STUDIES IN THE CHEMICAL BEHAVIOUR OF SOME COMPOUNDS OF SULPHUR

Part II. Reaction Between Disulphur Monoxide and Hydrogen Iodide

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INTRODUCTION

B. S. RAO[1] obtained disulphur monoxide in the form of an orange-yellow solution in carbon tetrachloride and found that the oxide was stabilised by elemental sulphur. Stamm and Wiebusch[2] suggested that the orange-yellow solution consisted of " Polysulphur oxide ". They studied the reaction between this liquid and a solution of hydrogen iodide in anhydrous formic acid and reported the reaction to be

$$S_xO + 2HI \rightarrow xS + H_2O + 2I.$$

Preliminary experiments by the present author, on the reaction between hydrogen iodide and the so-called " Polysulphur oxide " solution, showed that the reaction was far more complicated than had been realised by Stamm and his coworkers. For instance, it was found that hydrogen sulphide was one of the products of reaction. Its formation had not been reported by previous workers. A detailed study of the reaction was therefore undertaken.

EXPERIMENTAL

Carbon tetrachloride

Carbon tetrachloride (C.P. quality) was shaken with mercury for several hours to remove traces of sulphur. After filtration, the liquid was dried over phosphorus pentoxide and distilled in an all-glass apparatus, provided with a spray trap. The distillate was tested with mercury and found to be entirely free from sulphur. In storing, the dry tetrachloride was carefully protected from atmospheric moisture.

Anhydrous formic acid

Preparation of anhydrous formic acid presents certain difficulties. Methods for the preparation of the anhydrous acid have been reviewed by Weissberger and Proskauer.[3] The azeotropic process[4] has been successfully employed for the commercial preparation of anhydrous formic acid, but cannot conveniently be used on the laboratory scale. Common desiccants like calcium chloride or phosphorus pentoxide are unsuitable, as they react with the acid. Boric anhydride however, is quite satisfactory.

Pellets of boric anhydride were prepared by carefully heating recrystallised boric acid in a stainless steel dish to 900° C. in an electric furnace and pouring the molten mass into carbon tetrachloride kept at − 16° C. The pellets were removed and kept in a vacuum desiccator and freed from carbon tetrachloride by evacuation.[5, 6, 7]

Formic acid (Merck, A. R.) containing about 1% water was freed from moisture by keeping in a flask in contact with pellets of boric oxide for about a week. It has to be pointed out that it is not desirable to store anhydrous formic acid in a stoppered flask for any length of time. There were three accidents in this laboratory owing to the bursting of stoppered flasks in which anhydrous formic acid had been stored. The cause of the accidents was found to be the development of pressure due to carbon monoxide, liberated by slow decomposition of formic acid (*cf.* Coolidge[8]). In storing the anhydrous acid, the stopper of the flask should be fitted with a safety U-tube filled with boric oxide pellets, and open to the atmosphere. Before use, the anhydrous acid was always freshly distilled under reduced pressure (12 to 18 mm. of Hg) at 22 to 25° C. in an all-glass apparatus. The acid was found to be free from water as determined by the critical solution temperature technique described by Ewins,[9] with benzene as solvent.

Anhydrous Hydrogen Iodide

Heisig and Lingane[10] have critically examined methods for the preparation of hydriodic acid and recommend the production of hydrogen iodide by the union between hydrogen and iodine vapour in presence of platinised asbestos as catalyst.

In the present investigation, the apparatus used by Heisig and Lingane was suitably modified to deliver pure dry hydrogen iodide. The hydrogen iodide was frozen in a tube cooled by liquid air and conveyed by sublimation to previously evacuated storage flasks one of which is shown in Fig. 1 giving a sketch of the apparatus employed.

