

STUDIES IN THE CHEMICAL BEHAVIOUR OF SULPHUR COMPOUNDS

Part II. Disulphur Oxide

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Introductory

WHILE studying the properties of sulphur monoxide, it was noticed in this laboratory, that though sulphur monoxide was a colourless gas, yet the solution obtained by passing it into dry carbon tetrachloride had a deep yellow colour. This yellow solution lost its colour on keeping. Treated with sodium hydroxide immediately on preparation, the solution yielded sulphide, sulphite, and thiosulphate (Experiment *a*), but when the same solution was kept for 24 hours, sodium sulphite was practically the only product obtained in the aqueous layer, on treatment with the alkali (Experiment *b*). This indicated that an unstable oxide of sulphur, hitherto unknown, was present. The ratio of sulphur to oxygen in this compound could be obtained from the analytical values of (*a*) the experiment in which the fresh solution was treated with alkali and (*c*) an experiment in which the oxide was decomposed by mercury and the sulphur dioxide liberated was estimated. The sulphur in the oxide was practically equal to the sulphur corresponding to the soluble compounds of the element, obtained in experiment (*a*), while its oxygen corresponded to that of the sulphur dioxide liberated in (*c*). It was found that the ratio of S to O was approximately 2 : 1 indicating that the oxide had the formula S_2O and was disulphur oxide. An account of the preparation and the properties of the oxide is given in this paper.

Experimental

Sulphur monoxide was obtained by Schenk and his co-workers in a variety of ways (Cordes and Schenk,² Schenk and Platz,¹⁶ Schenk and Triebel,²¹ Schenk¹⁷). The method that was found most convenient for purposes of the present investigation was the combustion of sulphur under reduced pressure of oxygen (Schenk¹⁷). The apparatus employed was essentially the same as described by Schenk. It was however found advantageous

to use a quartz tube for the actual combustion. The oxygen pressure was maintained at 5 to 10 mm. of mercury. In the present investigation, the products of combustion were passed through 40 to 50 c.c. of pure dry carbon tetrachloride contained in a suitable absorption vessel maintained at -12 to -18° C. by a bath of alcohol cooled by carbon dioxide snow. When the gas was passed through the solvent, a deep yellow colour was produced, which as already stated, was found to be due to disulphur oxide. Before the solution could be employed for a study of the properties of the oxide, it was necessary to remove the sulphur dioxide present. To accomplish this, the combustion was stopped, but the current of oxygen continued and the sulphur dioxide pumped off. Investigations with sulphur dioxide solution in carbon tetrachloride had shown that this treatment was adequate for the removal of dissolved sulphur dioxide. It had also been found that it was unnecessary to replace the oxygen by an inert gas like nitrogen for this purpose.

It was found that the freshly obtained solution of disulphur oxide in carbon tetrachloride had a characteristic absorption spectrum (Plate XXI *a*), there being absorption of light from the ultra-violet end upto a wave-length of 4700 \AA . The same solution, however, when kept at the laboratory temperature for 2.5 hours gave an absorption spectrum (XXI *b*) which was identical with (XXI *c*) that of a synthetic solution containing sulphur dioxide and sulphur in quantities corresponding to the disulphur oxide originally present, thereby confirming the nature of the decomposition. A constant deviation spectrograph (supplied by Messrs. Adam Hilger, Ltd.) was used for studying the absorption spectrum.

The solution, as obtained in the combustion experiment (after removal of sulphur dioxide), was found to need dilution before the disulphur oxide could be accurately estimated. It was therefore diluted with a known weight of dry carbon tetrachloride. Three different sets of analytical experiments were then carried out:—

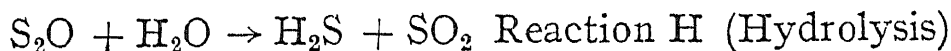
Experiment (a) : Hydrolysis of freshly prepared oxide with 2 N sodium hydroxide, containing cadmium hydroxide in suspension.—A dry stoppered bottle containing a thin-walled sealed tube filled with the alkali (and cadmium hydroxide) was weighed and a portion of the carbon tetrachloride solution was then introduced and the sealed tube immediately broken to effect hydrolysis, the contents being shaken for 3 minutes. The bottle was then reweighed and the weight of the carbon tetrachloride solution used, calculated. When hydrolysis was complete, the carbon tetrachloride layer was removed, a separating funnel being used. The aqueous layer was filtered

