THIONYL IODIDE

Part I. Formation of Thionyl Iodide

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Introduction

Thionyl Chloride was prepared by Persoz and Block[1] in 1819 and the bromide by Michaelis[2] in 1891. An attempt to prepare thionyl iodide was made by Bessen[3] by trying the action of thionyl chloride on cooled hydrogen iodide; but the reaction mixture yielded only hydrogen chloride, iodine, sulphur dioxide and free sulphur. While studying the reactivity of chlorine atom in thionyl chloride, Perret and Perrot[4] shook up a solution of thionyl chloride in carbon tetrachloride, with an acidified aqueous solution of potassium iodide. They noticed, however, that the reaction yielded only iodine, sulphuric acid and small quantities of thionic acids. Thus the preparation of thionyl iodide either in a state of purity or in the form of solution, has not so far been successful.

It has been shown by the author[5] that sulphur iodide can be prepared by shaking dry solid potassium iodide with a solution of sulphur chloride in carbon tetrachloride. It was felt that by a similar reaction, thionyl iodide also could be prepared. But when a solution of thionyl chloride in carbon tetrachloride was shaken up with solid potassium iodide, it was observed that the resulting solution, had a deep violet colour which was practically identical with a solution of iodine in carbon tetrachloride. But when the shaking was done in absence of light, the solution was not quite violet in colour but had an yellowish tinge. It was further noticed that when kept in sunlight, the yellow shade completely disappeared giving rise to the pure violet. The yellow tinge persisted for a longer time at 0° C. than when kept at 30° C. This difference in colour was suspected to be due to thionyl iodide and a systematic investigation was undertaken to study the nature of the compound formed.

Experimental

Reagents used:

1. *Potassium iodide.*—Merck's extra pure potassium iodide was finely powdered and dried over phosphorus pentoxide in a vacuum desiccator.

2. *Carbon tetrachloride.*—Sulphur free carbon tetrachloride was dried over phosphorus pentoxide and distilled.

3. *Thionyl chloride.*—Merck's purest sample of thionyl chloride was distilled in an all glass apparatus and a weighed quantity of the middle fraction added to a known amount of the dry carbon tetrachloride. The chloride solution was preserved in a bottle from which the liquid could be transferred to the weighing pipette without being contaminated by atmospheric moisture.

Analysis of thionyl chloride solution.—The strength of the thionyl chloride solution was determined by a quantitative estimation of the products of hydrolysis of the chloride in presence of alkali. Schiff[6] studied the action of thionyl chloride on sodium hydroxide and stated that sulphite and chloride were the only products of hydrolysis. Preliminary experiments by the present author however, showed that small quantities of sulphide were also produced. The following method was therefore employed to estimate the products of hydrolysis. The stock solution (18 gm.) was diluted with carbon tetrachloride (400 gm.) and shaken up with 25 c.c. of 2 N sodium hydroxide containing cadmium hydroxide suspension. The cadmium hydroxide converted the sulphide into the insoluble cadmium sulphide thus preventing any side reaction between the sulphide and the sulphite. The reaction of the alkali with the thionyl chloride could be completed by shaking the mixture for 10 minutes, after which the carbon tetrachloride layer was separated and washed twice with distilled water and the wash water added to the alakli solution. The carbon tetrachloride was then dried over phosphorus pentoxide and the dissolved sulphur was estimated by a slight modification of the method developed in this laboratory, by B. S. Rao and M. R. A. Rao.[7] A weighed quantity of carbon tetrachloride solution was distilled over mercury till the volume was reduced to about 20 c.c. The hot mixture was shaken up on a shaking machine for 30 minutes to convert the sulphur to mercuric sulphide. The residual carbon tetrachloride was distilled off. It was noticed that the distillation of the solvent did not carry away any sulphur with it. The mercuric sulphide formed was treated with a concentrated solution of hydrogen iodide and the hydrogen sulphide produced estimated iodometrically. In some experiments, the mercuric sulphide did not easily react with the hydrogen iodide. On warming, however, the reaction went to completion without any difficulty.

The aqueous layer was filtered and the cadmium sulphide was acidified with 10 c.c. of 2 N acetic acid and estimated iodometrically. The filtrate was made up to 250 c.c. and aliquots were used for the estimation of sulphite and thiosulphate by the method of Kurtenacker and Wollak.[8] The total amount of the sulphur compounds in the filtrate was determined by oxidising 10 c.c. of the solution with sodium hypobromite and estimating the total sulphate as barium sulphate. Pregl's micro method was adopted for the estimation of barium sulphate. In order to determine the chlorine content, 10 c.c. of the filtrate were treated with 5 c.c. of 4 N nitric acid to oxidise the sulphur compounds and the chloride present was precipitated as silver chloride. The silver chloride was estimated by the micro method described by Pregl. The results are presented in Table I.

