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STUDIES ON THE REACTIONS OF THIONYL FLUORIDE

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Abstract—Thionyl fluoride undergoes quantitative oxidation with chloramine-T and reduction with lithium aluminium hydride and sodium borohydride. At elevated temperatures, (> 150°C) it reacts with metals such as copper, silver, zinc and lead forming the corresponding metal sulphides, fluorides and sulphur dioxide. With the respective metal oxides, the metal fluorides and sulphur dioxide are formed.

INTRODUCTION

Although thionyl fluoride is a long known compound, there is still a wide scope to study its chemistry and explore the possible uses in diverse fields.

While carrying out investigations on the preparation and properties of sulphur oxyhalides, we have standardised a method for the preparation of sulphuryl chlorofluoride[1] which involves the fluorination of sulphuryl chloride by lead fluoride in acetonitrile medium. It is observed, in the present investigations, that under similar conditions thionyl chloride is fluorinated to thionyl fluoride.

In the present paper,the method adopted for the preparation of thionyl fluoride based on the above observations is described. Sulphur is present in +4 oxidation state in thionyl fluoride and it is possible to carry out oxidation or reduction of this compound with suitable reagents. Its reactions with chloramine-T ($CH_3C_6H_4SO_2NClNa$), lithium aluminium hydride, sodium borohydride and a few metals and metal oxides have been studied and results reported.

EXPERIMENTAL

Preparation of thionyl fluoride

The experimental procedure was similar to that reported earlier[1] for the preparation of sulphuryl chlorofluoroide. To a suspension of lead fluoride (70 g) in acetonitrile (100 ml) in the reaction flask, thionyl chloride (5 ml) in acetonitrile (15 ml) was added over a period of 45 min. The contents of the flask were refluxed for a further period of 30 min. The reaction products swept by the current of nitrogen (carrier gas) were condensed in a trap cooled by liquid nitrogen. The products were subjected to low temperature fractional condensation to purify thionyl fluoride by removing small amounts of silicon tetrafluoride and hydrogen chloride. The pure thionyl fluoride was stored in a dry glass globe provided with vacuum stopcocks. Yield: 70–75%.

The purity of the sample was checked by IR spectrum and chemical analysis. IR bands: Reported [2] (cm^{-1}) 530 m, 748 s, 806 s and 1333 s. Observed (cm^{-1}): 530 m, 750 s, 805 s, 1335 s. The gas was analysed for its sulphur and fluorine contents. Sulphur was estimated iodometrically after alkaline hydrolysis of the gas sample[3]. The fluorine content was determined in another aliquot after oxidation spectrophotometrically[4]. Analytical results indicated a purity of 99.5%. Found (in %) S, 37.10; F, 44.0. Calcd. (in %) S, 37.20; F, 44.19.

*Oxidation by chloramine-*T

A known amount (20–50 mg) of thionyl fluoroide was treated with decinormal chloramine-T solution (25 ml) (acidified with 5 ml of 2N hydrochloric acid or made alkaline with 5 ml of 2N sodium hydroxide) in a reaction vessel fitted with appropriate ground glass joints and vacuum stopcocks. After keeping for about 1 hr at room temperature, a 10% solution of potassium iodide (10 ml) was added (this was followed by the addition of 10 ml of 2N hydrochloric acid when the oxidation was carried out in alkaline medium). The liberated iodine was titrated with standard sodium thiosulphate solution. A blank was also run and correction applied. From the amount of chloramine-T consumed, the number of equivalent of the oxidant used up per mole of thionyl fluoride was calculated. The results of a few experiments are presented in Table 1.

Reduction with lithium aluminium hydride

A known quantity (25–50 mg) of thionyl fluoride was introduced into a reaction vessel containing a suspension of lithium aluminium hydride (250–300 mg) in dry tetrahydrofuran. A white solid separated out following a vigorous reaction. After about 2 hr, the vessel was flushed with nitrogen, the exit gases passing through a bubbler holding a suspension of cadmium hydroxide in dilute sodium hydroxide solution. Lithium aluminium hydride in excess was destroyed by the addition of ethylacetate and water. 2N hydrochloric acid (10 ml) was added after the vigorous reaction subsided and the solution was warmed. Hydrogen sulphide liberated was held in the bubbler as cadmium sulphide. The amount of sulphide was estimated iodometrically. Fluoride present in the reaction vessel was estimated by spectrophotometric method [4]. The results of these experiments are given in Table 2.

Reduction with sodium borohydride

Thionyl flouride (25–50 mg) dissolved in benzene (5 ml) in a reaction vessel was treated with a solution of sodium borohydride (1.0 g) in diglyme (15 ml). 3–4 hr later the reaction vessel was swept with a nitrogen stream and the excess sodium borohydride was destroyed by adding water. The contents were acidified with hydrochloric acid. The hydrogen sulphide evolved and the fluorine content of the solution were estimated as already described. The results of these experiments are included in Table 2.