and the precipitate of cadmium sulphide (and excess cadmium hydroxide) was washed. The filtrate was diluted to 250 c.c. in a measuring flask and aliquots employed for estimation of sulphite and thiosulphate by the method of Kurtenacker and Goldbach.⁹ Another aliquot was oxidised with hydrogen peroxide and the sulphate formed, estimated by the method of Pregl. From this sulphate value it could be found if any thionate or sulphate had been formed during hydrolysis. No detectable amounts of thionate or sulphate were found when 2 N alkali was used for hydrolysis as the sulphate obtained corresponded to the sulphite and thiosulphate originally present. The elementary sulphur in solution in carbon tetrachloride was estimated by the method developed in this laboratory and described by B. S. Rao and M. R. A. Rao.¹³

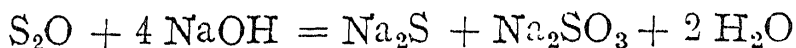
Experiment (b): Hydrolysis of oxide after keeping for 24 hours.—A weighed quantity of the disulphur oxide solution was kept in a carefully cleaned and dried bottle for a period of 24 hours and the sealed tube of alkali originally placed in it, was broken to effect hydrolysis of the oxide and the products were analysed as in experiment (a).

Experiment (c): Decomposition of disulphur oxide with mercury and estimation of sulphur dioxide liberated.—A hundred c.c. flask fitted with taps and suitable ground glass connections was weighed along with mercury (5 g.) placed in it, after complete displacement of the air by a stream of pure dry nitrogen. A suitable quantity of the freshly prepared disulphur oxide solution was then introduced into the flask and the flask weighed to obtain the weight of solution used. The sulphur dioxide liberated by the decomposition of the disulphur oxide was removed from the reaction vessel in a stream of dry nitrogen and absorbed in 2 N alkali (holding cadmium hydroxide in suspension). The flask was kept in a bath of boiling water to complete the reaction. The heating was continued till the major part of the carbon tetrachloride had distilled over. To the alkali in the absorption vessel glycerine was then added to inhibit the atmospheric oxidation of sulphite during the subsequent analytical operations. The cadmium hydroxide was filtered off, washed and analysed. No sulphide was found in it. Acetic acid and a known quantity of a standard solution of iodine were added to the filtrate and the excess of iodine left after reaction with the sulphite, was titrated with 0.01 N sodium thiosulphate.

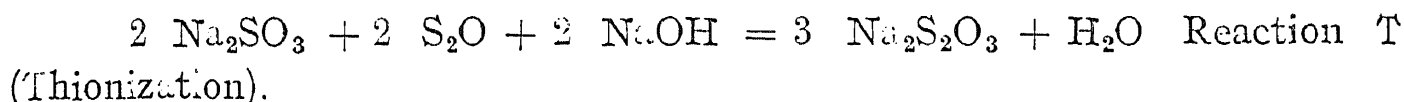
The results obtained can be explained on the basis of the following reactions: When brought in contact with alkali, the major part of the disulphur oxide produces the sulphide and the sulphite of sodium in equimolecular proportions (B. S. Rao¹⁴).



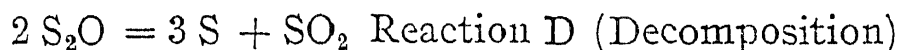
and in presence of sodium hydroxide



Part of the sulphite produced above, reacts with disulphur oxide to give sodium thiosulphate:—



At the same time, the disulphur oxide is decomposed into sulphur and sulphur dioxide:—



the sulphur dioxide liberated being absorbed by alkali to give sodium sulphite.

If S_2O corresponding to h atoms of sulphur, participates in reaction H, t atoms in 'T' and d atoms in D, the total quantity of disulphur oxide present in solution will be $h + t + d$, while $h = 2$ sulphide, $t = 2/3$ thio-sulphate, and $d = 4/3$ sulphur, formed in the course of the decomposition. It can be shown that the free sulphur should equal thiosulphate + 3 (sulphite-sulphide), all quantities being expressed in gram atoms of sulphur per gram of carbon tetrachloride used as solvent, since sulphide = $h/2$, sulphite = $h/2 - t/2 + d/4$, thiosulphate = $3 t/2$, and free sulphur = $3 d/4$.

