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HYDROLYSIS OF THIOPHOSPHORYL FLUORIDE

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SUMMARY

The hydrolysis of thiophosphoryl fluoride has been studied both in acid and alkaline medium. The products are phosphate, fluoride and varying amounts of sulphide, sulphite, thiosulphate and elemental sulphur depending on experimental conditions. The probable mode of formation of the different sulphur species has been explained on the basis of sulphur in a higher oxidation state in the thiophosphoryl fluoride molecule.

INTRODUCTION

An earlier communication [1] reports the preparation of pure thiophosphoryl fluoride and its oxidation, reduction reactions. This paper deals with the hydrolytic reactions of thiophosphoryl fluoride under different experimental conditions. Thiophosphoryl fluoride undergoes hydrolysis giving rise to fluoride, phosphate and varying proportions of sulphur, sulphide, sulphite and thiosulphate depending on experimental conditions. The phosphorus sulphur bond

(1.87Å) in thiophosphoryl fluoride is observed to be unusual in the sense it is shorter than the expected P = S (1.93Å). Triple bond character and ionicity are invoked to explain this multiple bond shortening [2,3]. The present results of hydrolytic reactions seem to lend further support for such a picture. The details of this investigation are reported in this paper.

EXPERIMENTAL

The pure gas, thiophosphoryl fluoride prepared [1] by the fluorination of thiophosphoryl chloride by sodium fluoride in acetonitrile medium is stored in a previously evacuated two litre glass globe. Known amounts of the gas are monitored and taken for hydrolytic reactions.

A known aliquot of the pure gas is taken in a previously evacuated glass reaction tube (4" height x 2" diameter) fitted with light weight vacuum stopcocks and ground glass joints. The gas is condensed in the tube by liquid nitrogen. To the condensed gas is added either (1) a suspension of cadmium hydroxide in alkali (mixture of 20 ml of sodiumhydroxide (2N) and 5 ml of cadmium acetate (10%)) or (2) dilute hydrochloric acid or nitric acid (20 ml)/concentrated hydrochloric acid or nitric acid (2 ml). The coolant is withdrawn and the reactants are allowed to attain room temperature (25°C). Reaction sets in as observed by the formation of yellow cadmium sulphide in the case of alkaline hydrolysis, or sulphur precipitation in the case of dilute acids and concentrated hydrochloric acid, or evolution of reddish brown nitrogen peroxide in the case of concentrated nitric acid. The cadmium sulphide formed is separated by filtration and estimated iodometrically.

The filtrate is made up to a known volume and aliquots are taken for the estimation of (1) sulphite and thiosulphate by iodometry; (2) Fluoride is determined spectrophotometrically [4] using cerium (IV) sulphate reagent. (3) Phosphate is precipitated as ammonium phosphomolybdate [5] and determined volumetrically. In the case of acid hydrolysis, the contents are made alkaline by the addition of 25 ml sodium hydroxide (4N) containing 10 ml of cadmium acetate. Any sulphide present in the reaction mixture gets fixed as cadmium sulphide. Sulphur that has precipitated out is associated with cadmium sulphide. The sulphide and elemental sulphur are oxidised to sulphate by sodium peroxide. The total sulphur is estimated gravimetrically as barium sulphate. In another aliquot the sulphide is estimated iodometrically. The amount of elemental sulphur formed is computed from the two results. The results of alkaline and acid hydrolysis are presented in Tables I and II.

RESULTS AND DISCUSSION

The hydrolysis of thiophosphoryl fluoride both in acid and alkaline medium goes to completion in about an hour. Phosphorus in thiophosphoryl fluoride is in +5 oxidation state and gets converted to phosphoric acid or sodium phosphate on hydrolysis. The fluoride ion is released as hydrogen fluoride which remains in solution. Both fluoride and phosphate could be estimated quantitatively. The other products in alkaline hydrolysis are sulphide, sulphite and thiosulphate. No elemental sulphur is produced. In acid medium the products are sulphur, sulphide and thiosulphate. No sulphite is present. With the oxidising acid, concentrated nitric acid, the sulphur in thiophosphoryl fluoride gets converted quantitatively to sulphate.