To remove traces of oxygen in the electrolytic hydrogen, the gas was passed over platinized asbestos heated electrically to 450° C. and the moisture formed was absorbed by phosphorus pentoxide. The hydrogen picked up iodine from bulb A kept at 160° C. (in an oil bath) and when passed over platinised asbestos maintained at 600° C., produced hydrogen iodide. The

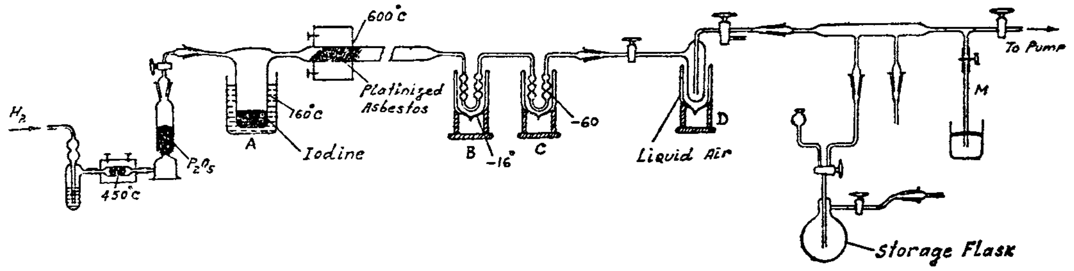

FIG. 1

uncombined iodine was frozen in B kept at −16° C. (freezing mixture) and the hydrogen iodide was completely stripped of iodine in C kept at −60° C. (alcohol cooled by solid carbon dioxide) and finally frozen in D, cooled by liquid air.

When sufficient hydrogen iodide had collected in D, the heating was stopped, but the stream of hydrogen was continued until the catalyst mass cooled down. After evacuation, the hydrogen iodide was allowed to evaporate into the storage flasks till the pressure rose to about 50 cm. of mercury as ascertained by momentary contact with the mercury manometer M.

The hydrogen iodide was quite free from iodine, there being no colouration when carbon tetrachloride was let into a storage flask.

Disulphur monoxide solution in carbon tetrachloride

The products of combustion of sulphur in oxygen at a pressure of 5–7 mm. of Hg were passed into an absorption vessel containing about 40 ml. of pure, dry carbon tetrachloride. The carbon tetrachloride was kept at − 16° C. (alcohol + carbon dioxide snow). An orange-yellow solution of disulphur oxide was obtained in about 30 minutes. To remove the sulphur dioxide present in the carbon tetrachloride, the combustion of sulphur was stopped and the stream of oxygen continued for 20 minutes. It was found that in this way, the sulphur dioxide could be completely removed. It was unnecessary to employ an inert gas to sweep off the sulphur dioxide (*cf.* B. S. Rao[1]). On removal of the sulphur dioxide, the carbon tetrachloride solution was transferred to a graduated weight-pipette of the Lung-Rey type containing an adequate amount of cooled carbon tetrachloride, to effect dilution.

Analysis of disulphur monoxide solution

The orange-yellow solution was analysed in the following way:—

(i) An aliquot was shaken up with mercury in an all-glass assembly, when the disulphur monoxide decomposed and formed sulphide of mercury, liberating sulphur dioxide. The mercury sulphide was estimated by the method of B. S. Rao and M. R. A. Rao.[11] The sulphur dioxide was swept away in a stream of hydrogen (or nitrogen) and absorbed in 2N caustic soda solution (holding some cadmium hydroxide in suspension) and the sulphite formed was determined iodometrically.

(ii) Another aliquot of the yellow solution was transferred to a storage flask containing hydrogen iodide under reduced pressure. The products of the reaction (which was rapid) were hydrogen sulphide, iodine and water. After 10 minutes, dry nitrogen (or hydrogen) was bubbled through the carbon tetrachloride for one hour and the liberated hydrogen sulphide was absorbed in alkali (holding cadmium hydroxide in suspension) and was estimated iodometrically. No sulphite could be detected in the alkali absorbent. Iodine present in the carbon tetrachloride solution was estimated, after shaking the solvent with a strong aqueous solution of potassium iodide and titrating the iodine in the aqueous phase with standard thiosulphate. The carbon tetrachloride was then tested for the presence of elemental sulphur. In general, no sulphur was present in the solvent.

