioamines in carbon tetrachloride were prepared and the solutions analysed for their nitrogen and sulphur contents. The ratio of N to S was 1.005 for tetraethyl-dithio-diamine, 2.008 for tetraethyl-thio-diamine and 1.003 for thionyl aniline.

Reaction with Hydrogen Iodide.—Dilute solutions of the compounds were introduced into bulbs containing hydrogen iodide.¹ The solution first acquired a reddish yellow tinge which finally changed to the characteristic purple of iodine (cf. Part II of this series). The iodine and hydrogen sulphide produced were estimated in the usual way. The experimental data are given in Table II. TABLE II

Compound	SI. No.	Thioamine used*	H2S produced	Iodine liberated in g. atoms×10 ^s per g. of solution	Ratio L : H ₂ S
Tetraethyl-dithio-diamine S_2 (NEt ₂) ₂	1 2 3 4	8.76 11.84 15.32 19.56	8.68 11.75 15.26 19.48	26-17 35-37 46-16 58-65	3.02 3.01 3.03 3.01
Tetraethyl-thio-diamine S (NEt ₂) ₂	1 2 3 4	7·58 12·46 17·25 22·85	7 • 48 12 • 36 17 • 18 22 • 78	30-30 49-68 69-23 91-33	4·05 4·02 4·03 4·01
Thionyl aniline C ₆ H ₅ NSO	1 2 3 4	8·78 15·36 22·25 28·64	8 · 69 15 · 28 22 · 12 28 · 58	52.31 92.11 132.9 172.3	6.02 6.03 6.01 6.03

Reaction between Hydrogen Iodide and Thioamines

* Quantities of sulphur and its compounds are expressed in terms of g. atoms of $S \times 10^6$ per g. of solution.

The results indicate that the reduction of the above compounds follows the equations:

$S_2 (NEt_2)_2 + 8 HI \rightarrow 2 H_2S + 2 NHEt_2.HI + 6 I$	(4)
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- $S(NEt_2)_2 + 6 HI \rightarrow H_2S + 2 NHEt_2.HI + 4 I$ (5)
- $C_{6}H_{5}NSO + 7 HI \rightarrow H_{2}S + C_{6}H_{5}NH_{2}HI + H_{2}O + 6 I$ (6)

(3) Hydrogen Iodide and Hydrogen Persulphides

Dihydrogen disulphide and dihydrogen trisulphide in carbon tetrachloride solution were found to liberate iodine on treatment with hydrogen iodide. A quantitative study of the reaction is given below.

Purified samples of dihydrogen disulphide and dihydrogen trisulphide were prepared by the distillation under reduced pressure of crude polysulphide oil (Walton and Parsons¹⁵). Stock solutions of the sulphides in dry carbon tetrachloride were prepared and analysed in the following way.

A known weight of the stock solution was shaken with about 5 g. of pure mercury in an all-glass apparatus. The hydrogen sulphide evolved was swept off in a current of dry nitrogen and estimated iodometrically. The mercury sulphide formed was determined by the method of B. S. Rao and M. R. A. Rao.¹⁶ The ratio of HgS to H₂S was 1.005 for the disulphide and 2.008 for the trisulphide.

The above analytical method was found to be more accurate than the procedure described by Feher, Talpay and Heuer,¹⁷ who decomposed the persulphide catalytically on glasswool and estimated the hydrogen sulphide argentimetrically and weighed the sulphur liberated.

Reaction with Hydrogen Iodide.—Known amounts of solutions of the persulphides were introduced into bulbs containing hydrogen iodide. The iodine, hydrogen sulphide and elemental sulphur (if any) produced in the reaction were estimated by methods described earlier. The data are given in Table III.

Compound	Expt. No.	Persulphide taken*	H ₂ S obtained	Iodine in g. atom × 10 ⁶ per g. of soln.	Ratio I : H ₂ S
Hydrogen disulphide	1	6.86	6.78	6.92	1.02
	2	11.54	11-46	11.81	1.03
	3	16.32	16-12	16.28	1.01
	4	22.65	22-48	22.92	1.02
Hydrogen trisulphide	1	5.95	5 • 84	7-82	1 • 34
	2	12.76	12 • 58	16-98	1 • 35
	3	18.28	18 • 12	24-11	1 • 33
	4	22.34	22 • 16	29-7	1 • 34

TABLE III

Reaction Between Hydrogen Iodide and Hydrogen Persulphide

* Quantities of sulphur and its compounds have been expressed in terms of g. atoms of $S \times 10^6$ per g. of solution,

A. R. VASUDEVA MURTHY

From the above results it may be concluded that the concerned reactions are:

 $H_2S_2 + 2 HI \rightarrow 2 H_2S + 2 I \text{ (Ratio of I to H_2S 1.0)}$ (7)

$$H_2S_3 + 4 HI \rightarrow 3 H_2S + 4 I \text{ (Ratio of I to } H_2S 1.33)$$
 (8)

The actual ratio of iodine to hydrogen sulphide was slightly more than unity for the disulphide. This was probably due to a small quantity of the trisulphide present as impurity. Known quantities of sulphur in carbon tetrachloride solution were added to solutions of the disulphide and the trisulphide, before treatment with hydrogen iodide. It was found that the dissolved sulphur, even in presence of persulphide, did not liberate any iodine from hydrogen iodide (cf. Part II of this series). There was thus no activation of the dissolved sulphur by the persulphide.

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