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Short Communication

The reaction of sulphur tetrafluoride with pyridine

D. K. PADMA

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012 (India)

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Sulphur tetrafluoride is known to behave as an electron acceptor with tertiary amines, forming weak adducts [1]. Thus it has been shown by vapour pressure measurements that sulphur tetrafluoride forms a 1:1 adduct with pyridine (Py) [2] and in this report the successful isolation of the following four adducts between sulphur tetrafluoride and pyridine is recorded: $SF_4 \cdot Py$, $SF_4 \cdot 2Py$, $SF_4 \cdot 4Py$ and $SF_4 \cdot 8Py$.

A solution of sulphur tetrafluoride (10 g) in 50 cm^3 of Freon (CCl_3F) was prepared at —78 °C [3] and to this various solutions of Freon containing different amounts of pyridine also at —78 °C were added. A gradual reaction occurred between the two reagents, a white adduct separating out from the mixture. The composition of the adduct was found to depend on the ratio of the reagents employed. Thus in the presence of a large amount of pyridine, a complex of composition $SF_4 \cdot 8Py$ was formed. However, as the pyridine content was decreased, adducts containing decreasing proportions of the amine were obtained corresponding to the compositions $SF_4 \cdot 4Py$, $SF_4 \cdot 2Py$ and $SF_4 \cdot Py$. The adducts were separated from the solution by filtration at —78 °C and freed from the reactants by washing with cold (—78 °C) Freon. Samples were dried at the pump at the same temperature and stored in an atmosphere of nitrogen at —78 °C. All operations were effected under dry conditions.

The composition of these adducts were established by the following chemical analyses:

Addition of aqueous hydroiodic acid (67%) at —78 °C reduced the sulphur in a sample of the compound (100 - 200 mg) to hydrogen sulphide, the latter being swept out in a current of nitrogen (over a period of 0.5 h) and absorbed by an alkaline suspension of cadmium hydroxide. In order to effect complete reduction, the reaction products were warmed up to 100 °C. The yellow cadmium sulphide formed was estimated iodometrically [4]. The calculated percentage of sulphur present is presented in Table 1.

The fluorine content was estimated by hydrolysis of a sample of the compound (100 - 200 mg) with cold alkali [KOH (4 mol l^{-1})]. This led to

TABLE 1

Analysis of the adducts of sulphur tetrafluoride and pyridine

Compound	Sulphur estimation				Fluorine estimation			
	Wt. of sample taken/mg	Sulphur present/mg	Calcd. %	Obtd. %	Wt. of sample taken/mg	Fluorine present/mg	Calcd. %	Obtd. %
$SF_4 \cdot Py$	120.00	19.84	17.11	16.54	792.00	320.00	40.65	40.40
	150.00	26.88		17.92	238.00	95.00		39.90
$SF_4 \cdot 2Py$	54.00	6.08	12.03	11.26	196.00	55.00	28.57	28.06
	130.00	15.68		12.00	480.00	140.00		29.17
$SF_4 \cdot 4Py$	134.30	9.92	7.50	7.38	432.20	74.50	17.92	17.64
	188.00	13.44		7.15	384.40	70.00		18.20
$SF_4 \cdot 8Py$	160.00	7.44	4.33	4.65	1124.00	105.00	10.27	9.35
	340.00	14.56		4.28	520.00	54.00		10.39
$SF_2 \cdot Py$	115.00	23.36	21.48	20.32	873.00	220.00	25.50	25.20
	138.00	29.12		21.10	218.00	54.00		24.70

the conversion of fluorine into the soluble fluoride ion; the colour of the solution becomes red during this process but addition of acid or the passage of time leads to the disappearance of this colour. The solution was made up to volume at room temperature (20 °C) and aliqouts taken for estimation of fluoride ion by titration with thorium nitrate using Alizarin Red and Methyl Blue as indicators [5]. The results obtained are also included in Table 1.

From the analytical results given in this table it follows that four adducts with the molecular formulae $SF_4 \cdot Py$, $SF_4 \cdot 2Py$, $SF_4 \cdot 4Py$ and $SF_4 \cdot 8Py$ are formed. It is interesting to note that these adducts are stable only below −30 °C and that above this temperature they undergo partial decomposition to give sulphur tetrafluoride (identified by its IR spectrum), a brown viscous liquid in the case of $SF_4 \cdot Py$ and white solids in the case of the other three adducts. The brown liquid (Table 1) corresponds to the molecular formula $SF_2 \cdot Py$, its IR spectrum demonstrating coordination through the nitrogen of the amine and an S—F bond frequency of *ca.* 840 cm^{-1}. A further interesting feature of the spectrum is the high shift of the 410 cm^{-1} band of pyridine to 480 cm^{-1}. The same high shift has also been observed in the case of the adduct between pyridine and hydrogen fluoride. Several other iminofluorides have been obtained from sulphur tetrafluoride and amines [6, 7] but pyridine iminosulphur fluoride has not hitherto been reported. The white solids mentioned above also exhibit an S—F bond frequency at *ca.* 840 cm^{-1} with all their available pyridine in an associated state.

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References

1 E. L. Muetterties, W. D. Phillips and W. C. Smith, U.S. Pat., 2,897,055 (1958); Chem. Abstr., 54 (1960) 1564.
2 E. L. Muetterties, J. Amer. Chem. Soc., 82 (1960) 1082.
3 D. Naumann and D. K. Padma, Z. Anorg. Allgem. Chem., 401 (1973) 53.
4 B. S. Rao and M. R. A. Rao, Proc. 10th Int. Congr. Chem., 3 (1938) 462.
5 H. H. Willard and O. B. Winter, Ind. Eng. Chem. Anal. Ed., 5 (1933) 7.
6 B. Cohen and A. G. MacDiarmid, Angew. Chem., 75 (1963) 207.
7 S. M. Williamson, Progr. Inorg. Chem., 7 (1966) 54.