

STUDIES IN THE CHEMICAL BEHAVIOUR OF SULPHUR COMPOUNDS

Part I. The Hydrolysis of Sulphur Chloride

BY BASRUR SANJIVA RAO

(Central College, Bangalore, Mysore University)

Received November 2, 1939

It is well known that the hydrolysis of sulphur chloride is a very complicated reaction, yielding sulphur and a number of sulphur compounds. The nature of the primary product has all along been a matter of controversy, because of its great reactivity and the consequent formation of various secondary products.

As far back as 1845, Plessy³² pointed out that sulphur chloride, when brought in contact with water, undergoes hydrolysis, yielding hydrochloric acid, elementary sulphur and several oxyacids of sulphur. Fordos and Gelis¹² suggested that pentathionic acid was the polythionic acid primarily formed. Debus⁷ attributed the formation of thiosulphuric acid as a product of the reaction, to the combination between nascent sulphur and sulphurous acid. Noack²⁹ showed that the products of hydrolysis were the same as those obtained by the reaction between hydrogen sulphide and sulphur dioxide in forming Wackenroder's solution. He suggested that the first stage of hydrolysis yielded thiosulphurous acid ($\text{H}_2\text{S}_2\text{O}_2$) which on decomposition would produce hydrogen sulphide and sulphur dioxide. Attempts by Noack to prepare thiosulphurous acid by the interaction between the two gases, in absence of water, failed. Neumann and Fuchs²⁸ pointed out that the hydrolysis was incomplete, as only 94% of the chloride reacted with water. The yield of sulphur was 65% and of the polythionic acids 32%, the principal acid being pentathionic acid (18%).

Olin³⁰ considered hydrogen sulphide and sulphur dioxide to be the primary products and assigned to sulphur chloride the structure $\text{S} : \text{S} (: \text{Cl}_2)$.

In all these investigations, as high concentrations of sulphur chloride had been used, the concentration of the primary product of hydrolysis was high and owing to its great chemical activity, a number of secondary reactions took place, yielding a variety of sulphur compounds. Furthermore, owing to the acidity developed during hydrolysis of the chloride, the secondary effects were rendered highly complex and a quantitative interpretation of the phenomenon was impossible.

In the investigations described in the present paper, the reaction has been elucidated by a new technique, the hydrolysis being carried out at the interface between very dilute solutions of sulphur chloride in carbon tetrachloride and aqueous alkali in presence of cadmium hydroxide. The alkali and the cadmium hydroxide circumscribed the scope of secondary reactions and rendered possible a quantitative interpretation of the phenomenon.

Experimental

Carbon Tetrachloride.—“Chemically pure” carbon tetrachloride was shaken with mercury to remove traces of sulphur. It was then 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 absolutely free from sulphur.

Sulphur Chloride.—A supply of C.P. quality from the British Drug House was mixed with 1% its weight of each of active charcoal and pure sulphur and heated at the temperature of the water bath for a period of four hours in an all-glass apparatus consisting of a flask, a reflux condenser and a device for the exclusion of atmospheric moisture. The chloride was then distilled under reduced pressure (28 mm.) at about 42° C. using a suitable all-glass apparatus (Harvey and Schuette¹⁷, Lowry, McHatton, and Jones²⁴). The middle fraction of the distillate was immediately diluted with purified carbon tetrachloride and stored in the dark in an apparatus in which the chloride was carefully protected from atmospheric moisture and from which portions of the solution could conveniently be withdrawn without exposure to atmospheric moisture. The sulphur chloride in the solution suffered no decomposition even after prolonged storage as could be gathered by periodical analysis.

Analysis of the Sulphur Chloride.—To analyse sulphur chloride, Kretov²⁰ digested a known weight of the chloride with 2 N alkali on the water bath and oxidised the products of hydrolysis with hydrogen peroxide to obtain the alkali chloride and sulphate. The chloride was determined by Volhard's method and the sulphate gravimetrically as barium sulphate. It was found in this laboratory (both by the author and by Mr. M. R. A. Rao) that while this method gave satisfactory values for chloride, the sulphur values were rather low owing to incomplete oxidation of elementary sulphur produced during hydrolysis. The sulphur could be estimated much more accurately by the following method developed in this laboratory (B. S. Rao and M. R. A. Rao²⁴). A known weight of the sulphur chloride solution was shaken up with pure mercury and the mercuric sulphide formed was treated in a suitable all-glass apparatus with a mixture of potassium iodide and

concentrated hydrochloric acid to which a small quantity of hypophosphorous acid had been added. A current of hydrogen was passed through the solution and the hydrogen sulphide liberated was quantitatively absorbed by a zinc hydroxide suspension in dilute alkali. The zinc sulphide was estimated iodometrically when macro quantities were present and colorimetrically (using the methylene blue reaction) when the quantity was small. The analytical results obtained with all the samples of sulphur chloride used in this investigation showed that in them the ratio of S to Cl was exactly unity. The author found no experimental evidence which could confirm the opinion of Terrey and Spong⁴⁵ that sulphur chloride purified by distillation with active charcoal had always a slight excess of sulphur.

Investigations carried out in this laboratory by M. R. A. Rao showed that sulphur chloride could very accurately be estimated by treatment with finely powdered and dried potassium iodide. The possibility of the iodometric estimation of sulphur chloride had been indicated by Spong.⁴² His method, however, yielded results of only moderate accuracy. The method developed by M. R. A. Rao was the following :

A known weight (8 g.) of an approximately 0.05 molar solution of the chloride in carbon tetrachloride was transferred to a stoppered bottle, which had been carefully dried previously and which contained 25 c.c. carbon tetrachloride and potassium iodide crystals dried in a vacuum desiccator over phosphorus pentoxide. The bottle was shaken for 10 minutes. Sulphur iodide was liberated and this decomposed completely on keeping for a few hours. After six hours, the liberated iodine was titrated with standard thiosulphate.

The results of a typical analysis of the stock solution of sulphur chloride are given below :

By Kretov's method of analysis it was found that 1 g. of the solution had Cl corresponding to 9.605×10^{-5} g. atoms. The S as determined by the method of B. S. Rao and M. R. A. Rao was found to be 9.560×10^{-5} g. atoms. Estimated by the method of M. R. A. Rao the sulphur chloride was found to correspond to 9.606×10^{-5} g. atom of sulphur per g. of stock solution.

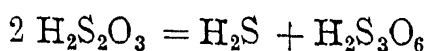
Hydrolysis of Sulphur Chloride.—A weighed quantity (about 18 g.) of the stock solution of the sulphur chloride was added to a known weight of dry carbon tetrachloride kept in a separating funnel. The requisite volume of an aqueous solution of sodium hydroxide was then added. To the alkali solution had been added previously 2 c.c. of a normal solution of pure cadmium chloride to furnish cadmium hydroxide for the removal of sulphide

produced by hydrolysis. (Kurtenacker and Goldbach²¹ employed cadmium carbonate for the removal of sulphide from aqueous solutions. In the present investigation it was found advantageous to use the more rapidly acting cadmium hydroxide.) The separating funnel was attached to a shaking machine and the contents shaken for 10 minutes. On standing for a while, the liquid in the funnel separated into two layers. The carbon tetrachloride layer was tapped off, a small quantity of the solvent was then added to the funnel and after shaking, a further separation effected. The total amount of dissolved sulphur present in the carbon tetrachloride layer was determined by employing an aliquot for analysis by the method already indicated (B. S. Rao and M. R. A. Rao³⁴).