In the following tables, free sulphur calculated on the basis of the above relationship has been termed S (Calculated) while the quantity actually determined by experiment is denoted as S (Found).

The method of calculation of results is indicated with reference to Experiment 1 in Table I. The quantities are expressed in gram atoms of sulphur per gram of carbon tetrachloride in the undiluted solution of disulphur oxide, and have been multiplied by 10^6 . The values of sulphur, h , t , and d have been obtained from the equations indicated above. In Experiment (c) the sulphite obtained is 4.62 while the sulphur in carbon tetrachloride solution is 32.85. Only the reaction D takes place in this case and so the S_2O present is four times the sulphite and the sulphur produced by decomposition of the S_2O is three times the sulphite.

$$\text{S}_2\text{O} = 18.48, \text{S} = 13.86.$$

TABLE I

No. of experiment	1		2		3		4		5		6		7	
	(a)	(b) Kept 2 hrs.	(a)	(b) Kept 24 hrs.	(a)	(b) Kept 6 hrs.	(a)	(b) Kept 24 hrs.	(a)	(b) Kept 24 hrs.	(a)	(b) Kept 24 hrs.	(a)	(b) Kept 24 hrs.
*Sulphite ..	4.96	4.66	4.7	3.87	5.36	3.46	1.60	2.22	2.12	3.73	7.47	5.12	6.59	4.87
Sulphide ..	5.85	0.41	6.3	0.17	5.65	0.45	3.14	0.07	4.72	0.12	10.63	0.54	9.25	0.47
Thiosulphate ..	6.22	1.63	6.85	1.24	4.47	1.73	4.95	0.43	8.89	0.75	9.54	2.86	9.38	2.52
Free Sulphur (Calcd.) ..	3.55	12.58	2.68	12.31	3.60	10.76	0.33	6.88	1.09	11.58	0.06	16.60	1.40	15.72
<i>h</i> ..	11.70	0.82	12.60	0.34	11.30	0.90	6.28	0.14	9.44	0.24	21.26	1.08	18.50	0.94
<i>t'</i> ..	4.15	1.69	4.59	0.73	2.98	1.15	3.30	0.29	5.93	0.50	6.36	1.91	6.25	1.68
<i>d</i> ..	4.73	16.77	2.77	16.45	4.80	14.35	0.44	9.17	1.45	15.44	0.08	22.13	1.87	20.96
<i>h</i> + <i>t'</i> + <i>d</i> ..	20.58	18.68	19.96	17.62	19.08	16.40	10.02	9.60	16.82	16.18	27.70	25.12	26.62	23.58
S ₂ O (Expt. c) ..	18.48	18.48	17.52	17.52	16.40	16.40	9.60	9.60	16.18	16.18	25.12	25.12	23.58	23.58
Activated Sulphur ..	2.10	0.20	2.44	0.10	2.68	..	0.42	..	0.64	..	2.58	..	3.04	..
<i>t</i> ..	2.05	0.89	2.15	0.73	0.30	1.15	2.88	0.29	5.29	0.50	3.78	1.91	3.21	1.68
S in CCl ₄ solution (Calcd.) ..	20.44	31.77	22.58	35.2	30.5	37.9	14.61	21.58	33.26	50.62
S in CCl ₄ solution (Found) ..	20.04	31.37	21.87	35.9	29.8	38.5	14.80	21.56	n.d.	n.d.	n.d.	n.d.	32.8	50.21
“Residual” S (Expt. c) ..	18.99	18.99	22.94	22.94	27.18	27.18	14.7	14.7	34.9	34.9
% hydrolysis ..	63.3	4.4	71.9	1.9	68.9	5.5	65.4	1.5	58.4	1.5	84.6	4.3	78.5	4.0
% thionization ..	11.1	5.9	12.3	4.2	1.8	7.0	30.0	3.0	32.7	3.1	15.1	7.6	13.6	7.1
% decomposition ..	25.6	90.7	15.8	93.9	29.3	87.5	4.6	95.5	8.9	95.4	0.3	88.1	7.9	88.9

* The quantities of disulphur oxide and of the products of its reaction have been expressed in gram atoms of sulphur per gram of the original solution and have been multiplied by 10⁶.