TABLE I

Estimation of the products of hydrolysis of $SOCl_2$

	Expt. 1	Expt. 2	Expt. 3
(1) Wt. of stock solution (gm.)	17·81	17·79	17·82
(2) CCl_4 used for dilution (gm.)	94·12	421·0	1493·0
(3) (g. atom of sulphur as CdS per gm. stock solution) × 10^6	0·4	0·5	0·3
(4) (g. atom of sulphur as Na_2SO_3 per gm. stock solution) × 10^6	100·6	101·8	99·0
(5) (g. atom of sulphur as $Na_2S_2O_3$ per gm. stock solution) × 10^6	Nil	Nil	Nil
(6) (g. atom of sulphur as total sulphur per gm. stock solution) × 10^6 ($BaSO_4$ method) ..	105·9	105·3	106·3
(7) (g. atom of chlorine as NaCl per gm. stock solution) × 10^6	211·5	212·6	211·9
(8) (g. atom of dissolved sulphur in CCl_4 per gm. stock solution) × 10^6	Nil	Nil	Nil

The following conclusions can be drawn from the analytical data. The average value for chlorine content is 212·0 and the average for the total sulphur compounds in the alkali solution ($BaSO_4$ + CdS) is 106·2. Thus within the limits of experimental error, the ratio of sulphur to chlorine in the thionyl chloride is as 1 : 2. This shows that the thionyl chloride is quite pure. The sulphite as estimated iodometrically (4th row) is about 5% less than the value obtained by the barium sulphate method (6th row). This is evidently due to the atmospheric oxidation of sulphite while shaking and filtering. Carius[9] has mentioned that thionyl chloride reacts with water producing free sulphur and sulphuric acid. But the present experiment shows that no sulphur is produced in the reaction. In order to test this point, the thionyl chloride solution was shaken up with a hot dilute solution of barium chloride in water. No detectable quantities of barium sulphate were produced. It was further noticed that the carbon tetrachloride did not contain any free sulphur. So it can be concluded that when a solution of thionyl chloride reacts with water or with alkali neither sulphuric acid nor free sulphur is produced. As discussed later, the sodium sulphide is probably obtained as a result of the hydrolysis of sulphur chloride which is a likely impurity in thionyl chloride.

Reaction of thionyl chloride with dry potassium iodide.—A weighed quantity of thionyl chloride solution (18 gm.) was introduced into a bottle containing a known amount (1,500 gm.) of carbon tetrachloride. Dry potassium iodide powder (10 g.) was added to the solution and the contents shaken up for 40 minutes. The solution was then kept in bright sunlight for 30 minutes when the yellow tinge completely disappeared. A portion of the solution (15 gm.) was then transferred to a colorimetric cup and its iodine concentration was estimated by comparison with a standard solution of iodine in carbon tetrachloride. The remaining portion of the solution was shaken up with 25 c.c. of 2 N sodium hydroxide containing cadmium hydroxide suspension till the carbon tetrachloride turned colourless. The carbon tetrachloride was separated and its sulphur content estimated as described already. The aqueous layer was filtered and it was noticed that the residue did not have any cadmium sulphide. The filtrate was made up to 250 c.c. and an aliquot used for the estimation of total sulphur compounds by the gravimetric method described already. On acidification, the filtrate gave rise to iodine. This indicated the absence of sulphite and thiosulphate. The iodine liberated on acidification was estimated. The results obtained are given in Table II.

TABLE II

Reaction of thionyl chloride with potassium iodide

	Expt. 1	Expt. 2
(1) Wt. of $SOCl_2$ solution (gm.)	17·82	17·79
(2) Wt. of CCl_4 used for dilution (gm.)	1529·0	1377·0
(3) (g. atom of sulphur in CCl_4/gm. stock solution) × 10^6 ..	50·2	49·2
(4) (g. atom of sulphur in aq./gm. stock solution) × 10^6 ..	52·8	53·4
(5) (g. atom of iodine in aq./gm. stock solution) × 10^6 ..	107·0	106·8
(6) (g. atom of iodine in CCl_4/gm. stock solution) × 10^6 (Colorimetric method) ..	210·0	208·9