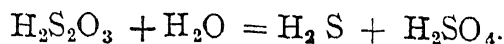
The cadmium sulphide along with the residual cadmium hydroxide was filtered and washed. The sulphide was then estimated iodometrically the precipitate being treated with 0.1 N iodine in presence of acetic acid and the excess of iodine estimated with standard thiosulphate. It was found desirable to add a small quantity of dilute hydrochloric acid, to complete the dissolution of the sulphide, prior to the estimation of residual iodine. The filtrate left after the removal of the cadmium sulphide was diluted to 250 c.c. in a measuring flask and aliquots employed for the estimation of sulphite and thiosulphate by the method of Kurtenacker and Goldbach.²¹ Another aliquot was oxidised with hydrogen peroxide in alkaline medium in a platinum dish and the sulphate estimated by the microanalytical method of Pregl. From this sulphate value, after deducting sulphur corresponding to sulphite and thiosulphate, one could determine sulphur originally present in solution as thionate and sulphate. Independent experiments based on the method suggested by Kurtenacker and Goldbach²¹ for the determination of sulphate in a solution containing a mixture of the oxyacids of sulphur, showed that measurable amounts of sulphate were produced in a few experiments. Trithionate was also found, usually associated with sulphate, in some cases. The quantities, however, were small.

Results

Under the experimental conditions described above, hydrolysis of sulphur chloride by alkali yielded free sulphur, and the sulphide, sulphite and thiosulphate of sodium (the sulphide reacting with cadmium hydroxide to give cadmium sulphide). Trithionate and sulphate formation (which is considered in the discussion) was noticed in experiments in which dilute alkali had been used for hydrolysis. The trithionate was due to the decomposition of thiosulphuric acid in the following way :



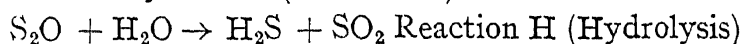
and therefore, in such cases the sulphide and the thiosulphate values were corrected on the following basis: Let a be the number of S atoms present as trithionate, b the observed sulphide and c the observed thiosulphate, in terms of sulphur atoms. Then corrected sulphide = $b - a/3$, and corrected thiosulphate = $c + 4a/3$. A similar correction was applied for sulphate formation on the basis of the reaction:



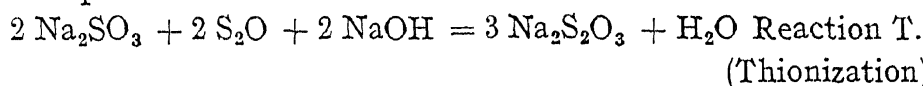
The free sulphur liberated in the reaction was mostly present in carbon tetrachloride solution and could be estimated by the method already indicated. When dilute alkali however, was used for hydrolysis a part of the sulphur was liberated in the "amorphous" condition as S_μ , in aqueous suspension along with the hydroxide and the sulphide of cadmium and could not conveniently be determined with any great accuracy. Such sulphur was therefore calculated by difference, in the majority of cases, the sulphur corresponding to sulphur chloride and to each of the products of hydrolysis being known.

It was found that the results could best be interpreted quantitatively on the basis that disulphur oxide (if not its highly unstable hydrate—the hypothetical thiosulphurous acid) is the primary product of hydrolysis. A solution of disulphur oxide (in carbon tetrachloride) has actually been obtained in this laboratory for the first time (B. S. Rao³³) and a paper on its preparation and properties will form Part II of the present studies.

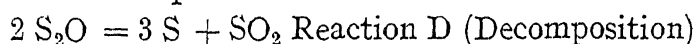
Disulphur oxide has been found to undergo three simultaneous reactions when brought in contact with alkali. The major part of the oxide produces the sulphide and sulphite of sodium in equimolecular proportions and in presence of sodium hydroxide (B. S. Rao³³):



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



At the same time, the disulphur oxide, in virtue of its instability, decomposes into sulphur and sulphur dioxide:



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

If S_2O corresponding to h atoms of sulphur participates in reaction H, t atoms in reaction T, and d atoms in reaction D, the total quantity of

disulphur oxide produced by the reaction between sulphur chloride and alkali will be $h + t + d$, while $h = 2$ sulphide, $t = 2/3$ thiosulphate, and $d = 4/3$ free sulphur, all quantities being expressed in gram atoms of sulphur. The values of h , t and d can therefore be calculated from the analytical data.

The following relationship between the products of reaction can easily be deduced :

Free Sulphur = Thiosulphate + 3 (Sulphite - Sulphide) for, the free sulphur = $3d/4$ while thiosulphate = $3t/2$, sulphite = $h/2 - t/2 + d/4$, and sulphide = $h/2$. Elementary sulphur could thus be determined directly and the quantity obtained compared with the value calculated on the basis of the above relationship. Close agreement between the two values cannot however be expected since the solutions were very dilute and there were inherent experimental errors in some of the determinations. These experimental errors are discussed in a later part of the paper.

In the first series of experiments (Table I) the effect of dilution of the sulphur chloride on the three parallel reactions was studied. The chief

TABLE I

Effect of Dilution of Sulphur Chloride on Hydrolysis by 2N Alkali

No. of experiment	1	2	3	4	5	6	7
* S ₂ Cl ₂ ..	12.0	12.0	12.0	12.0	12.0	8.98	8.98
† Dilution ..	0.7	0.7	1.5	1.5	3.8	38.7	77.1
* Sulphide ..	3.25	3.23	4.11	4.10	4.55	3.98	4.06
* Thiosulphate ..	1.13	1.06	1.11	1.44	1.72	1.10	1.31
* Sulphite ..	4.11	4.20	4.74	4.55	4.56	3.68	3.61
* Sulphur (found)	3.64	3.82	2.55	2.38	1.43	0.21	..
* ,, (calculated)	3.71	3.97	3.00	2.79	1.75	0.20	..
% Hydrolysis ..	54.2	53.8	68.5	68.3	75.8	88.6	90.4
% Thionization ..	6.2	5.9	6.2	8.0	9.6	8.1	9.7
% Decomposition	40.4	42.4	28.3	26.4	15.9	3.1	0.0
TOTAL ..	100.8	102.1	103.0	102.7	101.3	99.8	100.1

* In Table I, the quantities of sulphur chloride and of each of the products of reaction are expressed in gram atoms of sulphur and have been multiplied by 5×10^3 .

† In Table I, the dilution of sulphur chloride is expressed in grams of solvent per gram atom of sulphur as sulphur chloride and has been multiplied by 10^{-5}

features to be noticed are: (1) the remarkable decrease in decomposition as the dilution increases, the value dropping from 40% of the total sulphur to 0% as the dilution is raised from 0.7 to 77; (2) corresponding increase in hydrolysis from 54 to 90%; (3) the inappreciable effect of dilution on thionization.

