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REACTION BETWEEN HYDROGEN IODIDE AND SOME COMPOUNDS OF SULPHUR

By A. R. Vasudeva Murthy

(Department of General Chemistry, Indian Institute of Science, Bangalore-3)

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Hydrogen iodide, in absence of water, has energetic reducing action on sulphur compounds.[1] The oxygen in the sulphur compound is converted to water with simultaneous liberation of two atoms of iodine for each oxygen atom involved. Similarly elements such as nitrogen or halogen are converted to hydrides, the corresponding amount of iodine being set free. Sulphur is reduced to hydrogen sulphide, two atoms of iodine being set free for every molecule of hydrogen sulphide formed. The estimation of hydrogen sulphide as well as the iodine formed, is carried out in carbon tetrachloride medium from which the hydrogen sulphide can be swept off in a current of nitrogen (or hydrogen) and subsequently absorbed in alkali, whereas all the iodine remains in the carbon tetrachloride solution. Estimation of the hydrogen sulphide and the iodine can therefore be successfully made, thereby furnishing data for the determination of the composition of the sulphur compound. Since hydrogen iodide has no action on elemental sulphur at laboratory temperatures, it is possible to estimate separately the elemental sulphur present in a system containing sulphur compounds reduced by hydrogen iodide.

1. Hydrogen Iodide and Chlorides of Sulphur

The present author studied[2] the reaction between hydrogen iodide and the following chlorine compounds of sulphur; disulphur dichloride, sulphur dichloride, thionyl chloride and sulphuryl chloride. With all the four chlorides used, there was the formation of unstable intermediate compounds. The compound formed initially was, in each case, the iodine analogue of the chloride. When the chloride was in very dilute solution and the hydrogen iodide was in large excess, the intermediate compound suffered further reduction and hydrogen sulphide was quantitatively formed. The reactions taking place could be represented by the following equations:—

$$\begin{array}{lllll}
\text{I.} & (S_2Cl_2 & + 2HI & \longrightarrow S_2I_2 & + 2HCl) \\
 & (S_2I_2 & + 4\,HI & \longrightarrow 2H_2S & + 6\,I) \\
 & S_2Cl_2 & + 6\,HI & \longrightarrow 2H_2S & + 2HCl + 6\,I \\
\text{II.} & (SCl_2 & + 2\,HI & \longrightarrow SI_2 & + 2\,HCl) \\
 & (SI_2 & + 2\,HI & \longrightarrow H_2S & + 4\,I) \\
 & SCl_2 & + 4\,HI & \longrightarrow H_2S & + 2\,HCl + 4\,I. \\
\text{III.} & (SOCl_2 & + 2HI & \longrightarrow SOI_2 & + 2\,HCl) \\
 & (SOI_2 & + 4HI & \longrightarrow H_2S & + H_2O \quad + 6\,I) \\
 & SOCl_2 & + 6\,HI & \longrightarrow H_2S & + H_2O \quad + 2\,HCl + 6\,I \\
\text{IV.} & (SO_2Cl_2 & + 2\,HI & \longrightarrow SO_2I_2 & + 2\,HCl) \\
 & (SO_2I_2 & + 6\,HI & \longrightarrow H_2S & + 2\,H_2O + 8\,I). \\
 & SO_2Cl_2 & + 8\,HI & \longrightarrow H_2S & + 2\,H_2O + 2\,HCl + 8\,I.
\end{array}$$

When the sulphur chloride was in moderately dilute solution, further reduction of the intermediate compound did not take place with sufficient rapidity and there was consequently a partial decomposition of the intermediate compound yielding elemental sulphur. In the case of thionyl chloride and sulphuryl chloride, decomposition of the intermediate compound yielded sulphur dioxide which suffered partial reduction by hydrogen iodide.

The formation of the intermediate compound and its subsequent decomposition was confirmed by the author by spectrophotometric studies[2] with reference to disulphur diiodide, sulphur diiodide and thionyl iodide. It was also shown that thionyl iodide was formed when diethyl sulphite was made to react with hydrogen iodide.[3, 4] The presence of SO_2I_2, however, could not be confirmed by the spectrophotometric method as the compound was found to be highly unstable under the experimental conditions. It may be mentioned that M. R. A. Rao had obtained it in carbon disulphide solution at − 70° C. The evidence for the formation of iodine analogues of sulphur chlorides is supported by the work of M. R. A. Rao.