It is obvious that in addition to the sulphur produced by decomposition of S_2O , the carbon tetrachloride holds in solution extra sulphur. This sulphur has been designated "Residual Sulphur" for the sake of convenience. Its value in Experiment 1 is 32.85 less 13.86 , *i.e.*, 18.99 . This residual sulphur is due to the fact that during the production of disulphur oxide by combustion of sulphur, the oxide formed is continuously decomposing into sulphur and sulphur dioxide and is enriching the sulphur content of the carbon tetrachloride.

It will be noticed that the same solution of disulphur oxide when subjected to the three treatments (*a*), (*b*) and (*c*) described above, indicates varying amounts of disulphur oxide the value in (*a*) being 20.58 , in (*b*) 18.68 , and in (*c*) 18.48 . The difference between (*b*) and (*c*) is not very much above the experimental error and may perhaps be neglected since such differences between S_2O values for (*b*) and (*c*) have been noticed in only one other experiment (Experiment 2). The apparently higher value of S_2O in (*a*) is due to the fact that in carbon tetrachloride solution the disulphur oxide forms a molecular complex with dissolved sulphur as is revealed by molecular weight determinations by the cryoscopic method described later in this paper. When the complex is brought in contact with alkali, the disulphur oxide has the effect of activating a part of the dissolved sulphur and enables it to thionize the sulphite. The thiosulphate content of the solution thus increases and leads to an apparent increase in the amount of disulphur oxide. Thionization in Experiment (*a*) has therefore been denoted by t' which is higher than the true value t . The following mechanism for the activation of part of the dissolved sulphur can be suggested. When the complex between dissolved sulphur and disulphur oxide breaks up on treatment with alkali, it mainly splits up into sulphur and disulphur oxide. Small quantities of S_3O (trisulphur oxide), however, are formed and the extra sulphur present in the molecule thionizes sulphite to yield thiosulphate. It has already been pointed out in Part I of the present studies that S_3Cl_2 a chloride corresponding to S_3O is known to be present in sulphur chloride. The actual S_2O present in all the three cases is 18.48 and the activated sulphur in (*a*) is $(20.58 - 18.48) = 2.1$. This value has to be deducted from t' in (*a*) to give the correct value of t . It has to be pointed out that sulphur dissolved in carbon tetrachloride does not produce detectable quantities of sulphide, sulphite or thiosulphate under the experimental conditions of the hydrolytic treatment of disulphur oxide solutions with alkali.

Confirmation of the view that a part of the dissolved sulphur is activated by disulphur oxide and participates in thionization is afforded by the agreement between the observed and the calculated values of dissolved sulphur

present in the carbon tetrachloride layer in experiments 1 (a) and 1 (b). In 1 (a) the free sulphur in the solvent should be $(18.99 + 3.55 - 2.1)$ where 18.99 is the residual sulphur, 3.55 is the calculated amount of sulphur liberated during treatment with alkali and 2.1 is the activated sulphur. The free sulphur in experiment 1 (a) is 20.44 as calculated, and 20.03 as actually found by analysis. The value for free sulphur in 1 (b) is 31.77 (Calculated) and 31.37 (Found). The agreement in both the cases is good, considering the experimental difficulties involved in the accurate determination of sulphide, sulphite, thiosulphate and free sulphur in such dilute solutions. It has to be stated that the experimental error in the analytical determinations is of the order of 2 to 4%.

Effect of Duration of Combustion on Yield of Disulphur Oxide

The duration of combustion of sulphur was varied and the corresponding yields of disulphur oxide determined. The results are given in Table II and indicate that the quantity of disulphur oxide produced increased with time. The yields, however, were not reproducible. In two experiments, where the oxygen pressure and the heating of the combustion tube were practically constant and the combustion was carried out for 30 minutes, the S_2O produced corresponded to 17.28×10^{-6} and 19.80×10^{-6} gram atoms of sulphur per gram of solvent. In two similar experiments where the duration of combustion was 120 minutes, the yields were 55.66 and 77.62. The apparent yield per minute of combustion dropped as the duration of combustion increased.