In the second series of experiments (Table II) glycerine was employed along with the alkali. The object of using glycerine had been to prevent

TABLE II

Effect of Dilution of Sulphur Chloride on Hydrolysis by 2N Alkali in presence of 10% Glycerine

No. of experiment	1	2	3	4
* Sulphur chloride ..	9.61	9.61	9.61	9.61
† Dilution at hydrolysis ..	0.5	1.0	2.5	5.0
* Sulphide ..	1.86	1.99	1.73	2.01
* Thiosulphate ..	1.74	1.92	2.21	1.89
* Sulphite ..	2.43	2.41	2.12	2.47
* Sulphur (found) ..	3.52	3.24	3.46	3.37
* .. (calculated) ..	3.45	3.18	3.38	3.27
% Hydrolysis ..	38.7	41.4	36.0	41.8
% Thionization ..	12.1	13.3	15.3	12.8
% Decomposition ..	48.8	45.0	48.0	45.6
TOTAL ..	99.6	99.7	99.3	99.2

* In Table II, the quantities of sulphur chloride and of each of the products of reaction are expressed in gram atoms of sulphur and have been multiplied by 5×10^3 .

† In Table II, the dilution of sulphur chloride is expressed in grams of solvent per gram atom of sulphur as sulphur chloride and has been multiplied by 10^{-5} .

any possible oxidation of sulphite to sulphate. The glycerine, however, was found to have unexpected effects on the hydrolysis. It masked the effect of dilution on hydrolysis noticed in the first series of experiments, a ten-fold increase in dilution causing barely a 3% increase in hydrolysis and a 3% decrease in decomposition. Hydrolysis appeared to be inhibited considerably by the glycerine and decomposition correspondingly stimulated. Comparative experiments (Table III) were carried out to elucidate the influence of glycerine, the dilution of sulphur chloride at hydrolysis being the

TABLE III

Influence of Glycerine on Hydrolysis of Sulphur Chloride by Alkali

No. of experiment	1	2	3	4	5	6	7	8
Nature of experiment	No gly.	10% gly.	No gly.	5% gly.	No gly.	5% gly.	No gly.	5% gly.
* S ₂ Cl ₂	8.93	9.6	8.93	9.1	9.01	9.01	8.85	8.85
Alkali Strength	2N	2N	0.5N	0.5N	0.2N	0.2N	0.02N	0.02N
* Trithionate	0.91?	..	0.45	0.79	0.45
* Sulphate	0.10	0.24	0.12
* Sulphide (corrected)	3.45	1.94	2.97	2.19	2.88	2.03	1.60	1.37
* Thiosulphate (corrected)	0.54	1.60	1.04	4.30	1.55	3.71	5.52	4.98
* Sulphite	3.72	2.54	3.15	1.16	2.77	1.29	0.19	0.14
* Sulphur (found)	1.28	3.46	1.68	1.33	1.52	1.74	1.54	1.95
* ,, (calculated).. ..	1.35	3.40	1.58	1.21	1.22	1.52	1.29	1.29
% Hydrolysis	77.8	40.4	66.5	48.1	63.9	45.1	35.2	30.1
% Thionization	4.0	11.2	7.7	31.3	11.5	26.0	40.3	36.5
% Decomposition	19.3	48.0	25.1	19.6	22.4	25.8	22.6	28.6
TOTAL	100.6	99.6	99.3	99.2	97.8	96.9	98.1	95.2

* In Table III the quantities of sulphur chloride and of each of the products of reaction are expressed in gram atoms of sulphur and have been multiplied by 5×10^3 .

same in all the experiments. In experiment 2 it will be noticed that the proportion of glycerine is 10% while in experiments 4, 6 and 8, 5% glycerine has been employed. Owing to the higher concentration of glycerine in experiment 2, the hydrolysis is less and decomposition greater than in the other experiments though owing to the higher concn. of alkali in experiment 2, the percentage hydrolysis should have been greater. In presence of glycerine (excepting at the very small alkali concentration of experiment 8) thionization is promoted, it being 2 to 4 times that in absence of glycerine.

The interesting results obtained with glycerine prompted the author to try the influence of brucine on hydrolysis of sulphur chloride by alkali. Brucine, even in traces, has been found to have a remarkable inhibiting effect on the atmospheric oxidation of sulphite. Young⁴⁹ found that in alkaline solutions 0.000,005 M brucine hydrochloride reduced the velocity to one hundredth of the normal rate. About 3 milligrams of brucine were used with the alkali in each of the experiments (Table IV). Brucine was found to increase hydrolysis considerably, the effect being most marked at alkali concentrations upto 0.2 N. Thionization was much less, indicating that brucine inhibits the oxidation of sulphite to thiosulphate in the same manner as it reduces the oxidation of sulphite to sulphate.

The hydrolysis of sulphur chloride by baryta was also studied (Table V).

The general procedure was the same as that employed in the case of sodium hydroxide, but no cadmium hydroxide was used along with the baryta. The precipitate of barium sulphite was filtered off and washed. The sulphite was estimated by adding standard iodine solution in excess and then acidifying with weak hydrochloric acid. The filtrate containing the sulphide, thiosulphate and trithionate (if any), was treated with cadmium hydroxide and the sulphide formed estimated after filtration and washing. The thiosulphate was estimated iodometrically and the trithionate by the method already indicated. It has to be stated that the experimental errors are much greater when baryta is used for hydrolysis.

Though the alkali strength was the same in the comparative experiments with sodium hydroxide and baryta, a marked difference in the reactions was noticed. Reaction H was much less in the case of baryta, the value for hydrolysis for sodium hydroxide being over twice that for baryta in 0.5 N solutions and nearly seven times as great, when the quantity of alkali used was just sufficient to neutralise the acids liberated on hydrolysis. As is to be expected, thionization was much less with baryta, owing to the insoluble nature of barium sulphite. Since reaction H gets depressed, in the case of

TABLE IV
Influence of Brucine (3 mg.) on Hydrolysis of Sulphur Chloride by Alkali

No. of experiment	1	2	3	4	5	6	7	8
Nature of experiment	No Brucine	Brucine	No Brucine	Brucine	No Brucine	Brucine	No Brucine	Brucine
* S ₂ Cl ₂	8.92	8.92	8.92	8.92	9.01	9.01	9.1	9.1
Alkali Strength	2N	2N	0.2N	0.2N	0.1N	0.1N	0.02N	0.02N
* Trithionate	0.24	0.33?	0.71	0.09	0.79	0.20
* Sulphate	0.10	..	0.30	..	0.28	..
* Sulphide (corrected)	3.45	3.68	2.74	3.68	1.74	2.74	1.60	3.16
* Thiosulphate (corrected)	0.45	0.47	2.09	1.10	5.17	1.71	5.52	1.43
* Sulphite	3.72	3.92	2.59	3.63	0.61	2.77	0.19	2.98
* Sulphur (found)	1.28	1.05	1.62	0.78	1.59	1.75	1.54	1.21
* ,, (calculated).. ..	1.39	1.19	1.64	0.95	1.78	1.80	1.29	0.89
% Hydrolysis	77.3	82.0	60.8	81.7	39.0	61.4	35.2	69.5
% Thionization	4.0	3.6	15.5	8.1	38.7	12.8	40.3	10.4
% Decomposition	19.3	15.6	24.0	11.5	23.8	26.2	22.6	17.7
TOTAL	100.6	101.2	100.3	101.3	101.5	100.4	98.1	97.6

* In Table IV the quantities of sulphur chloride and of each of the products of reaction are expressed in gram atoms of sulphur and have been multiplied by 5×10^3 .