Explanation of the results of Table II.—The results given in Table II indicate that when thionyl chloride solution is shaken up with potassium iodide, the following reaction takes place quantitatively

$$2\,KI + SOCl_2 \rightarrow 2\,KCl + SOI_2.$$

The thionyl iodide being extremely unstable decomposes according to the equation

$$2\,SOI_2 \rightarrow SO_2 + S + 4\,I.$$

Thus, when the iodine in carbon tetrachloride is estimated colorimetrically, the value for iodine in experiment 1 (6th row) is 210 while the theoretical value is 212·4. The small difference between the observed and the calculated values is quite within the limits of experimental error. Since thionyl chloride is colourless, the colorimetric method of determination of iodine can be employed to find out the percentage of reaction between potassium iodide and thionyl chloride. Incidentally it may be mentioned that sulphur dioxide and iodine do not react with one another in absence of moisture.

When the solution is shaken up with alkali however, the sulphur dioxide is oxidised by the iodine to sulphuric acid (which forms sodium sulphate with the alkali). Half the iodine originally produced is utilised in this reaction :

$$SO_2 + I_2 + 2\,H_2O \rightarrow H_2SO_4 + 2\,HI.$$

Hence the iodine content after the alkali treatment (5th row, Table II) is half the original value (6th row). The average value (53·4) for the sulphate (4th row), is also in good agreement with the calculated value (53·1). The free sulphur in carbon tetrachloride (3rd row) however is only 50·2 or less, while the calculated value is 53·1. This is beyond the limits of experimental error which is about 1 %. The following procedure was adopted to find out whether any sulphur was adsorbed on the solid potassium iodide. The reaction between potassium iodide and thionyl chloride was repeated as described above and the carbon tetrachloride separated from the potassium iodide. The potassium iodide was washed well with carbon tetrachloride till there was no violet colour imparted to the washed liquid. When the solid was dissolved in water, it was noticed that a thin suspension of colloidal sulphur was produced in the aqueous layer. This was evidently due to the sulphur adsorbed on the solid potassium iodide. In order to determine the amount of sulphur deposited on the iodide, the colloidal sulphur was shaken up with mercury and the excess of water boiled off. Carbon tetrachloride (10 c.c.) was added to the solid residue and the mixture refluxed over a water-bath for 30 minutes and then shaken up for 20 minutes. The mercuric sulphide was estimated as outlined already. It was noticed that within the limits of experimental error, the amount of sulphur adsorbed on potassium iodide was equal to the difference between the observed and the calculated values for free sulphur.

The adsorption of sulphur by potassium iodide, leads one to suspect that the solid may take up other substances also. Preliminary experiments carried out indicated that the iodide adsorbed a small quantity of sulphur dioxide. A quantitative estimation of the adsorbed sulphur dioxide was effected in the following manner. The washed potassium iodide was dissolved in 25 c.c. of 0·2 N sodium hydroxide and the sulphur suspension removed by filtration and the filtrate was made up to 100 c.c. Aliquots of the filtrate were used to determine the sulphite both volumetrically and gravimetrically (by the $BaSO_4$ method, after oxidation). The volumetric method showed that $2 \cdot 2 \times 10^{-6}$ gm. atom of sulphur was present as sulphur dioxide while the gravimetric method indicated a value of $3 \cdot 5 \times 10^{-6}$. The lower value in the former case is due to the atmospheric oxidation of the sulphite.

Production of thionyl iodide during the reaction between thionyl chloride and potassium iodide.—It has been pointed out that when a solution of thionyl chloride in carbon tetrachloride is shaken up with potassium iodide, a violet solution with a distinct yellow tinge is produced. If this yellow tinge is due to the presence of thionyl iodide, its reaction with alkali must be similar to that of thionyl chloride with alkali. To test this point, a study of the hydrolysis of the yellow tinged solution with alkali was undertaken.

A known amount of the thionyl chloride solution (18 gm.) was mixed with a weighed quantity of carbon tetrachloride (1500 gm.) and the solution shaken up with dry potassium iodide (10 gm.) in a bottle wrapped in a black cloth. After shaking the mixture for 40 minutes, the bottle was taken to a dark room and a weighed sample of the solution was withdrawn from the bottle to test for the completion of the reaction between thionyl chloride and potassium iodide. The colorimetric estimation of iodine in this sample (after the disappearance of the yellow tinge) showed decisively that the thionyl chloride had reacted completely with the solid potassium iodide.