The results which are given in Table I show that the sulphur oxide held in solution by the carbon tetrachloride is disulphur monoxide. The sulphur

TABLE I

Reactions of Disulphur Monoxide

Serial No. of S_2O soln.	Decomposition by mercury				Reduction with hydrogen iodide				
	SO_2 obtained*	Elemental sulphur	Ratio of elemental sulphur to SO_2 S:SO_2	S+S_2O present	H_2S obtained	Iodine liberated in g. atoms × 10^6	Ratio of iodine to sulphur as H_2S	Elemental sulphur	S_2O corresponding to H_2S
1	14·95	45·4	3·01	60·35	60·86	183·3	3·01	..	60·86
2	6·01	17·83	2·96	23·83	23·75	72·85	3·06	..	23·75
3	27·68	82·15	2·97	109·83	109·05	329·86	3·02	1·08	109·05
4	23·10	68·20	2·96	91·30	89·85	270·4	3·00	1·21	89·85
5	10·86	33·50	3·08	44·36	44·50	132·4	2·98	..	44·5
6	18·96	56·85	3·07	75·81	75·05	225·1	3·00	1·15	75·05

Average 3·01 Average 3·01

* The quantities of disulphur monoxide taken and of the products of its reaction have been expressed in g. atoms of sulphur per g. of the original solution and have been multiplied by 10^6.

in combination with oxygen is quantitatively converted into hydrogen sulphide, and for every gram molecule of hydrogen sulphide formed, 3 gram atoms of iodine are liberated, the reaction being:

$$S_2O + 6HI \rightarrow 2H_2S + H_2O + 6I.$$

The experiments in which the carbon tetrachloride solution is treated with mercury also show that the sulphur oxide in solution is disulphur monoxide, for we get 3 gram moles of mercuric sulphide for every gram mole of sulphur dioxide, in terms of the equation

$$2S_2O + 3\,Hg \rightarrow 3\,HgS + SO_2.$$

Non-reducibility of elemental sulphur by hydrogen iodide at laboratory temperatures

For the purposes of the present investigation it was of importance to know if hydrogen iodide had any reducing action on sulphur at laboratory temperatures. A solution of known concentration of elemental sulphur in carbon tetrachloride was brought in contact with hydrogen iodide, air being carefully excluded. No iodine was liberated and quantitative estimations showed that the sulphur was entirely in the elemental state at the end of the experiment. Similar experiments were also carried out with elemental sulphur formed on keeping for a long time carbon tetrachloride solutions of disulphur monoxide, the sulphur dioxide formed during the decomposition of the lower oxide, being completely removed. No iodine was at all liberated.

Reaction between sulphur dioxide and hydrogen iodide

It is known that hydrogen iodide reduces sulphur dioxide to hydrogen sulphide. In the present investigation, it was necessary to examine the quantitative aspects of the reaction. A carbon tetrachloride solution of pure sulphur dioxide was standardised iodometrically. Aliquots were introduced into bulbs containing hydrogen iodide. The quantity of hydrogen iodide employed in each case was of the order of 600 to 650×10^{-6} g. mole per g. of the carbon tetrachloride solution. There was immediate reaction and the solvent turned yellowish violet. On keeping however, the normal colour of iodine in carbon tetrachloride solution was obtained. This suggested the possibility of the intermediate formation of the iodide or oxyiodide of sulphur.

This aspect of the reaction has been studied in detail and will be dealt with in a separate paper.

When the decomposition of the intermediate compound was complete, dry nitrogen (or hydrogen) was bubbled through the bulb and the gaseous products were observed in 2N alkali holding some cadmium hydroxide in suspension. The sulphide and sulphite formed, were determined iodometrically. Iodine and free sulphur present in solution in carbon tetrachloride were also estimated by methods described earlier. The results are given in Table II.