M. R. A. Rao[5–10] prepared the iodine analogues of chlorides and oxychlorides of sulphur by a new technique which consisted in treating a dilute carbon tetrachloride solution of the chlorides with potassium iodide powder. He found that these iodides and oxyiodides of sulphur were highly photosensitive, decomposing into sulphur or sulphur dioxide and iodine. It was observed by M. R. A. Rao that the hydrolysis of sulphur iodide was similar to that of sulphur chloride (*cf.* B. S. Rao[11, 12]). The following unstable compounds were prepared by M. R. A. Rao: disulphur diiodide (S_2I_2), sulphur diiodide (SI_2), thionyl iodide (SOI_2) and sulphuryl iodide (SO_2I_2).

The attempts of earlier workers[13–21] to prepare sulphur iodide, thionyl iodide and sulphuryl iodide by the reaction between hydrogen iodide and the corresponding chloride of sulphur had been unsuccessful because of the relatively high concentration of chloride employed. In the present investigation, very dilute solutions were employed to minimise decomposition and it was therefore practicable to obtain the highly unstable compounds.

Recently, Kapustinski and Golutvin[22] claimed that S_2I_2, SI_2, SI_4 and SI_6 could be formed in carbon disulphide solution by the interaction of iodine and sulphur. The evidence of formation of the unstable iodides was based on surface tension and density measurements. Such physical measurements had been carried out by a number of workers[23–37] but had not revealed any evidence of the existence of the iodides of sulphur.

In the opinion of the present author, evidence of compound formation, based on physico-chemical measurements, is not conclusive. Experimental work carried out by the author seems to show that the decomposition of sulphur iodide into its constituent elements is irreversible. It is therefore very doubtful if the iodides of sulphur can at all be prepared by direct union between sulphur and iodine.

2. HYDROGEN IODIDE AND SULPHUR NITRIDE

Sulphur nitride (S_4N_4) is the parent substance of several compounds containing sulphur and nitrogen. Many investigations have been carried out on the controversial subject of the structure of sulphur nitride.[38–47]

Goehring[48] studied the hydrolysis of sulphur nitride and its tetrahydro derivative and concluded that sulphoxylic acid (sulphur dihydroxide) was the primary product of hydrolysis. He investigated also the reaction between sulphur nitride and a solution of potassium iodide in anhydrous formic acid and found that per atom of nitrogen in S_4N_4 three atoms of iodine were liberated.

The present author studied[49] the action of hydrogen iodide on (*a*) sulphur, nitride, (*b*) tetrahydrosulphur nitride ($H_4S_4N_4$) and (*c*) hexasulphamide (S_6NH_2). The products of reaction were hydrogen sulphide, ammonia and iodine, the equations being:—