TABLE II

No. of experiment	1 (a)	1 (b)	2 (a)	2 (b)	3 (a)	3 (b)	4 (a)	4 (b)	5 (a)	5 (b)	6 (a)	6 (b)
	30 minutes			60 minutes			120 minutes			180 minutes		
Duration of Combustion ..												
* Sulphite ..	5.06	4.04	5.29	3.82	11.00	7.83	13.48	11.04	15.81	16.39	20.43	15.58
Sulphide ..	7.72	0.29	7.51	0.17	14.35	0.12	21.27	0.86	26.06	0.39	33.42	1.35
Thiosulphate ..	8.08	2.11	7.10	1.17	11.87	2.08	26.19	6.61	36.98	6.42	42.18	14.14
Sulphur (Calculated) ..	0.10	13.36	0.44	12.12	1.82	25.21	2.82	37.15	6.23	54.42	3.21	56.83
<i>h</i> ..	15.44	0.58	15.02	0.34	28.70	0.24	42.54	1.72	52.12	0.78	66.84	2.70
<i>t'</i> ..	5.39	1.41	4.73	0.78	7.91	1.39	17.46	4.41	24.65	4.28	28.12	9.43
<i>d</i> ..	0.13	17.81	0.59	16.16	2.43	33.61	3.76	49.53	8.31	72.56	4.28	75.77
<i>h + t' + d</i> ..	20.96	19.80	20.34	17.28	39.04	35.24	63.76	55.66	85.08	77.62	99.24	87.90
S ₂ O ..	19.80	19.80	17.28	17.28	35.24	35.24	55.66	55.66	77.62	77.62	87.90	87.90
S' = Activated Sulphur ..	1.16	Nil	3.06	Nil	3.80	Nil	8.10	Nil	7.46	Nil	11.34	Nil
<i>t</i> ..	4.23	1.41	1.67	0.78	4.11	1.39	9.36	4.41	17.19	4.28	16.78	9.43
S in CCl ₄ soln. (Calculated) ..	29.19	..	26.52	..	53.76	..	81.0	..	106.5	..	122.4	..
S in CCl ₄ soln. (Found) ..	28.55	43.61	26.95	41.26	54.75	80.34	83.5	123.4	101.1	162.1	130.0	192.8
Residual sulphur ..	30.25	30.25	29.14	29.14	55.13	55.13	86.25	86.25	107.7	107.7	136.0	136.0
% <i>h</i> ..	78.0	2.9	86.9	2.0	81.5	0.7	76.5	3.1	67.1	1.0	76.1	3.1
% <i>t</i> ..	21.4	7.1	9.7	4.5	11.6	3.9	16.7	7.9	22.2	5.5	19.1	10.7
% <i>d</i> ..	0.6	89.9	3.4	93.5	6.9	95.4	6.8	89.0	10.7	93.5	4.8	86.2
Dilution ..	3.3	..	5.8	..	4.05	..	2.1	..	1.7	..	1.7	..

* The quantities of disulphur oxide and of the products of its reaction have been expressed in gram atoms of sulphur per gram of the original solution and have been multiplied by 10⁶.

TABLE III

Duration of Combustion in minutes	30	60	120	180
Average yield of S ₂ O (g. atoms of S × 10 ⁻⁶) as S ₂ O per g. solvent	18.54	35.24	66.64	87.9
Apparent yield per minute	0.62	0.59	0.56	0.49

The ratio of "Residual Sulphur" to sulphur as disulphur oxide was found to be fairly constant, the values for the five experiments being as follows:—

No. of experiment (Table II) ..	1	2	3	4	5
Ratio Residual S to S as S ₂ O ..	1.53	1.69	1.56	1.39	1.55

Mean value 1.55

Rate of Decomposition of Disulphur Oxide

Information about the stability of disulphur oxide in carbon tetrachloride solutions could be obtained from the data presented in Table I. The results (Table IV) showed that no correlation could be established between the rate of decomposition and the concentration of disulphur oxide or of residual sulphur. The stability of the disulphur oxide was found to depend mainly on the condition of the glass surface of the vessel in which the oxide solution was kept.

TABLE IV

Decomposition of Disulphur Oxide (in Carbon Tetrachloride Solution) Stored in Glass Bottles

No. of Expt.	S ₂ O in 400 g. soln. in g. atoms × 10 ⁻⁶	Duration of storage in hours	% Decomposition	"Residual sulphur"	Ratio S : S ₂ O
1	18.68	2	90.7	19.0	1.02
2	17.62	24	93.9	22.94	1.30
3	16.40	6	87.5	27.20	1.66
4	9.6	24	95.5	14.7	1.53
5	16.2	24	95.4	n.d.	n.d.
6	25.1	24	88.1	n.d.	n.d.
7	23.6	24	88.9	34.9	1.48

Further studies on the stability of disulphur oxide solutions showed that dissolved sulphur had a noticeable stabilising effect on the oxide. This effect, however, was often masked by the catalytic decomposition taking place at the glass surface. The stabilising effect of dissolved sulphur was analogous to that of the element on the stability of persulphides of hydrogen (Sabatier¹⁵).