TABLE II

Reaction between Sulphur Dioxide and Hydrogen Iodide

Expt. No.	SO_2 taken*	H_2S obtained	SO_2 unreacted	Free sulphur liberated	Iodine liberated (in g. atoms × 10^6 per g.)	Ratio of Iodine to Sulphur I : S	% SO_2 reduced to H_2S	% SO_2 reduced to S	% SO_2 unreacted	% SO_2 accounted for
1	10·30	10·25	..	..	62·10	6·05	99·5	..	..	99·5
2	3·27	3·25	..	..	20·10	6·19	99·4	..	..	99·4
3	6·95	6·90	..	..	41·13	5·98	99·3	..	..	99·3
4	85·70	41·20	25·40	19·30	290·6	7·05	48·7	22·5	29·6	100·8
5	64·6	30·80	18·36	15·60	225·4	7·30	47·7	24·1	28·5	100·3
6	352·0	3·5	256·0	93·60	452·0	129·0	1·0	26·6	72·7	100·3

* Quantities of sulphur and its compounds have been expressed in g. atoms of S × 10^6 per g. of solution.

The results given in the table show that under favourable conditions, hydrogen iodide reduces sulphur dioxide quantitatively to hydrogen sulphide in terms of the equation:

$$SO_2 + 6HI \rightarrow H_2S + 2H_2O + 6I.$$

For the above reaction to be quantitative, two conditions however, have to be fulfilled: (*a*) The sulphur dioxide concentration in carbon tetrachloride should be low (of the order of 10 × 10^{-6} g. mole per g. of solvent); (*b*) A large excess of hydrogen iodide should be present. The iodide employed should be at least ten times the amount required to react with the sulphur dioxide.

In experiments 4 to 6, Table II, the concentration of hydrogen iodide remained the same as in the earlier experiments while that of sulphur dioxide increased. As a result, the reduction of sulphur dioxide was incomplete, about 25% of the oxide being left unreacted in experiments 4 and 5 and about 70% in experiment 6. When the initial concentration of sulphur dioxide was of the order of 75 g. atoms × 10^{-6} per gram of the solution only 50% of the sulphur dioxide that had reacted, was converted into hydrogen sulphide (the final product of reduction). In the last experiment where the concentration of sulphur dioxide was about 350×10^{-6} g. atom per g. of solution, only 1 to 2% of the sulphur dioxide was reduced to hydrogen sulphide.

As will be shown in a subsequent paper, the reaction between sulphur dioxide and hydrogen iodide takes place in several stages. The intermediate products are thionyl iodide and sulphur iodide, while the final product of reduction is hydrogen sulphide. The intermediate compounds are highly unstable and if the concentration of hydrogen iodide is inadequate to bring about rapidly, further reduction, these intermediate compounds suffer decomposition and yield elemental sulphur.

Reaction of disulphur monoxide solution in carbon tetrachloride with hydrogen iodide solution in formic acid

As already indicated, Stamm and Wiebusch[2] thought that " polysulphur oxide " was formed when the products of combustion of sulphur under low pressure of oxygen were passed through cold carbon tetrachloride. For analysis of the oxide, they employed formic acid solutions of hydrogen iodide or of potassium iodide and added water before estimating the iodine liberated. They calculated the oxygen in combination with sulphur on the assumption that each atom of oxygen corresponded to 2 atoms of iodine. The present author has found that hydrogen sulphide is formed when the orange yellow solution in carbon tetrachloride is treated with hydrogen iodide. Failure on the part of Stamm, *et al.*, to detect the hydrogen sulphide was due to the fact that on liberation of iodine, they added water to the reaction mixture. In presence of water, the iodine reacted with hydrogen sulphide, and also with sulphur dioxide, if any was present. Another unsuspected complication has been the catalytic decomposition of the lower oxides of sulphur by the formic acid employed as a solvent for hydrogen iodide by Stamm, *et al.* Such decomposition would materially reduce the production of hydrogen sulphide. Analytical determinations by the present author, employing hydrogen iodide without any formic acid have shown that the " poly-sulphur oxide " reported by the previous workers is practically pure disulphur monoxide. A detailed study was made of the influence of anhydrous formic acid on the reduction of the oxides of sulphur by hydrogen iodide.

Whether iodine (in carbon tetrachloride solution) had any action on sulphur dioxide or on hydrogen sulphide, in presence of anhydrous formic acid was first determined. To aliquots of iodine solution ($134 \cdot 8 \times 10^{-6}$ g. atoms per g. of carbon tetrachloride) in an all-glass apparatus out of contact with air, were added sulphur dioxide solutions ($66 \cdot 6 \times 10^{-6}$ g. atom of S per g.)

in carbon tetrachloride and 50 ml. of anhydrous formic acid. After various intervals ranging from 1 to 24 hours the contents were analysed for sulphur dioxide and iodine. It was observed that no iodine was consumed by the sulphur dioxide. Similar results were obtained when hydrogen sulphide was used instead of sulphur dioxide.