Immediately after the removal of the sample, 25 c.c. of 2 N sodium hydroxide containing cadmium hydroxide suspension, was added to the main portion of the solution and the mixture shaken up for 10 mintues to complete the reaction between the solution and the alkali. The carbon tetrachloride was separated and washed and the sulphur dissolved in it estimated as described already. The aqueous layer was analysed for sulphide, sulphite, thiosulphate, and total sulphur compounds as outlined under the analysis of thionyl chloride. Since the aqueous solution had the sulphate along with other sulphur compounds, the sulphate alone was determined separately by the method suggested by Kurtenacker and Goldbach.[10] It was noticed that within the limits of experimental error, the sulphate obtained by this method was equal to the difference between the total sulphate (by the oxidation method) and the sum of thiosulphate and sulphite (determined iodometrically). Hence it was concluded that the products of hydrolysis in the alkali solution were sulphide, sulphite, thiosulphate and sulphate. The free sulphur adsorbed on the potassium iodide, remained along with the cadmium sulphide when the aqueous solution was filtered and did not introduce any complications in the analytical work. Since a portion of the sulphur remained in the aqueous layer, the amount of free sulphur produced in the reaction was indirectly calculated by subtracting from 106·2 (the total sulphur content) the sum of the values in the rows 3 and 7 of Table III. The results are given in Table III.

TABLE III

Hydrolysis of thionyl iodide in presence of 2 *N alkali.*
1 *gm. stock solution had* $106{\cdot}2 \times 10^{-6}$ *gm. atom of sulphur as thionyl chloride*

	Expt. 1	Expt. 2	Expt. 3
(1) Wt. of $SOCl_2$ solution (gm.)	17·78	17·81	17·82
(2) Wt. of CCl_4 used for dilution (gm.)	1538·0	1508·0	1489·0
(3) (gm. atom of sulphur as sulphide per gm. stock solution) × 10^6	0·3	0·4	0·45
(4) (gm. atom of sulphur as sulphite per gm. stock solution) × 10^6	0·7	0·8	1·2
(5) (gm. atom of sulphur as thiosulphate per gm. stock solution) × 10^6	9·4	10·2	9·9
(6) (gm. atom of sulphur as free S in CCl_4 per gm. stock solution) × 10^6	25·4	25·2	25·3
(7) (gm. atom of sulphur as total S compounds per gm. stock solution) × 10^6 ($BaSO_4$ method) ..	78·5	78·9	79·1
(8) (Calculated value for the free sulphur per gm. stock solution) × 10^6 (106·2—rows 3 + 7) ..	27·4	26·9	26·6

Interpretation of the results of Table III.—It has already been shown (by the colorimetric estimation of iodine) that the solution got by shaking the thionyl chloride with potassium iodide, does not contain any unreacted thionyl chloride. The solution contains only thionyl iodide and its decomposition products as given by the equation

$$2\,SOI_2 \rightarrow S + SO_2 + 2I_2. \qquad (A)$$

On shaking with alkali, the sulphur remains unaffected, the sulphur dioxide forms sulphite and the iodine forms iodide and hypoiodite. The thionyl iodide itself partly undergoes hydrolysis as represented by the equation

$$SOI_2 + H_2O \rightarrow 2\,HI + SO_2 \qquad (B)$$

the hydrogen iodide and the sulphur dioxide forming their sodium salts. A portion of the thionyl iodide however, appears to decompose according to the equation

$$2\,SOI_2 \rightarrow S_2O_2 + 2I_2 \qquad (C)$$

momentarily giving rise to thiosulphuric anhydride (disulphur dioxide). The anhydride reacts with alkali forming sodium thiosulphate. The iodine produces sodium iodide and sodium hypoiodite on reacting with alkali. The hypoiodite formed in reactions A and C is completely reduced by the sulphite obtained in the reactions A and B. Thus the production of sulphite, sulphate and thiosulphate is completely explained by the above mechanism. It has to be pointed out that (in the absence of alkali) reaction C is probably the first step in the decomposition of thionyl iodide. The disulphur dioxide (thus produced), being unstable, decomposes into sulphur and sulphur dioxide giving for thionyl iodide, the decomposition products indicated in equation A.