As in the case of persulphides, the dissolved sulphur formed complexes with the disulphur oxide. Decomposition of persulphides of hydrogen is known to be less in glass vessels whose surface has been treated with hydrogen chloride (Butler and Maass¹). It was found that hydrogen chloride had similar stabilising effect on disulphur oxide.

Effect of Dilution of Disulphur Oxide on the Reaction with Alkali

When disulphur oxide solutions at different dilution were treated with 2 N alkali the relative proportions of the three reactions: H (hydrolysis), T (thionization), D (decomposition) changed as indicated in Table V.

TABLE V

*Effect of Dilution of S₂O Solutions on the Reaction with 2 N Alkali
(Dilution has been expressed in g. of CCl₄ holding S₂O
corresponding to 1 g. atom of S, and has been
multiplied by 10⁻⁵)*

Dilution	..	1.7	1.7	2.1	3.1	3.3	3.5	3.7	4.05	5.8
Hydrolysis	..	67.1	76.1	76.5	73.1	78.0	73.7	71.7	81.5	86.9
Thionization	..	22.1	19.1	16.7	21.4	21.4	19.5	26.9	11.6	9.7
Decomposition	..	10.7	4.8	6.8	5.2	0.6	6.8	1.4	6.9	3.4

The effect of dilution was not consistent probably because of the influence of dissolved sulphur (present in varying amounts), but it was noticed that in general, dilution tended to increase hydrolysis and decrease thionization as well as decomposition.

In Part I of the present studies, it was pointed out that the hydrolysis by alkali of sulphur chloride solutions could best be interpreted by assuming that disulphur oxide (or its highly unstable hydrate—the hypothetical thio-sulphurous acid) was the primary product of hydrolysis. It is of interest therefore to compare the above results with those obtained in the study of the effect of dilution on the hydrolysis of sulphur chloride (Table VI). It will be noticed that at the same dilution, disulphur oxide and sulphur chloride give approximately the same values for hydrolysis. Thionization, however,

is more in the case of disulphur oxide and decomposition is less. The difference in thionization seems to be due to the fact that in the case of the disulphur oxide solutions we are dealing with a complex between the oxide and dissolved sulphur. This complex presumably is a better thionizing agent than disulphur oxide itself.

Complex formation, resulting in greater stability of the disulphur oxide, may also be responsible for the smaller decomposition noticed with the oxide solutions. An alternative explanation, however, is possible. In consonance with the fact that the lower oxides of sulphur are more stable than their corresponding oxyacids, disulphur oxide is more stable than thiosulphurous acid, which has so far not been isolated though its esters are known and have been studied (Noack,¹² Meuwsen,¹⁰ Hellmuth,⁸ Stamm and Wintzer²³). If thiosulphurous acid itself (and not disulphur oxide) is considered to be the primary product of hydrolysis of sulphur chloride, it is easy to account for the greater decomposition noticed in the case of sulphur chloride hydrolysis.

TABLE VI

*Effect of Dilution of Sulphur Chloride on its Reaction with 2 N Alkali
(Dilution has been expressed in g. of CCl₄ holding S₂O
corresponding to 1 g. atom of S, and has been
multiplied by 10⁻⁵)*

Dilution ..	0.7	1.5	3.8	38.0	77.1
Hydrolysis ..	54.2	68.5	75.8	88.6	90.4
Thionization ..	6.2	6.2	9.6	8.1	9.7
Decomposition ..	40.4	28.3	15.9	3.1	0.0

The effect of (a) temperature, (b) strength and nature of alkali, and (c) reagents like formalin and brucine on the hydrolytic decomposition of disulphur oxide have been studied and will be the subject of another paper in this series. In general, the effects are analogous to those noticed in the hydrolytic decomposition of sulphur chloride.