Aliquots of the orange-yellow solution (of disulphur oxide in carbon tetrachloride) were introduced into each of three bulbs A, B and C. A contained hydrogen iodide, B had the same quantity of the halide but dissolved in anhydrous formic acid (50 ml.) and C contained 50 ml. of the formic acid and about 0·5 g. of powdered potassium iodide that had been previously dried. Air in the bulb C had been removed before the introduction of the orange-yellow solution.

Iodine was liberated in all the three bulbs. After ten minutes, the contents of the bulbs were carefully analysed, using dry nitrogen to sweep away hydrogen sulphide and sulphur dioxide and to absorb them in alkali, in presence of cadmium hydroxide. The sulphide and sulphite formed were determined. No thiosulphate was found. The iodine and sulphur present in the carbon tetrachloride were also estimated. The data thus obtained were employed in calculating the extent of each of the reactions that took place.

The reactions were:

$$S_2O + 6HI \rightarrow 2H_2S + H_2O + 6I \qquad (A)$$

$$2S_2O \rightarrow SO_2 + 3S \qquad (B)$$

$$SO_2 + 6HI \rightarrow H_2S + 2H_2O + 6I \qquad (C)$$

If 0·5 a g. mole of S_2O undergoes Reaction A, and 0·25 b g. mole of S_2O takes part in Reaction B and c g. mole of the oxide undergoes Reaction C, it can be shown that quantities of the final products formed will be as follows:

$$\text{Sulphide} = a + c; \quad \text{Sulphite} = 0{\cdot}25\, b - c.$$

$$\text{Sulphur} = 0{\cdot}75\, b; \quad \text{Iodine} = 3a + 6c.$$

From the above, the extent of each of the Reactions A, B and C can be calculated. The results are given in Table III.

Two other reactions are possible:

(1) The hydrogen sulphide formed may, in presence of formic acid, react with sulphur dioxide to form sulphur and water, and (2) the sulphur dioxide may be reduced by the hydrogen iodide to sulphur:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad (D)$$

$$SO_2 + 4HI \rightarrow S + 2H_2O + 4I \qquad (E)$$

TABLE III

Influence of Formic Acid on the Reaction between Hydrogen Iodide and Disulphur Monoxide

Reaction between HI and S_2O	Experiment 1			Experiment 2		
	*a**	*b**	*c**	*a*	*b*	*c*
Sulphide** (H_2S) ..	54·8	46·45	10·95	18·30	5·60	3·60
Sulphite (SO_2) ..	..	5·77	8·00	..	1·93	2·69
Free Sulphur (S) ..	..	32·48	35·95	..	10·80	12·15
Iodine (g. atom $\times 10^6$ per g.) ..	164·6	64·82	45·05	55·05	22·05	15·25
Iodine (calc.) ..	164·4	64·53	44·79	54·90	21·81	15·09
Disulphur monoxide used ..	54·80	54·70	54·90	18·30	18·33	18·35
% S_2O reduced to H_2S ..	100·0	20·5	12·7	100·0	21·4	11·8
% S_2O catalytically decomposed ..	..	78·8	87·3	..	78·7	88·1
% Conversion to H_2S of SO_2 produced in reaction B	..	46·8	33·5	..	46·4	35·4
% S_2O accounted for ..	100·0	99·3	100·0	100·0	100·1	99·9

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

*a** had S_2O in CCl_4 and HI in CCl_4; *b** had S_2O in CCl_4 and HI in anhydrous formic acid; *c** had S_2O in CCl_4 and KI in formic acid.

As shown later in this paper, the reaction between hydrogen sulphide and sulphur dioxide is rather slow. It may, therefore, be ignored. The concentration of sulphur dioxide which is produced by the decomposition of disulphur monoxide is rather small, and to simplify the calculations it may be assumed, that the sulphur dioxide which has undergone reduction has produced only hydrogen sulphide and no sulphur.