TABLE I

Alkaline hydrolysis of thiophosphoryl fluoride

Concentration of alkali	Expt. No.	Amount of P ₂ S ₅ in mg.	Sulphide* (% of total sulphur)		Sulphite* (% of total sulphur)		Thio-sulphate* (% of total sulphur)		Total Sulphur in mg.		Phosphorus in mg.		Fluoride in mg.	
			Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.
4N	1	72.5	3.244 (16.7)	3.488 (17.95)	12.580 (64.8)	19.420	18.620	19.312	19.420	18.620	18.720	34.110	34.430	
	2	88.6	3.968 (16.77)	4.786 (20.21)	14.550 (61.5)	23.670	22.760	23.304	23.670	22.760	22.880	41.600	42.080	
2N	1	64.9	2.930 (16.89)	3.185 (18.35)	11.160 (64.28)	17.360	16.680	17.280	17.360	16.680	16.750	30.650	30.820	
	2	104.4	4.300 (15.43)	5.400 (19.31)	17.920 (64.28)	27.880	26.810	27.620	27.880	26.810	26.960	49.050	49.600	
1N	1	55.8	2.372 (15.96)	2.690 (18.05)	9.768 (64.8)	14.900	14.310	14.830	14.900	14.310	14.400	26.300	26.510	
	2	52.2	2.153 (15.44)	2.690 (19.30)	8.960 (64.27)	13.940	13.350	13.803	13.940	13.350	13.470	24.500	24.790	
0.1N	1	122.00	4.710 (14.45)	4.300 (13.19)	23.600 (72.41)	32.590	31.350	32.610	32.590	31.350	31.490	57.700	57.950	
	2	244.5	9.390 (14.31)	8.770 (13.43)	46.970 (71.93)	65.310	62.820	65.130	65.310	62.820	63.100	115.000	116.10	
0.05N	1	93.600	3.250 (13)	3.300 (13.2)	18.370 (73.5)	25.000	24.000	24.920	25.000	24.000	24.150	44.100	44.460	
	2	140.2	4.850 (12.95)	5.000 (13.36)	27.500 (73.43)	37.440	36.000	37.350	37.440	36.000	36.170	66.300	66.590	

* expressed in milligrams of sulphur.

TABLE II

Acid hydrolysis of thiophosphoryl fluoride

Acid strength	Expt. No.	Amount of P ₂ S ₅ in mg.	Sulphide*		Thio Sulphate*		Elemental sulphur*	Sulphate*	Total Sulphur in mg		Total Phosphorus in mg		Total Fluoride in mg	
			(% of total sulphur)	(% of total sulphur)	(% of total sulphur)	(% of total sulphur)			Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.
Hydrochloric acid 2N	1	36.5	0.838 (8.59)	6.876 (70.5)	1.935 (19.89)	-	-	9.650	9.750	9.352	9.426	17.270	17.340	
	2	120.2	2.665 (8.30)	22.320 (69.5)	6.752 (21.03)	-	-	31.737	32.100	30.910	31.000	56.900	57.000	
Nitric acid 2N	1	127.3	3.848 (11.32)	28.030 (82.45)	2.020 (5.94)	-	-	33.898	34.000	32.700	32.850	60.000	60.460	
	2	138.9	4.220 (11.37)	29.980 (80.54)	2.800 (7.57)	-	-	37.000	37.100	35.650	35.850	65.500	66.000	
Concentrated hydrochloric acid	1	71.2	4.820 (25.35)	9.649 (50.76)	4.500 (23.67)	-	-	18.900	19.070	18.360	18.380	33.600	33.830	
	2	105.7	6.850 (24.28)	14.940 (52.99)	6.320 (22.39)	-	-	28.110	28.230	27.150	27.270	50.000	50.200	
Concentrated Nitric acid	1	66.6	-	-	-	17.718	-	17.718	17.790	17.180	17.196	31.500	31.620	
	2	140.0	-	-	-	37.310	-	37.310	37.400	36.050	36.130	66.200	66.410	

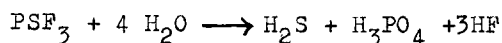
* expressed as milligrams of sulphur

In alkaline hydrolysis, the sulphide content varies from 13 to 16% over the concentration range 0.05N to 4N alkali while the sulphite and thiosulphate vary between 13 to 20% and 73 to 61% respectively. The yield of sulphide and sulphite increases at higher concentration of alkali while the thiosulphate decreases. This trend is similar to that observed when elemental sulphur [6], sulphur chloride [7] and sulphur bromide [8] are hydrolysed by alkali.

In the case of acid hydrolysis (2N), no sulphite is formed whereas about 20% elemental sulphur is released. The yield of sulphide is around 8% and that of thiosulphate is 70%. In concentrated hydrochloric acid the yield of sulphide increases to 25% and thiosulphate decreases to 53%. The amount of elemental sulphur remains around 22%. Concentrated nitric acid oxidises all the sulphur to sulphuric acid.