TABLE V
Comparative Study of Hydrolysis of Sulphur Chloride with Baryta and Sodium Hydroxide

No. of experiment	1	2	3	4	5	6	7	8
Concn. Alkali	0.5N NaOH	0.5N Ba(OH) ₂	0.5N NaOH	0.5N Baryta	0.2N NaOH	0.2N Baryta	Theoretical amt. NaOH	Theoretical amt. Baryta
% Hydrolysis	66.5	30.9	63.2	24.9	60.8	15.3	30.5	4.6
% Thionization ..	7.7	3.8	10.4	4.3	15.5	5.3	40.0	7.6
% Decomposition	25.1	72.8	25.5	78.2	24.0	84.6	25.7	89.7
TOTAL ..	99.3	107.5	99.1	107.4	100.3	105.2	96.2	101.9

baryta, the disulphur oxide suffered much greater decomposition, the value being three times that for sodium hydroxide.

In Table VI is indicated the effect of dilution of sodium hydroxide on the three parallel reactions. A tenfold dilution of alkali (2 N to 0.2 N) causes a 5% increase in decomposition and nearly a fourfold increase in thionization, the corresponding decrease in hydrolysis being about 17%. Further tenfold dilution (0.2 N to 0.02 N) of alkali causes a 25% decrease in hydrolysis and a 25% increase in thionization.

TABLE VI

Effect of Alkali Strength on Hydrolysis of Sulphur Chloride

Alkali	2N	0.5N	0.2N	0.1N	0.02N	Alkali just required for neutralisation
% Hydrolysis ..	77.3	66.5	60.8	39.0	35.2	30.5
% Thionization ..	4.0	7.7	15.5	38.7	40.3	40.0
% Decomposition ..	19.3	25.1	24.0	23.8	22.6	25.7
TOTAL ..	100.6	99.3	100.3	101.5	98.1	96.2

To study the effect of temperature on the three reactions, comparative experiments were carried out at 0° C. and at 25° C. (Table VII) the sulphur chloride dilution being kept constant. There was in general a 5% increase in hydrolysis and a corresponding decrease in decomposition when the temperature was raised from 0° to 25°C.

TABLE VII

Effect of Temperature Increase on the Hydrolysis of Sulphur Chloride by Alkali

No. of experiment	1	2	3	4	5	6
Alkali Concn.	2N	2N	0.2N	0.2N	0.02N	0.02N
Temperature	0°	25°	0°	25°	0°	25°
% Hydrolysis	78.6	83.7	55.1	60.8	30.8	35.2
% Thionization	2.6	3.0	14.5	15.5	39.2	40.3
% Decomposition	20.4	14.0	30.0	24.0	26.6	22.6
TOTAL ..	101.6	100.7	99.6	100.3	96.6	98.1

The view that during hydrolysis of sulphur chloride, thiosulphate is mainly produced by the reaction between sulphite and disulphur oxide, obtained support from the following experiments:—Hydrolysis by 0.1 N alkali was carried out in presence of 10 c.c. of formalin (40%) and the results compared with those obtained when no formaldehyde was used. The formaldehyde was expected to bind the sulphite and thus suppress thio-sulphate formation. Owing to the presence of the aldehyde the sulphite could not be estimated iodometrically and had to be determined gravimetrically in the following way: sodium carbonate was added to an aliquot of the solution in a platinum dish and the contents evaporated to dryness. The dish was then heated by a Meker burner, a little nitre being used to complete the oxidation of sulphite and thiosulphate to sulphate. The sulphate was then estimated by the microanalytical method of Pregl, and the sulphite value obtained, taking into account the thiosulphate present in the original solution.

TABLE VIII

Effect of Formaldehyde on Hydrolysis of Sulphur Chloride by 0.1 N Sodium Hydroxide

	No Formalin	Formalin present
% Hydrolysis ..	39.0	57.7
% Thionization ..	38.7	3.7
% Decomposition	23.8	33.5
TOTAL ..	101.5	94.9

The fact that reaction T is one of the three parallel reactions was indirectly confirmed by carrying out hydrolysis with 0.2 N alkali in presence of a known amount of freshly prepared sodium sulphite (6×10^{-5} g. atom of S per g. of CCl_4 soln.). In calculating sulphite produced by hydrolysis, the sulphite originally added was deducted from the sulphite found in solution after hydrolysis. The experiment (Table IX) showed that owing to the larger concentration of sulphite, greater thionization took place.

TABLE IX

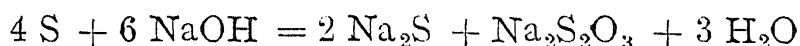
Alkali	0.2 N NaOH	0.2 N NaOH + Sulphite
% Hydrolysis	60.8	59.7
% Thionization	15.5	24.4
% Decomposition	24.0	15.8
TOTAL ..	100.3	99.9

Whether the sulphur liberated in the reaction would unite with sulphite and produce thiosulphate was determined by the following experiments. A quantity of 75 % saturated solution of sulphur in carbon tetrachloride was added to the sulphur chloride in expts. 2 and 3 and the same quantity of pure carbon tetrachloride added to the sulphur chloride solution in experiment 1. 2 N alkali was used for hydrolysis. Results are indicated in Table X.

TABLE X

No. of experiment	1	2	3
		Extra sulphur	Extra sulphur
% Hydrolysis	84.9	83.3	85.5
% Thionization	3.5	3.5	3.7
% Decomposition	11.0	12.0	11.0
TOTAL	99.4	98.8	100.2

Sulphur is known to react with alkali to yield sulphide and thiosulphate in terms of the following equation:



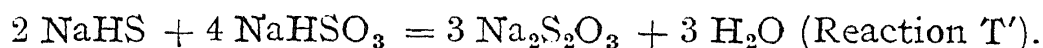
(Tartar and Davies,⁴⁴ Bullock and Forbes⁵). The possibility of sulphur formed in reaction D uniting with alkali to yield sulphide and thiosulphate was therefore examined. It was found that under the conditions of the present investigation, there was no measurable reaction between the sulphur and alkali.

Experiments were also carried out to determine if reaction D ($2S_2O = 3S + SO_2$) was reversible. A sulphur dioxide solution in carbon tetrachloride (corresponding to ten times the sulphur content of the stock solution of sulphur chloride) was mixed with an equal volume of a saturated solution of sulphur in dry carbon tetrachloride and the liquid kept for 24 hours in a dry bottle and then shaken with 2 N sodium hydroxide. Neither sulphide nor thiosulphate was formed in detectable quantities.

Solutions of hydrogen sulphide and sulphur dioxide in carbon tetrachloride were mixed together and shaken with dilute alkali and the carbon tetrachloride and aqueous layers analysed. No measureable quantity of free sulphur or thiosulphate was found. This experiment is of importance as showing that the production of free sulphur or of thiosulphate in sulphur chloride hydrolysis cannot be due to any interaction between hydrogen

sulphide and sulphur dioxide that might primarily be formed in sulphur chloride hydrolysis.