$$S_4N_4 + 24\,HI \longrightarrow 4\,H_2S + 4\,NH_4I + 20\,I$$

$$H_4S_4N_4 + 20\,HI \longrightarrow 4H_2S + 4\,NH_4I + 16\,I$$

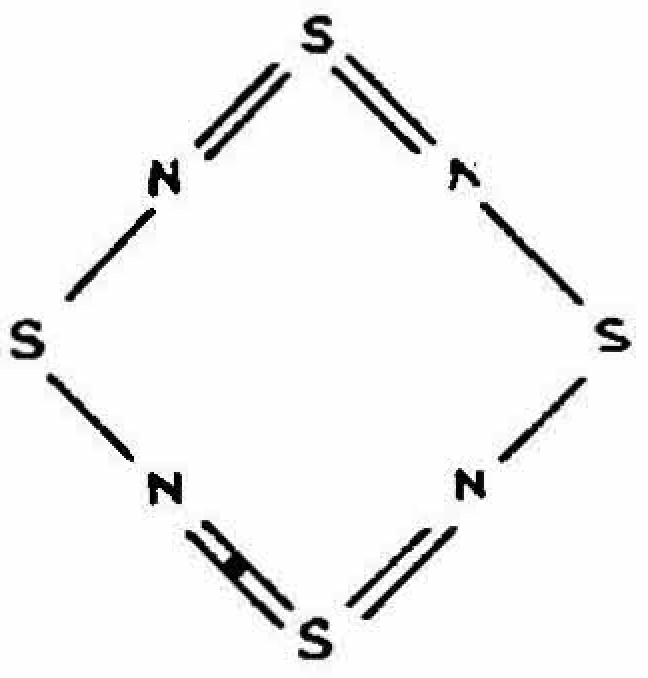
$$S_6NH_2 + 14\,HI \longrightarrow 6\,H_2S + NH_4I + 13\,I$$

. The liberation of iodine in the above reactions was interpreted by Goehring as being evidence of the oxidising power of sulphoxylic acid—the primary product of hydrolysis. As already discussed the reaction is to be attributed to the energetic reducing action of hydrogen iodide. If this reaction between hydrogen sulphide is taken into account, we find that the experimental results of Goehring are in agreement with the findings of the present author. It may also be pointed out that failure on the part of Goehring to notice the formation of hydrogen sulphide was due to the addition of water to the system, on the liberation of iodine. As already stated, the iodine which was in excess consumed the hydrogen sulphide present. Tetrahydro sulphur nitride reacted in the same way with hydrogen iodide.

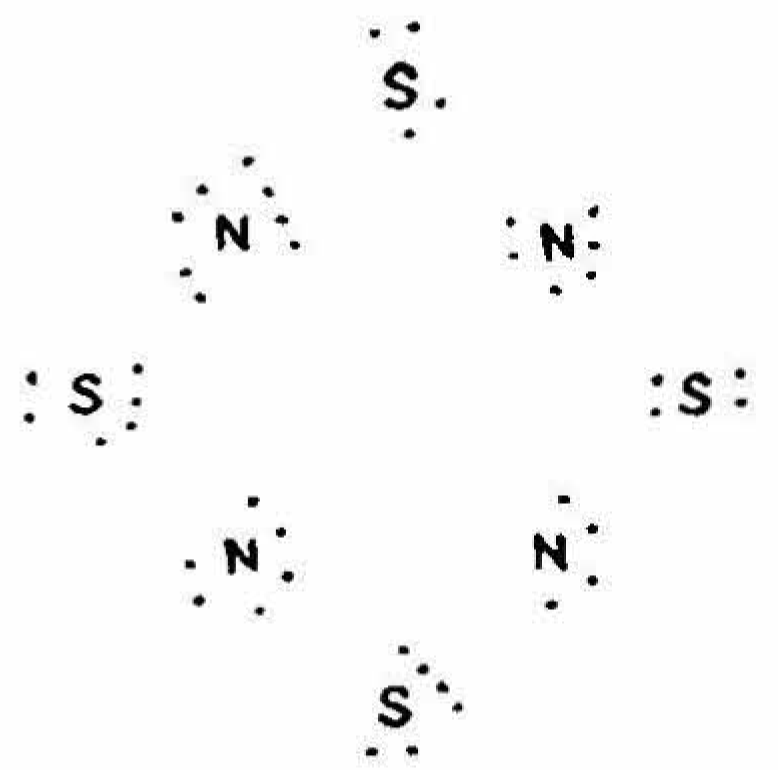
It is of interest to note that in the case of hexasulphamide there has been a controversy about the exact number of hydrogen atoms in the molecule of the compound.[41, 50] One view has been that the formula is $(S_6NH_2)_3$ while the other formula suggested is $S_{18}N_3H_5$. Exact determination of hydrogen directly has been found to be very difficult.

The data obtained by the present author regarding the ratio of iodine liberated to hydrogen sulphide formed supports the formula $(S_6NH_2)_3$.