Reaction with metals and metal oxides

The metal or metal oxide in the form of a fine powder and a known amount of thionyl fluoride were taken in a pyrex reaction tube (25 × 4 cm) provided with suitable joints and stopcocks. The reaction tube was heated in a tubular furnace to a temperature of 150–350°C, where the reaction was observed to occur. The reactants were kept at that temperature for 10–15 hr. The gaseous products were identified by their IR spectra. The solid products were identified by qualitative analyses and X-ray powder diffraction technique. The "*d*" spacings found from the powder pattern were compared with the values reported in literature for individual compounds.

The following metals and metal oxides were used:—

Metals. Copper, silver, zinc and lead.

Metal oxides. Cupric oxide, silver oxide, zinc oxide and lead dioxide.

Table 1. Oxidation of thionyl fluoride by chloramine-T

Expt. No.	Medium	Amount of SOF_2 taken (mole x 10^{-4})	Amount of chloramine-T consumed (equivalent x 10^{-4})	No. of equivalents of CAT consumed per mole of SOF_2
1	Acidic (0.3N HCl)	4.710	9.316	1.98
2		3.407	6.785	1.99
3		4.233	8.507	2.01
4	Alkaline (0.3N NaOH)	5.128	10.230	1.99
5		3.616	7.191	1.99
6		3.384	6.653	1.98

Table 2. Reduction of thionyl fluoride by lithium aluminium hydride and sodium borohydride

		Lithium aluminium hydride			Sodium borohydride		
		Expt.			Expt.		
		1	2	3	1	2	3
Amount of SOF_2 taken (mole x 10^{-4})		5.58	3.56	3.74	5.16	5.95	4.52
Amount of sulphur (mole x 10^{-4})	Expected	5.58	3.56	3.74	5.16	5.95	4.52
	Found as H_2S	5.57	3.53	3.69	5.11	5.92	4.46
	% reduction	99.8	99.0	98.7	99.1	99.5	98.5
Amount of fluoride (mole x 10^{-4})	Expected	11.16	7.12	7.48	10.32	11.90	9.04
	Found	11.05	6.99	7.42	10.21	11.79	8.95
	% Fluoride found	99.0	98.4	99.1	98.9	98.9	99.0

RESULTS AND DISCUSSION

Of the several methods described in literature[5–10] for the preparation of thionyl fluoride, the one suggested by Tullock and Coffman[10] is supposed to be the most convenient for laboratory scale preparation. The present method is an alternative method. The fluorination reaction may be represented as

$$SOCl_2 + PbF_2 \xrightarrow{CH_3CN} SOClF + PbClF$$

$$SOClF + PbF_2 \xrightarrow{CH_3CN} SOF_2 + PbClF.$$

The reaction is expected to occur in two steps. It appears that the second step is as fast as the first one resulting in the replacement of two chlorine atoms by fluorine atoms simultaneously. As result, no chlorofluoride is detected in the product.

The residue in the reaction vessel is found to contain lead chlorofluoride as the X-ray powder pattern indicated. This is to be expected in the light of the thermodynamic data. The energetics involved in the formation of lead chlorofluoride are more favoured compared to lead chloride.

Oxidation of thionyl fluoride

Chloramine-T oxidises thionyl fluoride in acid, alkaline and neutral media. The oxidation of S(+4) to S(+6) is quantitative. Two equivalents of the oxidant are consumed by 1 mole of thionyl fluoride as the results in Table 1 indicate. This is expected for the reaction

$$SOF_2 + 2H_2O + (O) \rightarrow H_2SO_4 + 2HF.$$

This reaction is quantitative and hence could be adopted for the quantitative determination of sulphur in a sample of thionyl fluoride.

Reduction of thionyl fluoride

The results in Table 2 indicate that both lithium aluminium hydride in THF and sodium borohydride in diglyme reduce thionyl fluoride quantitatively. These complex metal hydrides react with thionyl fluoride giving a solid complex containing metal sulphide and metal fluoride. The complexes on acidification, liberate hydrogen sulphide quantitatively. The fluoride present in the reaction vessel can be estimated and accounted quantitatively for that expected from the amount of thionyl fluoride taken. The exact nature of the complexes, however, could not be studied. Characterisation of the complexes will help to throw some light on the mechanism of reduction.

Reaction with metals and metal oxides

It has been reported [5] that thionyl fluoride does not react with metals even at 125°C, but no experimental details are given. The present studies indicate that it does not react with metals or metal oxides at room temperature (25 ± 5°C). However, at elevated temperatures (150–350°C) it reacts with metals and metal oxides.