Bassett and Durrant³ have found that the sulphide and sulphite of sodium can co-exist in alkaline solutions without any interaction taking place. It is known however, that sodium hydrogen sulphide and sodium hydrogen sulphite do interact to yield thiosulphate in terms of the following equation as pointed out by Foerster and Mommsen :¹⁰



This raised the possibility that in the hydrolysis of sulphur chloride by alkali, the hydrogen sulphide and sulphur dioxide produced in reaction H might form momentarily, at the carbon tetrachloride interface with the aqueous solution, the two acid salts in view of the production of hydrochloric acid during hydrolysis. It was deemed advisable therefore to obtain an idea of the speed with which reaction T' takes place. The following experiments were carried out :

To 20 c.c. of freshly prepared 0.1 N NaHS solution was added 20 c.c. of freshly made 0.2 N NaHSO₃ solution. The mixture was kept at 25° C. for 10 minutes to allow reaction T' to take place. The reaction was then stopped by the addition of 10 c.c. of 2 N sodium hydroxide. Cadmium hydroxide was added to precipitate the residual sulphide and the filtrate titrated with iodine after addition of formaldehyde and acetic acid. If the reaction T' had been completed in 10 minutes, thiosulphate corresponding to 30 c.c. of 0.1 iodine would have been formed. Actually 7.4 c.c. of 0.1 N iodine were required for the titration of the thiosulphate. When 5% glycerine had been added to the solution of the two salts at the start of the reaction T', the titration value was 7.2 c.c., time of reaction being 10 minutes as in the previous experiment. With brucine (3 mg.) it was 6.4 c.c. and when formalin was employed the value was 0.15 c.c. These experiments show that the reaction T' is comparatively slow and that its velocity is influenced by reagents like brucine. It may therefore be concluded that reaction T' is not of any significance in the formation of thiosulphate in the sulphur chloride hydrolysis experiments.

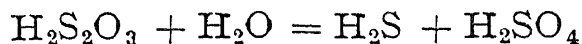
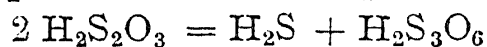
Discussion

In discussing the hydrolysis of sulphur chloride (in carbon tetrachloride solutions) under the influence of aqueous sodium hydroxide it has to be pointed out that the reaction is very rapid even when exceedingly dilute solutions of the chloride are employed. The yellow colour of the carbon tetrachloride solution disappears within a minute or two when the chloride solution is shaken up with the alkali. Absence of sulphur chloride in the

carbon tetrachloride layer can be confirmed by withdrawing the solvent, drying it rapidly with phosphorous pentoxide and testing with dry potassium iodide. No violet colour (due to iodine) develops if the sulphur chloride has completely reacted. This sensitive reaction, it may be stated, is not only suitable for the detection of traces of sulphur chloride but can also be employed for the colorimetric estimation of small quantities of the chloride. The test is far more satisfactory than the one proposed by Castiglioni⁶ in which a violet colour develops when the sulphur chloride solution is added to an ammoniacal solution of alcohol. By applying the sensitive potassium iodide test described above, it was confirmed that the reaction between dilute sulphur chloride solutions and alkali was complete, well within two minutes. The rapidity of reaction is of importance as it considerably minimises the secondary reactions that possibly can take place in the system. It may be stated that with a view to cut down secondary effects, the filtration and the analysis of the aqueous layer was carried out as rapidly as possible and scarcely took more than 20 minutes.

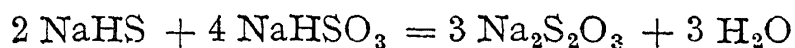
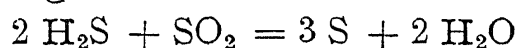
Owing to the use of cadmium hydroxide, the sulphide produced in reaction H (Hydrolysis) is quickly immobilised and does not take part in secondary reactions. The removal of sulphide eliminates for instance, the catalytic influence the sulphide would otherwise have exerted on the thionization of sulphite by free sulphur liberated during the reaction (Hargreaves and Dunnigham¹⁶, Watson and Rajagopalan⁴⁸, Bassett and Durrant³).

Besides reaction H, the decomposition of thiosulphuric acid under favourable pH conditions can produce sulphide:



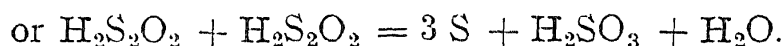
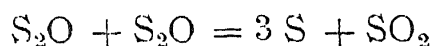
Both these types of decomposition occur to a small extent when very dilute alkali is used for sulphur chloride hydrolysis. As already stated a suitable correction has been applied for sulphide values in such cases. The sulphide therefore correctly represents the magnitude of reaction H.

It will be noticed that sulphite is in excess of sulphide when alkali concentration is greater than 0.2 N but on the other hand is lower than sulphide produced when more dilute solutions of alkali are employed for hydrolysis. If reaction H was the only one taking place, the sulphite obtained should equal the sulphide. It has already been pointed out that under the conditions of hydrolysis, the hydrogen sulphide and sulphur dioxide produced by reaction H do not interact to yield sulphur or thiosulphate by the following reactions:



It is therefore to be concluded that in the case of hydrolysis by stronger solutions of alkali there is some reaction producing sulphite in excess of sulphide and that when the alkali is dilute, the deficiency of sulphite is due to its removal as a result of some reaction. Reaction D (Decomposition) and reaction T (Thionization) have been found to be responsible for the observed difference between sulphite and sulphide values.

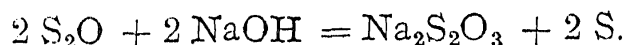
The decomposition of disulphur oxide (Reaction D) seems to be governed largely by dilution. In expt. 7 (Table I) it dropped to zero while in expts. 1 and 2 it was over 40% of the disulphur oxide primarily formed. The decomposition is due to a reaction between two S_2O (or $H_2S_2O_2$) molecules :



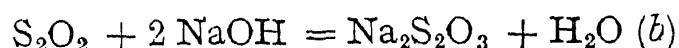
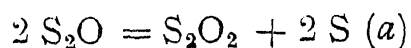
The extent of reaction D seems to be determined by the frequency of fruitful collisions between S_2O molecules. This frequency is dependent on the proximity between two S_2O molecules when they are formed by hydrolysis. The concentration of sulphur chloride (the source of the disulphur oxide) therefore determines the extent of reaction D. If the reaction is to be eliminated during hydrolysis (*cf.* expt. 7, Table I) it seems to be necessary (when 2 N alkali is used) to have in solution a molecular ratio of sulphur chloride to carbon tetrachloride of the order of 1 : 100,000.

Reaction T (Thionization) seems to be mainly responsible for the formation of thiosulphate. It has already been pointed out that under the experimental conditions of this investigation, no measurable amount of thiosulphate is produced either by the reaction between hydrogen sulphide and sulphur dioxide or by the reaction between free sulphur and sodium sulphite. On the other hand there is definite evidence (which has already been indicated) that part of the sulphite produced in reaction H is converted into thiosulphate. The powerful thionizing agent responsible for this oxidation of sulphite seems to be disulphur oxide. Sulphite thionization seems to be considerable when alkali concentration is low, as can be gathered from the small sulphite concentrations (in comparison with corresponding sulphide values) in such experiments (Table III, expts. 7 and 8, Table IV, expts. 5 and 7).