From the above results, it may be concluded that in presence of an excess of hydrogen iodide, disulphur monoxide is completely reduced to hydrogen sulphide and water (Reaction A). In presence of anhydrous formic acid however, owing to the catalytic influence of the acid, only a part of the oxide is reduced by hydrogen iodide, while the major portion undergoes decomposition to sulphur dioxide and sulphur (Reaction B). Part of the sulphur dioxide produced during the Reaction B, is reduced by the hydrogen iodide to form hydrogen sulphide (Reaction C.) The reducing capacity of a formic acid solution of potassium iodide is far less than that of a solution of hydrogen iodide in formic acid. Relatively less hydrogen sulphide is therefore formed in potassium iodide solutions.

The effect of anhydrous formic acid on the reduction of sulphur dioxide by hydrogen iodide was also studied following the same technique as had been employed for disulphur monoxide. The results are given in Table IV.

TABLE IV

Influence of Formic Acid on the Reaction between Hydrogen Iodide and Sulphur Dioxide

Reaction of HI and SO_2	Experiment 1			Experiment 2		
	*a**	*b**	*c**	*a*	*b*	*c*
SO_2** used	7·83	7·83	7·83	12·76	12·76	12·76
SO_2 unreacted	..	1·30	2·25	..	2·05	3·15
H_2S formed	7·78	2·76	1·85	12·68	3·80	3·10
Sulphur liberated	..	3·65	3·65	..	6·85	6·51
Iodine liberated	48·05	32·20	25·90	77·85	50·65	45·00
Iodine calculated	46·98	31·20	25·74	76·56	49·96	44·64
% SO_2 reduced to H_2S	99·4	66·4	54·8	99·4	65·5	58·2
% SO_2 converted to free S	..	15·6	15·6	..	16·1	24·6
% SO_2 unreacted	..	16·6	28·7	..	17·9	17·1
% SO_2 accounted for	99·4	98·6	99·1	99·4	99·5	99·9

** Quantities of sulphur and its compounds have been expressed in g. atoms of S × 10^6 per g. of solution.

a * had SO_2 in CCl_4 and HI in CCl_4 ; *b* * had SO_2 in CCl_4 and HI in anhydrous formic acid and *c* * had SO_2 in CCl_4 and KI in anhydrons formic acid.

The data presented show that in presence of anhydrous formic acid, the reduction of sulphur dioxide to hydrogen sulphide by hydrogen iodide, is incomplete. Only two-thirds of the sulphur dioxide is reduced to hydrogen sulphide, 12 to 18% of the dioxide does not at all react, while 16 to 19% of the oxide is reduced to elemental sulphur. The percentage of unreacted sulphur dioxide is much higher when the reductant is potassium iodide.

Reaction between sulphur dioxide and hydrogen sulphide in presence of anhydrous formic acid

The reaction between sulphur dioxide and hydrogen sulphide in presence of anhydrous formic acid was studied, employing dilute solutions of sulphur dioxide and of hydrogen sulphide in carbon tetrachloride. It was found that the two gases did react to give sulphur and water. The reaction was rather slow.

At the end of the experiment (6 hours) dry nitrogen was bubbled through the reaction vessel to sweep away the unreacted gases which were absorbed by 2N sodium hydroxide having some cadmium hydroxide suspension. The sulphide and sulphite formed in the absorption vessel and elemental sulphur present in carbon tetrachloride were estimated in the usual way. No thiosulphate was found. The results are given in Table V.

TABLE V

Reaction between Sulphur Dioxide and Hydrogen Sulphide in Presence of Formic Acid

Reaction between SO_2 and H_2S	Experiment			
	1	2	3	4
SO_2* taken	26·38	18·97	38·72	16·23
H_2S taken	28·80	33·63	78·60	35·50
SO_2 unreacted	13·89	4·55	5·85	2·50
H_2S unreacted	4·50	4·85	12·46	6·86
S produced	36·90	43·25	98·74	41·65
% SO_2 unreacted	52·60	24·00	15·10	15·40
% SO_2 reacting with H_2S	46·60	76·02	85·00	85·10
% SO_2 accounted	99·20	100·02	100·10	100·50
Ratio of H_2S to SO_2	1·08	1·77	2·02	2·19

* Quantities of sulphur and its compounds have been expressed in g. atoms of S × 10^6 per g. of solution.