Complex Formation between Disulphur Oxide and Dissolved Sulphur

To throw light on the molecular condition of the disulphur oxide in solution, an attempt was made to determine the molecular weight of the oxide by the cryoscopic method. The cryoscopic constant for carbon tetrachloride is particularly high (360° for a g. mole in 100 g. solvent). This enabled reasonably accurate determinations even with highly dilute solutions.

The ordinary Beckmann apparatus was employed, the freezing bath being alcohol to which adequate amounts of carbon dioxide snow were added from time to time, to maintain a temperature of -24°C ., the refrigerant being kept in a Dewar bottle. Preliminary experiments were carried out with dilute solutions of sulphur in carbon tetrachloride, the sulphur concentration being of the order of 20×10^{-6} g. atom per g. of solvent. For the atomicity of the sulphur molecule the values obtained were 8.06 and 8.18 (mean value 8.12). A solution of disulphur oxide was prepared and divided into two portions. One sample was treated with 2 N alkali to determine the S_2O and the residual sulphur present. The other sample was used for the cryoscopic work. The freezing point depression observed was of the order of 0.5° . After determination of the freezing point, the solution was treated with alkali to determine S_2O still left in solution. It was noticed that on an average, 3 to 4 % of the S_2O originally present had decomposed. Three determinations were carried out. The results are given in Table VII.

TABLE VII

Cryoscopic Work on Disulphur Oxide Solutions in Carbon Tetrachloride

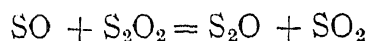
No. of Experiment	1	2	3
Fr. pt. lowering	0.500°	0.785°	0.527°
Moles of complex $\times 10^{-6}$ per g. of soln.	13.89	21.81	14.64
$\text{S}_2\text{O} \times 10^{-6}$	72.9	103.8	68.76
"Residual Sulphur"	99.9	147.7	70.28
$\text{S}_2\text{O} + \text{S}$	172.8	251.5	139.04
S atoms per mol. of complex	12.44	11.53	9.49
S_2O per mol. of complex	5.25	4.76	4.70
Sulphur per mol. of complex	7.19	6.77	4.78
Molecules of S_2O in union with mole of sulphur (S_8)	2.92	2.81	3.90

The results indicated that the disulphur oxide in solution formed a complex with the dissolved sulphur. The number of moles of S_2O associated with a mole of sulphur varied with the concentration. It is of interest to note that Schenk¹⁸ found that when sulphur monoxide was condensed by refrigeration, the sulphur residues, after removal of the monoxide, contained oxygen in combination. He suggested that the monoxide gave off sulphur dioxide and formed complexes between the sulphur liberated and the residual monoxide.

In the opinion of the present author, there is definite formation of disulphur oxide when sulphur monoxide is passed into cold carbon tetrachloride and not mere complex formation between sulphur and sulphur monoxide. He also considers it very probable that disulphur oxide is produced when sulphur monoxide is condensed by refrigeration as in Schenk's experiments. The production of sodium sulphide when the carbon tetrachloride solution is treated with alkali cannot easily be accounted for, excepting on the basis of formation of disulphur oxide. The quantitative study presented in this paper, of the reaction between the solution of the products of combustion of sulphur in oxygen at low pressure and alkali has shown that disulphur oxide and sulphur are the only constituents in solution after the removal of sulphur dioxide.

Decomposition of Sulphur Monoxide to Disulphur Oxide

From their investigations on the free energy of sulphur monoxide, Montgomery and Kassel¹¹ have concluded that the gas is moderately stable with respect to sulphur and sulphur dioxide at flame temperatures but that it is unstable below 1000° K. Cordes and Schenk⁴ have claimed that sulphur monoxide can be stored for two days in a quartz tube without complete decomposition. The stability of sulphur monoxide has been further considered by them in a later paper.⁵ It is of interest to note that more recently Cordes⁶ has thrown doubt on the very existence of sulphur monoxide and has stated that the absorption band (which has been of great value in studying the gas) merely indicates the existence of metastable S₂. Schenk¹⁹ on the other hand considers that a reactive oxygen compound of sulphur is responsible for the phenomena observed. By postulating the production of disulphur oxide (containing the S = S linkage) as caused by the decomposition of sulphur monoxide primarily formed, the divergent views expressed by the original discoverers of sulphur monoxide may be bridged. The disulphuroxide seems to be formed by the following reaction between sulphur monoxide and the disulphur dioxide:—



Disulphur dioxide, it may be pointed out, is readily formed by the polymerisation of the monoxide. From their investigations on sulphur monoxide, Schenk and Platz²⁰ have concluded that nearly two-thirds of the monoxide is associated as disulphur dioxide in the vapour state. Cordes and Schenk³ also assumed polymerisation of sulphur monoxide to account for their observation that on condensation, sulphur monoxide cannot again be completely vapourised.