Besides reaction T, the following reaction D' can possibly form thio-sulphate :



This reaction may be considered to be taking place in two steps :



The difference between reactions T and D' is that in the former case the sulphur liberated in step (a) is assumed to thionize sulphite to thiosulphate while in D' elementary sulphur is actually liberated. Reaction T therefore involves the participation of sulphite. When barium hydroxide is used, or when formalin is added to the sodium hydroxide employed in hydrolysis, the sulphite is immobilised and reaction T cannot take place. A small quantity of thiosulphate however is still formed (Tables V and VIII) and it is therefore to be concluded that reaction D' does occur to a slight extent. While S_2O is necessary for thiosulphate formation from sulphite, the latter is not at all required for conversion of S_2O into thiosulphate in terms of reaction D'. It may be pointed out that in the case of hydrolysis of sulphur chloride by moderately strong solutions of alkali, it is possible to represent the chemical phenomenon by reactions H, D' and D (without introducing reaction T) but in cases of hydrolysis by dilute alkali, reaction T cannot be ignored in any quantitative interpretation of the hydrolysis.

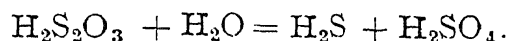
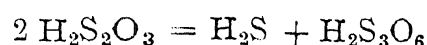
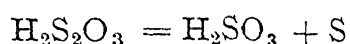
It is difficult to estimate reaction D' as separately occurring from the reaction T and so, as an approximation, it has been assumed that only one reaction, namely T, is responsible for the production of thiosulphate. This assumption raises the values for reaction D by a few per cent., as the sulphur produced in D' is attributed to reaction D.

The sulphur produced by reaction D is entirely found in carbon tetrachloride solution, when alkali concentration is at least 0.5 N. This is significant in view of the fact that sulphur produced by the interaction between hydrogen sulphide and sulphur dioxide in presence of water is principally as S_μ (Brownlee⁴). This lends indirect support to the view that in sulphur chloride hydrolysis the sulphur is not the product of any reaction between hydrogen sulphide and sulphur dioxide. No doubt alkaline solutions have been found to hasten the conversion of amorphous sulphur into the ordinary soluble sulphur (Smith and Brownlee;⁴¹ McKee²⁵) and there is therefore the possibility that elementary sulphur liberated in hydrolysis is in the first instance amorphous and is converted into ordinary sulphur under the catalytic influence of the alkali. The rate of conversion of amorphous sulphur into ordinary sulphur has been studied by the present author and he finds that this is not fast enough to account for the formation, in the course of the hydrolysis experiments (whose duration was 15 to 20 minutes) of sulphur entirely soluble in carbon tetrachloride.

When dilute alkali is used for hydrolysis, an appreciable amount of the liberated sulphur is in the amorphous condition. It is also found that in such cases there is thionate formation as well. Both the production of

amorphous sulphur and the formation of thionate seem to be due to the decomposition of thiosulphuric acid in cases of hydrolysis by dilute alkali, owing to the fact that the hydrolysis of sulphur chloride is accompanied by the liberation of hydrochloric acid which produces at the interface between carbon tetrachloride and water local zones of acidity conducive to the decomposition of thiosulphuric acid.

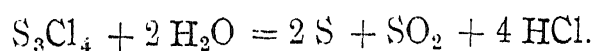
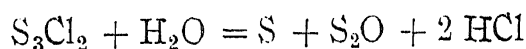
The decomposition of thiosulphuric acid has been a subject of extensive investigation (Bassett and Durrant,³ Deines,⁸ Reisenfeld and Sydow,³⁷ Schaffer and Böhm,³⁹ Kurtenacker and Ivanov,²² Râyand Maulick,³⁶ Hansen,¹⁴ Foerster and Umbach¹¹). Three reactions are possible :



The first of these three reactions probably accounts for part of the amorphous sulphur, the second for the presence of thionate and the third for the presence of sulphate in certain hydrolysis experiments. Smith and Brownlee⁴¹ have found that the sulphur precipitated by the addition of acid to sodium thiosulphate is in the first instance 100% amorphous sulphur. The presence of sulphate in the products of hydrolysis is not likely to be due to atmospheric oxidation of sulphite, for it would then have been produced in all cases of hydrolysis though, to a varying degree owing to the influence of alkali on sulphite oxidation (Kolthoff and Furman).¹⁹ Production of sulphate, owing to auto-reduction or auto-oxidation of sulphite (*cf.* Mellor,²⁶ Kurtenacker and Kaufmann,²³ Foerster and Hornig⁹) can also be ignored in the present investigations as the analysis of the aqueous layer was carried to completion within 20 minutes of the actual hydrolysis of sulphur chloride.

It will be noticed that it has been assumed that the thionate found is entirely as trithionate. That thionates higher than the trithionate are formed in thiosulphuric acid decomposition has often been suggested, but even if this be the case, the higher polythionates will readily decompose in alkaline media and finally give trithionate (Hansen¹⁵). Hansen points out that even the trithionate is not very stable and gives sulphate in acid and weakly alkaline solutions and sulphite in solutions more alkaline than 1 N. The decomposition of trithionate yielding sulphite, introduces a small error in the calculation of the reactions H, T and D, for which it is not practicable to apply a suitable correction. Such decomposition, however, takes place only in strongly alkaline solutions, but in such solutions the formation of trithionate is itself unlikely.

Investigations on sulphur chloride by several authors have indicated that S_3Cl_2 and S_3Cl_4 possibly exist in sulphur chloride (Lowry, McHatton and Jones,²⁴ Trautz,⁴⁶ Baroni,² Spong⁴²). The presence of these chlorides however, does not vitiate the consideration of sulphur chloride hydrolysis as being made up of the three reactions H, T and D, for the hydrolysis of these impurities in sulphur chloride may be pictured as follows :



The experimental errors inherent in the analysis of sulphur and the different sulphur compounds produced by hydrolysis may now be discussed. The error in the estimation of sulphur, in carbon tetrachloride solutions was not more than 2% (*cf.* Rao, B. S. and Rao, M. R. A.,³⁴), at the concentrations met with in these investigations. Amorphous sulphur, formed as a suspension in aqueous medium could not be accurately estimated.

The estimation of sulphide was quite satisfactory except in cases where hydrolysis had been effected by dilute alkali (0.1 N) wherein appreciable errors were caused by the adsorption of sulphite. Experiments were carried out to determine the extent of adsorption of sulphite by the cadmium sulphide and cadmium hydroxide precipitates. No measurable adsorption of sulphite took place in solutions above 0.1 N in alkalinity, but in feebly alkaline solutions 2 to 3% of the sulphite present was brought down by the sulphide precipitate. Even on prolonged washing with water the adsorbed sulphite could not be removed. 0.2 N alkali however was much more effective in the removal of adsorbed sulphite. It has to be pointed out that when cadmium sulphide containing sulphite is treated with iodine in presence of acid, both sulphide and sulphite react with iodine exclusively, and the interaction between sulphide and sulphite is negligible. In experiments with baryta, it was noticed that there was appreciable adsorption of sulphide by the barium sulphite precipitate. This probably accounts for the much greater experimental error noticed in hydrolytic experiments with baryta.