It has been found, that a small quantity of sulphide is also produced during the reaction of thionyl chloride with alkali. The sulphide is probably due to the hydrolysis of sulphur chloride present in traces as an impurity in thionyl chloride. B. S. Rao[11] has shown that sulphide is one of the principal products in the hydrolysis of sulphur chloride by 2 N alkali as:

$$S_2Cl_2 + 2\,H_2O \rightarrow H_2S + SO_2 + 2\,HCl.$$

It may be pointed out that on a commercial scale, thionyl chloride is generally obtained by the reaction between sulphur chloride and sulphur trioxide. On treatment of thionyl chloride with potassium iodide, the sulphur chloride present as impurity, forms sulphur iodide[5] whose reaction with alkali is analogous to that of sulphur chloride as:

$$S_2I_2 + 2\,H_2O \rightarrow H_2S + SO_2 + 2\,HI. \qquad (D)$$

The hydrogen sulphide, the sulphur dioxide and the hydrogen iodide combine with the alkali to form the sodium salts.

The extent to which the reactions A, B, C and D take place can be calculated in the following manner. Free sulphur is produced only in the reaction A. Therefore twice the amount of the free sulphur corresponds to the extent to which the reaction A takes place. Hence the iodine, the sulphur dioxide and the free sulphur produced in A can be calculated. Similarly since the thiosulphate is produced only in C, the extent to which reaction C takes place can also be calculated. Sulphide is formed only in D and twice this amount corresponds to the sulphur taking part in this reaction. The extent to which the reaction B takes place, can be calculated by two methods. In the first method, the value is calculated (in gm. atoms of sulphur) by subtracting from the total sulphur compounds (Table III, 7th row) in the aqueous layer, the quantity $\left(c + \frac{a}{2} + \frac{d}{2}\right)$ where a, c and d represent the number of gm. atoms of sulphur taking part in each of the reactions A, C and D respectively. This value is referred to as B_1, in Table IV. In the second method the extent of reaction B can be calculated by subtracting from the total sulphur (*i.e.*, 106·2, Table I, 6th row), the quantity $(a + c + d)$. This has been referred to as B_2 in Table IV. The extent of each of the reactions A, B, C and D, has been expressed in Table IV, as percentages of gm. atoms of sulphur taking part in each reaction.

TABLE IV

Reactions A, B, C and D during the hydrolysis of thionyl iodide in presence of 2 N alkali

Reactions	% (A)	% (C)	% (D)	% (B_1)	% (B_2)
Experiment 1	51·2	8·9	0·6	39·1	39·3
Experiment 2	51·4	8·6	0·8	39·7	39·2
Experiment 3	51·0	9·3	0·8	39·3	38·9

The agreement between the two values B_1 and B_2 is quite good.

The experimental results of Table III can also be examined from another point of view. If A, B, C and D are the only reactions that take place when the solution reacts with alkali, it is obvious that the sulphate produced in the experiment must correspond to the sulphite that is oxidised by the iodine formed during the reaction. The total sulphite formed is equal to $\left(\frac{a}{2} + b + \frac{d}{2}\right)$. The observed value for the sulphite oxidised = (total sulphite formed − unoxidised sulphite) $= \frac{a}{2} + b + \frac{d}{2}$ − unoxidised sulphite (Table III, 4th row). This value for the sulphite is represented as the observed value for the sulphite oxidised. Similarly the gm. atoms of iodine liberated must be equal to $2a + 2c$. The calculated value for the oxidised sulphite is $(a + c)$, *i.e.*, half the iodine, since two atoms of iodine oxidise one molecule of sulphur dioxide. This is given as the 'Calculated value' for the oxidised sulphite. The following table represents the 'Calculated' and 'Observed' values for the oxidation of sulphite :

TABLE V

	% of sulphite oxidised	
	Calculated	Observed
Experiment 1 ..	60·1	64·3
Experiment 2 ..	60·0	65·0
Experiment 3 ..	60·3	64·0

It is noticed that the calculated values for the oxidation of sulphite are lower than the observed values. This is due to the atmospheric oxidation of the sulphite. Similar oxidation of the sulphite is also observed in the analysis of thionyl chloride (Table I, 4th and 6th rows), where about 5–6% of the sulphite formed is oxidised by air during shaking and filtration.