It is well known that the union of hydrogen sulphide and sulphur dioxide is catalysed by moisture. As formic acid is also a highly polar liquid, it may be expected to catalyse the reaction. Formic acid does catalyse the reaction but the effect is comparatively small. It has been shown that in formic acid solutions, iodine oxidises neither hydrogen sulphide nor sulphur dioxide. In presence of water however, both the gases are oxidised by iodine. Thus, though water and formic acid are both highly polar, there is a marked difference in their influence on the chemical reactivity of hydrogen sulphide and sulphur dioxide.

Reaction between hydrogen sulphide and sulphur dioxide in presence of potassium iodide in formic acid

The reaction between hydrogen sulphide and sulphur dioxide was also studied in presence of potassium iodide in anhydrous formic acid. The experimental technique was the same as already described. The following three reactions are possible:

$$(1)\quad SO_2 + 6HI \rightarrow H_2S + H_2O + 6I \qquad (C)$$

$$(2)\quad SO_2 + 4HI \rightarrow S + 2H_2O + 4I \qquad (E)$$

$$(3)\quad 2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad (D)$$

Interaction between hydrogen sulphide and sulphur dioxide, though catalysed by formic acid, is slow. The formation of sulphur by this reaction may therefore be ignored and it may be assumed that the sulphur produced is entirely got by the reduction of sulphur dioxide by hydrogen iodide. When this simplifying assumption is made, it is possible to calculate the extent of each of the two Reactions C and E. The results are presented in Table VI.

TABLE VI

Reaction between Sulphur Dioxide and Hydrogen Sulphide in Presence of Potassium Iodide in Formic Acid

Reaction between SO_2 and H_2S	Experiment		
	1	2	3
SO_2* taken	12·96	9·95	12·46
SO_2 unreacted	4·05	3·06	4·08
H_2S taken	10·80	12·56	14·83
Ratio of $H_2S : SO_2$	0·83	1·26	1·19
H_2S at end of reaction	15·15	15·56	18·25
H_2S surplus	4·35	3·00	3·42
Sulphur produced	4·53	3·89	4·87
% SO_2 reduced to H_2S (Reaction C)	33·5	30·1	27·4
% SO_2 reduced to sulphur (Reaction E)	35·0	39·1	39·0
% SO_2 unreacted	31·20	30·5	32·7
% sulphur accounted for	99·7	99·7	99·1
Free iodine found	45·14	33·87	40·46
Free iodine (calc.)	44·58	33·56	40·00

* Quantities of sulphur and its compounds have been expressed in g. atoms of S × 10^6 per g. of solution.

The data show that when the reductant is potassium iodide dissolved in formic acid, the sulphur dioxide is reduced to hydrogen sulphide to an extent of 25 to 30% while with hydrogen iodide in absence of formic acid, the reduction of sulphur dioxide to hydrogen sulphide was practically complete (Table II).

Stability of disulphur monoxide

It was reported in Part I[12] of this series that when the products of combustion of sulphur in oxygen at a pressure of 5 to 7 mm. of mercury were condensed at – 70° C. all the sulphur dioxide present volatalised, leaving practically pure disulphur monoxide as an orange-yellow solid. The disulphur monoxide thus obtained, when warmed to – 16° C. appeared to be insoluble in carbon tetrachloride (also at – 16° C.) though solutions containing the pure oxide could be obtained by passing the products of combustion directly into carbon tetrachloride at – 16° C. and removing the sulphur dioxide present in solution. It was therefore of interest to investigate the reaction of the solid towards hydrogen iodide in presence of carbon tetrachloride.

The reaction was studied by the technique described earlier. The results are presented in Table VII.