Owing to the fact that in the iodometric estimation of thiosulphate 2 atoms of sulphur correspond to an atom of iodine (while for sulphite and sulphide 0.5 atom of the element corresponds to an iodine atom) the experimental error in the estimation of thiosulphate is proportionately greater. In the calculation of free sulphur by the relationship :

$$S = \text{Thiosulphate} + 3 (\text{sulphite} - \text{sulphide})$$

any experimental error in the estimation of sulphite or sulphide gets considerably magnified in computing the sulphur value. In some of the earlier hydrolysis experiments (Table I) the agreement between sulphur (found)

and sulphur (calculated) is not satisfactory, but in later experiments the agreement was far more satisfactory, except in cases where the inherent experimental errors due to adsorption and other causes, were much greater.

The highly unstable sulphur iodide (whose existence has been questioned in the past) has been prepared in this laboratory by M. R. A. Rao by the action of dry potassium iodide on sulphur chloride solutions (Rao, M. R. A.³⁵). He has studied the hydrolysis of sulphur iodide by moderately strong solutions of alkali and it is of interest to compare the values for the reactions H, T and D obtained with the two halides of sulphur. In his paper (sent for publication) results of hydrolysis of sulphur iodide have been expressed in terms of reactions H, D' and D of the present paper. Since then, it has been found necessary to introduce reaction T in place of D' to explain the results of hydrolysis by dilute alkali. In Table XI, the values obtained by M. R. A. Rao have been recalculated on the basis of the reactions H, T and D.

TABLE XI

Comparative Study of the Hydrolysis of Sulphur Iodide and Sulphur Chloride by 2 N Sodium Hydroxide at Different Dilutions

		Sulphur Iodide Hydrolysis				Sulphur Chloride Hydrolysis		
Dilution	..	8.5	18.1	42.5	162.4	3.8	38.7	77.1
% Hydrolysis	..	1.4	2.3	6.8	26.6	75.8	88.6	90.4
% Thionization	..	14.2	15.7	18.3	13.5	9.6	8.1	9.7
% Decomposition	..	82.1	78.2	75.1	53.1	15.9	3.1	0.0
TOTAL		97.7	96.2	100.2	93.2	101.3	99.8	100.1

If disulphur oxide is the primary product of hydrolysis of the sulphur halides by alkali, it may be expected that the values for the three parallel reactions should approximately be the same for corresponding dilutions of iodide and chloride. Further work on sulphur iodide is undoubtedly needed before the marked differences in results of hydrolysis can be explained satisfactorily, but at present two possible explanations may be offered. One explanation is that sulphur iodide exists in a polymerized condition, in carbon tetrachloride solutions even at great dilutions. The effect of such polymerisation is to increase the proximity between S₂O (or H₂S₂O₂) molecules formed by hydrolysis of the iodide, thus rendering greater, the chances of decomposition in terms of reaction D. Owing to the great instability of sulphur iodide, it has not yet been possible to determine in this laboratory the molecular

weight of the iodide by cryoscopic methods. It is very probable, however, that sulphur iodide molecules are polymers of S_2I_2 . It may be mentioned that appreciable polymerization has been noticed in the case of sulphur chloride, in carbon tetrachloride solutions by Patrick and Hackerman.³¹

Another possible explanation is that the structure of the sulphur iodide molecule is markedly different from that of the molecule of sulphur chloride. Several experimental investigations have in recent years been carried out on the structure of sulphur chloride. From a study of the reactions of the complex $AlCl_3 \cdot 2S_2Cl_2$, Ruff and Golla³⁸ favoured the structure $S : S (: Cl_2)$. The same structure has been assigned to the chloride by Trivedi⁴⁷ from his work on absorption spectra. Electron diffraction studies by Ackerman and Mayer¹ however, have given evidence of the structure $Cl.S.S.Cl$. Scheibe and Stoll⁴⁰ favour the structure $RO-SS-OR$ for esters of thiosulphurous acid as a result of Raman spectra and dipole moment investigations. To determine the structure of the hypothetical thiosulphurous acid and of its chloride S_2Cl_2 , Giacomello¹³ studied the behaviour of sulphur chloride solutions in benzene towards phenols and concluded that sulphur chloride is an equilibrium mixture of $S : S (: Cl_2)$ (Structure A) with $Cl-S-S-Cl$ (Structure B) and that the latter form is stabler and is in greater proportions in the mixture. Structure A was considered by him to indicate a more reactive form of the chloride than B. When sulphur halides are hydrolysed, we may therefore expect to get as the primary products the two forms of thiosulphurous acid corresponding to structures A and B of sulphur chloride. The proportion of the two forms, in the thiosulphurous acid obtained, is likely to depend on the relative amounts of A and B originally present in the halide. Sulphur chloride is known to have form B in excess and if it be assumed that in sulphur iodide form A preponderates the greater decomposition noticed in sulphur iodide hydrolysis can be explained. Experimental determination of the structure of sulphur iodide, by suitable methods, may therefore be expected to throw light on the observed difference in the hydrolysis of the two halides of sulphur.

Finally the question whether disulphur oxide or thiosulphurous acid is the primary product of sulphur chloride hydrolysis, may be considered. From theoretical considerations it is obvious that thiosulphurous acid would be formed first, by the hydrolysis of sulphur chloride. But the question is whether the unstable acid acts as such in the three reactions H, T and D or whether it splits off water and forms disulphur oxide before undergoing further transformation. In spite of the increasing attention that has been paid to thiosulphurous acid and its alkyl derivatives in recent years, the acid still continues to be a hypothetical substance (Meuwsen²⁷, Hellmuth¹⁸, Stamm

and Wintzer⁴³). Owing to the presence of the elements of water in the molecule, thiosulphurous acid seems to be extremely unstable and it is only when the molecule is rendered less active by replacing the hydrogen by an alkyl group that stability is secured. Disulphur oxide, on the other hand, has actually been prepared in the form of a solution in carbon tetrachloride (B. S. Rao³³) and until we have definite evidence of the existence of thiosulphurous acid in the free state, it is perhaps appropriate to look upon disulphur oxide as the primary product of the hydrolysis of sulphur chloride. Judging however, from the difference in behaviour on hydrolysis between sulphur chloride and sulphur iodide, and also between sulphur chloride and disulphur oxide (Part II of these studies) there is reason to believe that at least a part of the thiosulphurous acid formed by hydrolysis of sulphur halides, reacts as such without splitting off water (to give rise to disulphur oxide). The precise nature of the primary product has therefore to be left open for the present, but the experimental work described in this paper makes it clear that the primary product is either disulphur oxide or its hydrate the hypothetical thiosulphurous acid. The fact that disulphur oxide has been prepared, it may be claimed, has made the existence of thiosulphurous acid itself, more probable.

Summary

(1) The hydrolysis of sulphur chloride has been studied by carrying out the reaction at the interface between very dilute solutions of the compound in carbon tetrachloride and aqueous alkali, in presence of cadmium hydroxide. The alkali and the cadmium hydroxide circumscribed the scope of secondary reactions and rendered possible a quantitative interpretation of the phenomenon.

(2) The products of hydrolysis were free sulphur, sulphide, sulphite and thiosulphate, and were estimated by suitable analytical methods. The free sulphur was mostly present in the carbon tetrachloride layer. When dilute alkali was used for hydrolysis, a part of the sulphur appeared in the amorphous condition, and sulphate and trithionate were formed in small quantities, owing to decomposition of thiosulphuric acid.