Reaction between iodine and a mixture of sulphite and thiosulphate in alkaline solutions.—It has been assumed hirtherto, that the sulphate formed during the hydrolysis of thionyl iodide in presence of alkali, is entirely due to oxidation of the sulphite produced in the reaction. Ashley,[12] Kolthoff[13] and others[14] however have shown that iodine in alkaline solutions, oxidises thiosulphate to sulphate. It was therefore deemed advisable to ascertain the action of iodine on an alkaline mixture of sulphite and thiosulphate. The following method of investigation was adopted. Sodium thiosulphate solution (5 c.c. of N/100) was mixed with sodium sulphite (5 c.c. of N/100) and the mixture was made alkaline with 25 c.c. of 2 N sodium hydroxide. The alkaline mixture was shaken up with 400 gm. of a dilute solution of iodine in carbon tetrachloride containing iodine enough to oxidise the sulphite solution. After the reaction, the aqueous solution was separated and analysed for sulphite and thiosulphate. It was noticed that about 94% of the iodine oxidised the sulphite to sulphate while the remaining 6% reacted with the thiosulphate. Even when the iodine content of the carbon tetrachloride had 1·5 times the previous concentration, only 98% of the sulphite present was oxidised. No detectable quantities of tetrathionate were produced. Hence it is to be concluded that when a mixture of sulphite and thiosulphate in alkaline solutions, is treated with iodine in carbon tetrachloride, only a small portion of the thiosulphate is oxidised to sulphate.

It is of interest to study the hydrolysis of thionyl iodide using water instead of aqueous sodium hydroxide. Hydrolysis of the iodide when (along with water) cadmium carbonate is used as a neutralising agent, is also of interest. If thiosulphuric acid is produced during the hydrolysis when water is used, the acid will not be oxidised to sulphate by the iodine but is converted into tetrathionate. So in the case of water, the tetrathionate content of the solution will indicate the total amount of reaction C. The following experiments were therefore tried.

Reaction of thionyl iodide solution in presence of water and water, holding cadmium carbonate in suspension.—Thionyl iodide solution prepared by the method described above was transferred to four bottles (weighed with their contents) containing the following reagents: Bottle (1) had 25 c.c. of 2 N sodium hydroxide with cadmium hydroxide suspension. Bottle (2) had 25 c.c. of distilled water and bottle (3) had 25 c.c. of distilled water containing cadmium carbonate suspension. Bottle (4) had been carefully dried and contained no reagents. Bottle (1) was shaken up immediately after the introduction of the thionyl iodide solution, till there was no violet colour in carbon tetrachloride. The products of hydrolysis were then determined by the method outlined already. The results of this experiment indicated the amount of thionyl iodide present in the solution and also the extent to which the reactions A, B, C and D took place when the iodide was shaken up with 2 N alkali.

After the introduction of the solution, the bottles (2) and (3) were wrapped with a dark cloth and kept on a shaking machine. The mixture had to be shaken up for several hours before all the thionyl iodide decomposed. After the reaction was complete, the bottles were weighed and the carbon tetrachloride layer separated. The carbon tetrachloride had the dissolved iodine and sulphur. To find the iodine content, a known weight of the solution was shaken up with 20 c.c. of 0·2 N alkali till there was no iodine in the carbon tetrachloride. The sodium hydroxide layer was separated and acidified with 15 c.c. of 2 N sulphuric acid and the iodine liberated was estimated. It had previously been experimentally found that when an iodine solution decolourised by 0·2 N alkali is acidified, the original iodine content is liberated. The carbon tetrachloride layer (after shaking with alkali) was used to determine the dissolved sulphur.

After the separation of the carbon tetrachloride layer, the aqueous solution was filtered to remove the cadmium carbonate and the filtrate was analysed for free iodine, sulphate and tetrathionate. The cadmium carbonate was found to be free from sulphide. The tetrathionate was estimated by the potassium cyanide method suggested by Kurtenacker and Goldbach.[10] The filtrate (50 c.c.) was mixed with potassium iodide (2 gm.) and the excess of iodine removed by titration with sodium thiosulphate. Pure potassium cyanide (1 gm.) was added to the resulting solution and kept for 5 minutes. It was then acidified with 20 c.c. of 2 N sulphuric acid and the thiosulphate developed was estimated. The addition of potassium iodide was essential, otherwise the results obtained were found to be abnormal—sometimes 3–4 times the expected value. But in presence of potassium iodide normal values were obtained for the tetrathionate. Potassium cyanide and tetrathionate react with one another according to the equation:

$$Na_2S_4O_6 + 3\ KCN + H_2O \rightarrow K_2SO_4 + KCNS + 2\ HCN + Na_2S_2O_3.$$

It was noticed that no tetrathionate was produced in the contents of the bottle having aqueous cadmium carbonate while only traces of the thionate were detected in the bottle in which the thionyl iodide solution was shaken up with mere water. The analytical results were used to calculate the extent of the reactions A, B, etc., in the two cases.