Earlier reports [9,10] of the hydrolytic studies of thiophosphoryl fluoride indicate the presence of sulphide in the alkaline medium. No quantitative evaluation of sulphide and other sulphur compounds were made. As the estimation of sulphur in thiophosphoryl fluoride was carried out by oxidation with sodium peroxide in alkaline medium, the formation of sulphite and thiosulphate escaped the attention of the earlier workers.

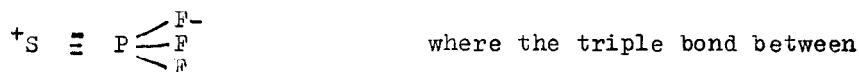
If thiophosphoryl fluoride were to undergo hydrolysis in terms of the equation



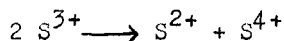
all the sulphur should have come out in the form of hydrogen sulphide. But the results of the present investigations show

less than 20% is converted into sulphide. Sulphite, thiosulphate and sulphur are the other products.

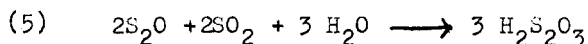
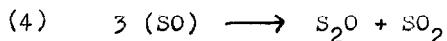
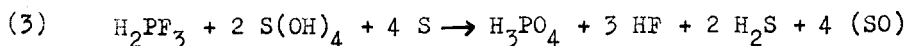
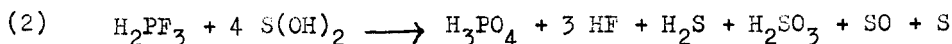
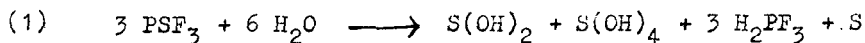
The results of the hydrolytic reactions can be explained on the basis of the formation of highly reactive intermediate species, $S(OH)_2$ and $S(OH)_4$. In such species the oxidation state of sulphur will be +2 and +4 respectively. It is reasonable to expect such primary products of hydrolysis from one of the resonance structures of the thiophosphoryl fluoride molecule



phosphorus and sulphur could be present. The oxidation state of sulphur in this form is +3. This could also be visualized as made up of two species S(II) and S(IV).



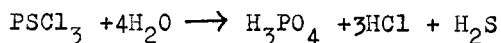
These highly reactive species can give rise to a variety of products such as sulphide, sulphite, thiosulphate and elemental sulphur. These reactions could be represented by the following equations:



It has to be pointed out that it is not possible to evaluate quantitatively the extent of each one of these reactions because of

complexity. However, such postulates can qualitatively account for the formation of sulphur compounds. The intermediate compound H_2PF_3 is known [11] but it cannot be isolated here as it undergoes further reactions with the sulphur species.

It is of interest to compare the nature of hydrolysis of thiophosphoryl fluoride with thiophosphoryl chloride. When the hydrolysis of thiophosphoryl chloride is carried out in a two phases system (a solution of thiophosphoryl chloride in carbon tetrachloride is shaken with alkali (2N) containing cadmium hydroxide suspension for three hours on a waterbath) all the sulphur is quantitatively converted into hydrogensulphide [12]. The hydrolytic reaction could be represented by the equation:



On the other hand it has been found in the present investigation that the hydrolysis if carried out in a homogeneous medium (a solution of thiophosphoryl chloride in dioxan is stirred with sodium hydroxide (2N) containing cadmium hydroxide on waterbath for one hour) over 75% of the sulphur is converted to sulphide and the rest as sulphite and thiosulphate (Table III) In the case of thiophosphoryl fluoride only 16% of the sulphur gets converted to sulphide and the rest is present as sulphite and thiosulphate. This difference namely the increased yield of sulphide in the alkaline hydrolysis of thiophosphoryl chloride could be attributed to the lower value of the electronegativity of chlorine and consequently a decrease in the multiple bond character between phosphorus and sulphur.

TABLE III

Alkaline hydrolysis of thiophosphoryl chloride

Medium	Concentration of alkali	Expt. No.	Amount of PSCl_3 mg	Sulphide* (% of total sulphur)	Sulphite* (% of total sulphur)	Thiosulphate* (% of total sulphur)	Total Sulphur Expt.	Total Sulphur Calcd.
Carbon tetra-chloride (CCl_4)	2N	1	374.4	70.73	-	-	70.73	70.84
		2	502.3	94.89	-	-	94.89	95.04
Dioxan	2N	1	123.9	18.31 (78.12)	0.052 (0.22)	5.077 (21.66)	23.44	23.44
		2	125.5	18.35 (77.31)	0.055 (0.23)	5.201 (21.91)	23.61	23.74

* expressed in milligrams of sulphur

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