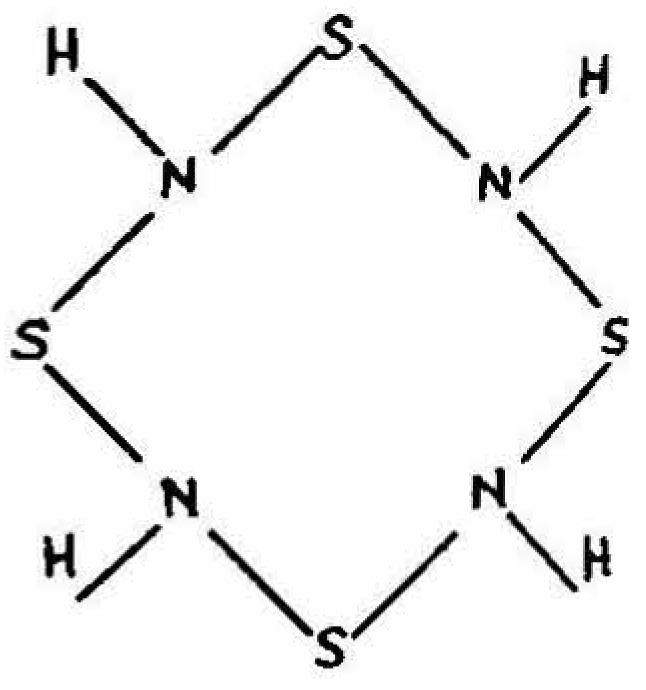
Goehring has discussed at length the different structures proposed for sulphur nitride and its tetrahydroderivative. In the light of his experimental results, he concluded that the following structures satisfactorily explain all their behaviour.



(C)



(D)



(E)

Structure D in which it is said that the double bonds are not rigid is to be preferred because it is in consonance with the magnetic properties exhibited by the sulphide. The structure of the tetrahydro derivative is E according to Goehring. Spectroscopic evidence (Infra-red) supports the above structure.

Experimental evidence obtained by the present author based on the reduction of nitrogen sulphide by hydrogen iodide seems to support the structure proposed by Goehring.[53] Sulphur iodide is presumably an intermediate step in the production of hydrogen sulphide, the final reduction product of sulphur nitride.

New derivatives of sulphur nitride such as $(SH)_3SX$, where $X = Cl, Br, NCS$ or SO_3H and N_2S_4, N_2S_5 and others have recently been announced.[51–53] It is proposed to study them by the hydrogen iodide technique described above.

3. HYDROGEN IODIDE, HYDROGEN PERSULPHIDES AND POLYSULPHIDES

Hydrogen disulphide and hydrogen trisulphide were, for a long time, the only known persulphides of hydrogen.[54–64] In 1928, however, hydrogen pentasulphide was isolated.[65] Recently, a new technique for the preparation of the polysulphides of hydrogen has been described by Feher and co-workers. According to these authors, hydrogen has the following polysulphides: H_2S_2, H_2S_3; H_2S_4 H_2S_5 and H_2S_6. The probable existence of H_2S_{10} and even of H_2S_{354} has been suggested.[65]

In view of the fact that hydrogen iodide can be used as a reagent to discriminate between sulphur in the elemental form and sulphur in combination, it can be used as a reagent to determine if all the sulphur present in the "polysulphides of hydrogen" is actually in combination or if some of it is only in solution in the elemental condition. To find out the suitability of hydrogen iodide in such studies, the present author investigated the action of hydrogen iodide on the di-and the trisulphide of hydrogen.

These persulphides in dilute carbon tetrachloride solutions liberated iodine from hydrogen iodide, the sulphur being converted into hydrogen sulphide. The concerned reactions were:—

$$H_2S_2 + 2\,HI \longrightarrow 2\,H_2S + 2\,I$$
$$H_2S_3 + 4\,HI \longrightarrow 3\,H_2S + 4\,I$$

Quantitative results showed that solutions of dihydrogen disulphide and of dihydrogen trisulphide could readily be obtained free from dissolved elemental sulphur. The method employed for the preparation of the two sulphides was that recommended by Walton and Parsons.[66]

The technique employing hydrogen iodide seems therefore to be quite suitable for the study envisaged above.

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