Bottle (4) was weighed after the introduction of the thionyl iodide solution and kept in sunlight for the decomposition of the iodide. The free iodine developed was estimated colorimetrically in a portion of the solution and it

TABLE VI

Hydrolysis of thionyl iodide in presence of water containing different substances

	Bottle (1) shaken up with 2 N alkali	Bottle (2) shaken up with aq. $CdCO_3$	Bottle (3) shaken up with mere water	Bottle (4) shaken up with water after complete decomposition
		Experiment I		
% of reaction A ..	48·2	94·9	97·7	100·0
,, ,, B ..	43·0	5·1	1·9	Nil
,, ,, C ..	7·9	Nil	Only traces less than 0·4%	Nil
,, ,, D ..	0·9	Nil	Nil	Nil
		Experiment II		
% of reaction A ..	40·1	94·2	97·2	100
,, ,, B ..	49·6	5·8	2·0	Nil
,, ,, C ..	9·0	Nil	Only traces less than 0·8%	Nil
,, ,, D ..	1·3	Nil	Nil	Nil

was noticed that there was no unreacted thionyl chloride. The remaining portion of the solution was shaken up with 25 c.c. of water. The carbon tetrachloride layer was used for the estimation of iodine and sulphur, while the aqueous solution was used to determine the iodine and the sulphuric acid present. Necessary corrections were applied for the sulphur and sulphur dioxide adsorbed on the solid potassium iodide (used in the preparation of thionyl iodide) which was analysed as described already. From the analytical data the percentages of the reactions A, B, C and D were calculated. The results are given in Table VI.

Since very little tetrathionate is formed when thionyl iodide is shaken up with water or with water containing cadmium carbonate, it can be concluded that the thiosulphuric anhydride is not actually present along with the thionyl iodide solution. Hence the anhydride has only a momentary existence. It is interesting to note that when thionyl iodide is shaken up with water, most of the iodide merely decomposes (reaction A) instead of hydrolysing (reaction B). Thus in experiment 1, although the solution has 51·8% of thionyl iodide only 1·9% hydrolyses in presence of water. When cadmium carbonate is present, owing to the lower acidity of the solution, a higher proportion of thionyl iodide (5·1%) hydrolyses.

Production of thiosulphate during the hydrolysis of thionyl bromide.—It has been shown that no thiosulphate is produced when thionyl chloride reacts with alkali but thiosulphate is obtained in quantity when thionyl iodide is treated with alkali. Presumably thionyl bromide is intermediate between the chloride and the iodide in its properties. It was therefore felt desirable to study the reaction of thionyl bromide with alkali. The following procedure was adopted in the investigation. To prepare the thionyl bromide, the methods described by Hartog and Sims[15] and by Mayes and Partington[16] were used with slight modifications. A solution of thionyl chloride in carbon tetrachloride was shaken at 60° C. with dry sodium bromide for a period of two hours when a deep yellow solution of thionyl bromide was obtained. Another sample of thionyl bromide was prepared by adding thionyl chloride to a solution of dry hydrogen bromide in carbon tetrachloride the temperature being maintained at 60° C. for a period of three hours. Both these samples were subjected to hydrolysis with 2 N sodium hydroxide at the laboratory temperature. It was noticed that about 2–3% of the thionyl bromide was converted into thiosulphate in both the samples. This shows conclusively that there is a regular gradation in the extent to which the reaction C takes place during the hydrolysis of the three thionyl halides.

Hydrolysis of thionyl iodide with alkali of different concentrations.—The experimental results presented in Table VI show that for the same sample of thionyl iodide solution, the decomposition (reaction A) is minimum when sodium hydroxide is used and maximum in the case of water. This indicates that at higher concentrations of the alkali, the decomposition might even be smaller. Hence the hydrolysis of the thionyl iodide solution in presence of alkali of different concentrations was tried. The thionyl iodide solution was introduced into four weighed bottles containing the alkali and a suspension of cadmium hydroxide. Bottle (1) had 25 c.c. of 5 N alkali, bottle (2) 25 c.c. of 2 N alkali, bottle (3) 25 c.c. of 0·7 N alkali and bottle (4) 50 c.c. of 0·2 N alkali. After the iodide was introduced, each of the bottles was shaken up to complete the reaction of the iodide with alkali and then weighed. The products of hydrolysis were determined. From the analytical data the percentages of each of the reactions A, B, C and D were calculated. The results are given in Table VII and indicate that at higher concentrations of the alkali, the decomposition of the thionyl iodide is less.