(3) The results can most satisfactorily be explained on the basis that disulphur oxide (if not its hydrate—the hypothetical thiosulphurous acid) is the primary product of hydrolysis. Disulphur oxide has now been obtained in carbon tetrachloride solutions. The oxide undergoes three parallel reactions: (a) hydrolysis, producing sulphite and sulphide in equimolecular proportions, (b) thionization, oxidising part of sulphite formed in hydrolysis to thiosulphate and (c) decomposition yielding, sulphur and sulphite:

$S_2O + 4 NaOH = Na_2S + Na_2SO_3 + 2H_2O$ (Reaction H) Hydrolysis.

$2 Na_2SO_3 + 2 S_2O + 2 NaOH = 3 Na_2S_2O_3 + H_2O$ (Reaction T) Thionization.

$2 S_2O + 2 NaOH = 3 S + Na_2S_2O_3 + H_2O$ (Reaction D) Decomposition.

(4) A method of calculating the extent of each of the three reactions from the analytical values of the products of hydrolysis, is indicated and it is shown that: Free Sulphur = Thiosulphate + 3 (Sulphite - Sulphide).

(5) The effect on hydrolysis, exercised by dilution of sulphur chloride, has been studied and found to be to increase reaction H and reduce D. When the molecular ratio of sulphur chloride to carbon tetrachloride is of the order of 1 : 100,000, reaction D drops to zero (2 N alkali being used for hydrolysis).

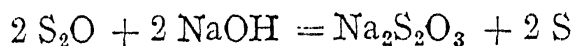
(6) Glycerine added to the alkali, has been found to reduce H and increase D and T; while brucine, even in small quantities, increases H and inhibits T.

(7) Hydrolysis by baryta has been found to be markedly different from that by sodium hydroxide. With baryta, hydrolysis and thionization are less but decomposition much more than with sodium hydroxide.

(8) Dilution of sodium hydroxide affects the three reactions differently. Hydrolysis diminishes, there is a small increase in decomposition, while thionization markedly increases.

(9) The effect of an increase in temperature on the three reactions is comparatively small.

(10) There is evidence to show that production of thiosulphate is to a certain extent due to the following reaction:



for, when sulphite is immobilised by the use of baryta or of formalin, thiosulphate is still produced, though to a much smaller extent.

(11) It is shown that sulphur and thiosulphate are not obtained as a result of any secondary reactions but are directly formed from the disulphur oxide.

(12) The behaviour of sulphur iodide (which has been prepared in this laboratory in carbon tetrachloride solutions) is compared with that of sulphur chloride towards alkali and tentative explanations are offered for the observed difference.

The author wishes to thank Mr. M. R. A. Rao for his valuable assistance in carrying out part of the analytical work.

REFERENCES

1. Ackerman and Mayer .. *J. Chem. Physics*, 1936, **4**, 377.
2. Baroni .. *Atti. R. Acad. Lincei*, 1932, **15**, 305.
3. Bassett and Durrant .. *J. Chem. Soc.*, 1927, **1416**.
4. Brownlee .. *J. Am. Chem. Soc.*, 1907, **29**, 1032.
5. Bullock and Forbes .. *Ibid.*, 1933, **55**, 252.
6. Castiglieni .. *Ann. Chim. Applicata*, 1934, **24**, 273.
7. Debus .. *Lieb. Ann.*, 1888, **76**, 244 ; *J. Chem. Soc.*, 1888, **53**, 278.
8. Deines .. *Z. anorg. Chem.*, 1928, **177**, 13.
9. Foerster and Hornig .. *Ibid.*, 1922, **125**, 86.
10. ——— and Mommsen .. *Ber.*, 1924, **57B**, 258.
11. ——— and Umbach .. *Z. anorg. Chem.*, 1934, **217**, 175.
12. Fordos and Gelis .. *Lieb. Ann.*, 1879, **199**, 97 ; 1882, **213**, 329.
13. Giacomello .. *Atti. Acad. Lincei*, 1935, **21**, 36.
14. Hansen .. *Ber.*, 1933, **66B**, 1000.
15. ————— .. *Ibid.*, 1933, **66B**, 1009.
16. Hargreaves and Dunningham .. *J. Soc. Chem. Ind.*, 1923, **147T**, 42.
17. Harvey and Schuette .. *J. Am. Chem. Soc.*, 1926, **48**, 2065.
18. Hellmuth .. *Ber.*, 1935, **68B**, 673.
19. Kolthoff and Furman .. *Volumetric Analysis*, 1928, **1**, 237.
20. Kretov .. *J. Chem. Ind. Moscow*, 1928, **5**, 1268.
21. Kurtenacker and Goldbach .. *Z. Anorg. Chem.*, 1927, **166**, 177.
22. ——— and Ivanov .. *Ibid.*, 1930, **185**, 337.
23. ——— and Kaufmann .. *Ibid.*, 1925, **148**, 225.
24. Lowry, McHatton and Jones .. *J. Chem. Soc.*, 1927, 746.
25. McKee .. *J. Chem. Edn.*, 1932, **9**, 249.
26. Mellor .. *Treatise on Inorganic Chemistry*, 1930, **9**, 207.
27. Meuwsen .. *Ber.*, 1935, **68B**, 121, 1011.
28. Neumann and Fuchs .. *Z. angew. chem.*, 1925, **38**, 277.
29. Noack .. *Z. anorg. Chem.*, 1925, **146**, 239.
30. Olin .. *J. Am. Chem. Soc.*, 1926, **48**, 167.
31. Patrick and Hackerman .. *J. Phys. Chem.*, 1936, **40**, 679.
32. Plessey .. *J. pr. chem.*, 1845, **36**, 239.
33. Rao, B. S. .. *Curr. Sci.*, 1938, **6**, 381.
34. ——— and Rao, M. R. A. .. *Pro. 10th International Congr. Chem.*, 1938, **3**, 462.
35. Rao, M. R. A. .. *Curr. Sci.*, 1937, **6**, 63.
36. Ray and Maulick .. *Z. anorg. chem.*, 1931, **199**, 353.
37. Reisenfeld and Sydow .. *Ibid.*, 1928, **175**, 49.

38. Ruff and Golla .. *Z. anorg. chem.*, 1924, **138**, 17.
39. Schaffer and Böhm .. *Ibid.*, 1929, **183**, 151.
40. Scheibe and Stoll .. *Ber.*, 1938, **71B**, 1571.
41. Smith, A. and Brownlee *Z. Phy. Chem.*, 1908, **61**, 209.
42. Spong .. *J. Chem. Soc.*, 1933, **1547**.
43. Stamm and Wintzer .. *Ber.*, 1938, **71B**, 2212.
44. Tartar and Davies .. *J. Am. Chem. Soc.*, 1924, **46**, 576.
45. Terrey and Spong .. *J. Chem. Soc.*, 1932, **220**.
46. Trautz .. *Z. elektrochem.*, 1929, **35**, 110.
47. Trivedi .. *Proc. Acad. Sci. U.P. (India)*, 1935, **4**, 263.
48. Watson and
Rajagopalan *J. Indian Inst. Sci.*, 1925, **8A**, 275.
49. Young .. *J. Am. Chem. Soc.*, 1902, **24**, 297.