The sulphur monoxide preparations obtained by Schenk and Platz²⁰ gave with 5 N alkali at 0° C. sulphite, sulphide and thiosulphate but no sulphate, hyposulphite (hydrosulphite) or polythionates. The formation of sulphide, without the concomitant production of sulphate is significant as it indicates the presence of disulphur oxide. For, sulphide formation from disulphur dioxide or sulphur monoxide is possible, only if sulphate is simultaneously formed:—

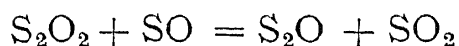


Hydrolysis of the above type does not take place with alkali and disulphur dioxide. It only takes place in strongly acid medium (Foerster and Umbach⁷). In their earliest communications, Cordes and Schenk^{2,3} claimed the production of sodium sulphoxylate and sodium hyposulphite when their sulphur monoxide preparations were brought in contact with alkali but in a subsequent paper, Schenk and Platz²⁰ state that they have not obtained any hyposulphite or sulphoxylate. Production of either of these salts can be looked upon as chemical evidence of the presence of sulphur monoxide. The present author has repeatedly tried the action of alkali on sulphur monoxide preparations but has failed to obtain any evidence of the formation of sulphoxylate or hyposulphite. Of particular significance is the fact that Scholder and Denk²² failed to obtain sodium sulphoxylate in aqueous solution. The reaction employed by them yielded only sodium thiosulphate. It is therefore to be concluded that there is scarcely any irreproachable chemical evidence of the existence of the monoxide in the liquid obtained by the refrigeration of the products of combustion of sulphur (in oxygen at low pressure) or in the cold carbon tetrachloride into which the combustion products are passed. The chemical evidence on the other hand supports the existence of disulphur oxide, though it does not exclude the probable presence of disulphur dioxide, which yields thiosulphate with alkali.

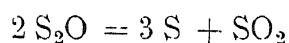
Summary

(1) When the products of combustion of sulphur in oxygen under highly reduced pressure are passed into cold carbon tetrachloride, disulphur oxide is produced.

(2) It is suggested that the primary product of combustion is probably the highly unstable sulphur monoxide. Part of the monoxide polymerises to yield disulphur dioxide and the reaction between the polymer and the monoxide produces disulphur oxide and sulphur dioxide:—



(3) Disulphur oxide (in carbon tetrachloride solutions) is unstable and decomposes into sulphur and sulphur dioxide :—



(4) As revealed by cryoscopic studies, disulphur oxide exists in carbon tetrachloride solutions, in the form of a complex with the dissolved sulphur present—a molecule of sulphur (S_8) uniting with 3 or 4 molecules of disulphur oxide.

(5) The complex in carbon tetrachloride solution gives an absorption band which extends from the ultra-violet end to a wave-length of 4700 Å.

(6) The dissolved sulphur (by forming a complex) renders the disulphur oxide more stable.

(7) The decomposition of dissolved disulphur oxide is greatly influenced by the nature of the glass surface of the containing vessel. Hydrogen chloride (as with persulphide solutions) retards the decomposition at the glass surface.

(8) When dilute solutions of disulphur oxide are treated with aqueous solutions (2 N) of sodium hydroxide, the major part of the oxide is hydrolysed to sodium sulphide and sodium sulphite which are formed in equimolecular proportions.

(9) The disulphur oxide thionizes part of the sulphite (formed by hydrolysis) to yield sodium thiosulphate.

(10) Owing to complex formation, a part of the sulphur present in carbon tetrachloride solution is activated by the disulphur oxide and rendered capable of converting sulphite to thiosulphate. The activation is probably due to the formation of small quantities of trisulphur oxide (S_3O) (corresponding to the chloride S_3Cl_2) when the complex breaks up in reacting with alkali.

(11) The effect of dilution on the hydrolysis of disulphur oxide is compared with that noticed in the case of sulphur chloride hydrolysis by 2 N alkali.

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