The main products of reaction with metals are the corresponding metal sulphides, sulphur dioxide and metal fluorides. It is necessary to point out that it is rather difficult to account quantitatively for the products of these reactions owing to secondary reactions of the reaction products. It is also observed that the metal fluorides react with glass releasing traces of silicon tetrafluoride. Thionyl fluoride alone does not attack glasss in the temperature range (150–350°C) employed for the study. The metal sulphide may react with sulphur dioxide giving rise to sulphate, oxide, etc. The reaction with the metals chosen may be broadly indicated in terms of the following equations

$$4Cu + 2SOF_2 \xrightarrow{250^\circ C} Cu_2S + 2CuF_2 + SO_2$$

$$6Ag + 2SOF_2 \xrightarrow{250\text{–}300^\circ C} Ag_2S + 4AgF + SO_2$$

$$3Zn + 2SOF_2 \xrightarrow{350\text{–}400^\circ C} ZnS + 2ZnF_2 + SO_2$$

$$3Pb + 2SOF_2 \xrightarrow{180\text{–}190^\circ C} PbS + 2PbF_2 + SO_2.$$

In the case of the reaction with metal oxides, the products are invariably the metal fluorides and sulphur dioxide. However, here again, it is difficult to account quantitatively for the reaction products for reasons already mentioned above for metals. In addition, these reactions give rise to metal sulphates also.

The reactions with metal oxides may be represented in terms of the following equations

$$CuO + SOF_2 \xrightarrow{280\text{–}300^\circ C} CuF_2 + SO_2$$

$$Ag_2O + SOF_2 \xrightarrow{250\text{–}275^\circ C} 2AgF + SO_2$$

$$ZnO + SOF_2 \xrightarrow{350\text{–}380^\circ C} ZnF_2 + SO_2$$

$$PbO_2 + SOF_2 \xrightarrow{250\text{–}300^\circ C} PbF_2 + SO_2 + 1/2O_2.$$

It may be noted that oxygen is liberated in addition to sulphur dioxide in the reaction with lead dioxide. Lead dioxide alone does not give out oxygen in that temperature range. Lead sulphate is also formed in this reaction, probably as a result of reaction of lead dioxide with sulphur dioxide[11]. Similarly, the formation of traces of sulphate is observed in other cases also.

It will be of interest to compare the reactions of thionyl fluoride with metals and metal oxides with those of thionyl chloride with the respective metals and metal oxides. Both thionyl chloride and thionyl fluoride react with metals forming sulphur dioxide, the corresponding metal sulphides and the metal halides. The reaction with metals in the presence of excess of thionyl chloride results in the formation of sulphur chloride (S_2Cl_2) along with the metal sulphide and metal chloride [12–14]. However, when thionyl fluoride reacted with metals under these conditions, the formation of sulphur fluoride (S_2F_2) is not observed.

With metal oxides, both thionyl chloride and thionyl fluoride give metal halides and sulphur dioxide. However, thionyl chloride, on reacting with lead dioxide produces sulphuryl chloride in addition to lead chloride and sulphur dioxide.

$$PbO_2 + 2SOCl_2 \rightarrow PbCl_2 + SO_2 + SO_2Cl_2.$$

On the other hand the reaction of thionyl fluoride with lead dioxide does not give rise to sulphuryl fluoride (SO_2F_2).

REFERENCES

1. D. K. Padma, V. Subrahmanya Bhat and A. R. Vasudeva Murthy, *J. Fluorine Chem.* **11**, 187 (1978).
2. J. Kenneth O'Loane and M. Kent Wilson, *J. Chem. Phys.* **23**, 1313 (1955).
3. A. Kurtenacker and R. Wollack, *Z. Anorg. Allg. Chem.* **161**, 201 (1927).
4. D. K. Pakma and S. K. Vijayalakshmi, *J. Ind. Inst. Sci.* **58**, 280 (1976).
5. H. S. Booth and F. C. Mericola, *J. Am. Chem. Soc.* **62**, 640 (1940).
6. U. Wannagat and G. Mennicken, *Z. Anorg. Allg. Chem.* **278**, 310 (1955).
7. K. Wiechert, *Z. Anorg. Allg. Chem.* **261**, 310 (1950).
8. H. C. Clark and H. J. Emeleus, *J. Chem. Soc.* 190 (1958).
9. F. Seel and L. Riehl, *Z. Anorg. Allg. Chem.* **282**, 293 (1955).
10. C. W. Tullock and D. D. Coffman, *J. Org. Chem.* **25**, 2016 (1960).
11. D. L. Hammick, *J. Chem. Soc.* **111**, 379 (1917).
12. W. C. Schumb and C. H. Hamblet, *J. Am. Chem. Soc.* **57**, 260 (1935).
13. H. B. North and A. M. Hageman, *J. Am. Chem. Soc.* **34**, 890 (1912).
14. A. M. Hageman, *J. Am. Chem. Soc.* **35**, 352 (1913).