TABLE VII

Reaction between Orange-Yellow Residue and Hydrogen Iodide in Presence of Carbon Tetrachloride

Reaction between S_2O and HI	Experiment		
	1	2	3
H_2S* evolved	12·36	8·96	20·77
Elemental sulphur	21·05	14·28	41·67
Iodine (g. atoms × 10^6)	58·55	41·45	104·5
% S_2O undecomposed	15·9	18·0	11·0
% S_2O decomposed	84·0	81·8	88·9

* Sulphur and its compounds have been expressed in terms of g. atoms of S × 10^6 per g. of solvent.

From the above experiments it was concluded that disulphur monoxide in absence of its solvent (carbon tetrachloride) decomposed rapidly. Only 11 to 18% of the oxide was left undecomposed when the oxide at – 70° C. was warmed to – 16° C. The apparent insolubility of the solid when brought in contact with carbon tetrachloride at – 16° C. was due to the fact that much of the disulphur monoxide had already decomposed to sulphur (and sulphur dioxide). The solubility of sulphur in carbon tetrachloride being small, the solid did not dissolve.

To show that carbon tetrachloride as solvent had stabilising action on disulphur monoxide, an aliquot of the solution of the oxide (obtained by passing the products of combustion into carbon tetrachloride at — 16° C. and freed from sulphur dioxide) was frozen at — 30° C., at which temperature there was no liquid solvent to keep the oxide in solution. The frozen mass was thawed and treated with hydrogen iodide in carbon tetrachloride at — 16° C., and the products of reaction analysed. The results are given in Table VIII.

TABLE VIII

Decomposition of Disulphur Monoxide in Carbon Tetrachloride Solutions, on Freezing

Decomposition of S_2O	Experiment		
	1	2	3
S_2O* taken	25·43	44·75	55·56
H_2S produced	16·72	15·4	14·30
Elemental sulphur	8·64	29·25	41·20
Iodine liberated	58·85	75·56	84·5
% S_2O undecomposed	54·3	12·6	1·0
% S_2O decomposed	45·3	87·2	98·86

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

It was concluded from the above results that when disulphur monoxide solutions in carbon tetrachloride were kept frozen for different periods, the oxide decomposed to the extent of 45 to 98%. It was noticed that the intensity of orange-yellow colour of the carbon tetrachloride solution depended on the disulphur monoxide left undecomposed. When the decomposition of the oxide was almost complete, the solution was practically colourless. Solid disulphur monoxide is markedly less stable than a solution of the oxide in carbon tetrachloride.

SUMMARY

1. The orange-yellow liquid obtained when the products of combustion of sulphur in oxygen at low pressure are passed into cooled carbon tetrachloride (at — 16° C.) and the sulphur dioxide is removed, is a solution of almost pure disulphur monoxide.

2. Anhydrous hydrogen iodide quantitatively reduces disulphur monoxide into hydrogen sulphide. A corresponding amount of iodine is liberated.

3. Sulphur dioxide is also quantitatively reduced to hydrogen sulphide by hydrogen iodide, provided the concentration of sulphur dioxide is small and that of hydrogen iodide is relatively large. When hydrogen iodide is present in moderate excess, only a part of the sulphur dioxide is reduced to hydrogen sulphide, the rest being reduced to sulphur.

4. In presence of anhydrous formic acid, owing to the catalytic influence of the acid, only a part of the disulphur oxide is reduced by hydrogen iodide, while the major portion undergoes decomposition to sulphur dioxide and sulphur. The reducing capacity of a formic acid solution of potassium iodide is far less than that of a solution of hydrogen iodide in formic acid.

5. Anhydrous formic acid also affects the reduction of sulphur dioxide by hydrogen iodide. In presence of the acid, the reduction of the oxide to hydrogen sulphide, is incomplete. The percentage of unreacted sulphur dioxide is much higher when the reductant is potassium iodide in formic acid.

6. The union of hydrogen sulphide and sulphur dioxide is slowly catalysed by anhydrous formic acid.

7. When the products of combustion of sulphur (in oxygen under reduced pressure) are cooled to – 70° C., disulphur monoxide is obtained as an orange yellow solid. The solid is far less stable than a solution of the oxide in carbon tetrachloride.

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