TABLE VII

Effect of concentration of the alkali on the hydrolysis of thionyl iodide

Strength of the alkali	5 N	2·5 N	0·7 N	0·2 N
% of reaction A	48·8	51·4	57·8	65·2
,, B	40·5	39·1	34·7	29·4
,, C	9·8	8·7	6·9	4·9
,, D	0·9	0·8	0·6	0·5

Attempts to prepare solutions of pure thionyl iodide.—To get an undecomposed sample of thionyl iodide, it would be necessary to adjust the experimental conditions so that the formation of the iodide takes place so quickly that during the period of reaction, the decomposition is negligible. It was found that the increase in the amount of potassium iodide and rise in the temperature of the reaction mixture would favour the rate of formation of thionyl iodide. Thus when the potassium iodide was ten times the normal quantity, the conversion of thionyl chloride into the iodide was brought about within six minutes of shaking. But even in this short interval about 32 % of the thionyl iodide formed had decomposed. The adsorption of sulphur by the solid potassium iodide indicates that the potassium iodide surface catalyses the decomposition. Hence the use of very large quantities of potassium iodide is of no advantage. When the effect of temperature on the reaction was tried, it was noticed that at 50° C. the formation of the iodide was complete within 15 minutes. But during this interval, 56% of the thionyl iodide formed decomposed. Since the rate of decomposition of thionyl iodide is considerably diminished at lower temperatures, the mixture of potassium iodide and thionyl chloride was shaken up at 0° C. After shaking for two hours, only 80% of the thionyl chloride reacted to form thionyl iodide, 50% of which had already decomposed. It has not therefore been possible so far to prepare a solution containing undecomposed thionyl iodide.

Conclusion

The experimental results presented in this paper show beyond doubt, that thionyl iodide though highly unstable, can be prepared by the method described. Two important factors should be borne in mind while attempting to prepare such unstable compounds. First and foremost, it is necessary to adjust the experimental conditions, such that the substance gets produced in the form of dilute solution, since the compound decomposes with great rapidity both in the pure state and in concentrated solutions. In fact, treatment of pure thionyl chloride with potassium iodide, yields but little thionyl iodide and results only in the formation of sulphur, sulphur dioxide and iodine. Similarly very little sulphur iodide[17] is produced when sulphur chloride is treated with potassium iodide. Secondly, it is also necessary to bear in mind the decomposing effect that light may have. In fact both sulphur iodide[5] and thionyl iodide (especially the latter) are easily decomposed by light. It is the neglect of these two factors, that is responsible for the failure of earlier workers in preparing these compounds. The method worked out by the author for the preparation of sulphur iodide[5] and thionyl iodide appears to be general in scope and applicable to the preparation of many new compounds.

Summary

(1) In chemical literature, thionyl iodide has been stated to have no existence. It has been shown in this paper that thionyl iodide can be prepared in carbon tetrachloride solutions by shaking a dilute solution of thionyl chloride (in carbon tetrachloride) with solid potassium iodide.

(2) The thionyl iodide is extremely unstable in presence of light and decomposes giving sulphur, sulphur dioxide and iodine. When kept in the dark, the iodide is more stable.

(3) The action of aqueous sodium hydroxide on thionyl iodide solutions has been investigated. When thionyl iodide reacts with alkali, apart from the decomposition of the halide, the principal reaction is the hydrolysis of the iodide represented by the equation :

$$SOI_2 + H_2O \rightarrow SO_2 + 2\,HI \qquad (1)$$

A portion of the iodide however, is converted into thiosulphate in terms of the equation.

$$2\,SOI_2 + H_2O \rightarrow H_2S_2O_3 + 2\,I_2. \tag{2}$$

In presence of alkali, these products of reaction form the corresponding sodium salts. A quantitative interpretation of the reaction with alkali is also given. The extent to which the hydrolysis takes place, is a function of the concentration of the alkali, the hydrolysis increasing with the strength of the alkali.

(4) Unlike thionyl chloride, the iodide decomposes into sulphur, sulphur dioxide and iodine, when it is shaken up with water, there being very little hydrolysis.

(5) When thionyl halides are hydrolysed by alkali, the formation of thiosulphate is greatest with the iodide and considerably less in the case of the bromide. No thiosulphate at all is produced during the hydrolysis of the chloride.

(6) The method described for the preparation of thionyl iodide in this paper, appears to be general in its scope and can be applied for the preparation of highly unstable compounds.

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