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A STUDY ON THE REACTION OF SILICON TETRAHALIDES WITH PHOSPHORUS PENTOXIDE AND OF ALKALI METAL FLUOROSILICATES WITH PHOSPHORUS PENTOXIDE AND SULPHUR TRIOXIDE

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SUMMARY

Silicon tetrahalides, SiX_4 (X=F, Cl, Br) and the fluorosilicates of sodium and potassium react with phosphorus pentoxide above 300°C. The tetrahalides give rise to the corresponding phosphoryl halides and silica, while the fluorosilicates form the corresponding metal fluorophosphates and silicon tetrafluoride. The reaction of the fluorosilicates of sodium and potassium with sulphur trioxide occurs at room temperature to give rise to the corresponding metal fluorosulphates and silicon tetrafluoride.

INTRODUCTION

It is well known that a silicon halogen bond undergoes the thermodynamically favoured reaction with oxygen containing compounds such as water, oxides and hydroxides very easily at room temperature [1] but high temperatures of the order of 700-800°C are needed in the reactions of silicon tetrafluoride with aluminium hydroxide [2] and arsenic (III) oxide [3].So it was of interest to study the

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reaction of phosphorus pentoxide on silicon halides and on fluorosilicates of sodium and potassium. Kolditz et al [4] have reported the reaction of sulphur trioxide on potassium fluoride and it was of interest to study the nature of the reaction of sulphur trioxide with fluorosilicates of sodium and potassium which contain the fluorosilicate ion. The details of these studies are presented below.

EXPERIMENTAL

1 Reactions of silicon tetrahalides with phosphorus pentoxide

a) Reaction of silicon tetrafluoride with phosphorus pentoxide

Into a quartz reaction vessel (30cm long having a capacity of 300 ml and fitted with appropriate ground glass joints and vacuum stopcocks) an excess of phosphorus pentoxide (previously sublimed in a stream of oxygen), ($\sim$1.0g, $\sim$3-5mmol) is taken and a known amount of silicon tetrafluoride ($\sim$0.208g; $\sim$2.0 mmol) is condensed over it. The reactants are heated for 4 hours at 300°C. The infrared spectrum of the product gases (recorded on a Perkin Elmer 599 spectrometer) indicated the characteristic absorption bands of phosphoryl fluoride [5] and unreacted silicon tetrafluoride. No other volatile products of silicon and phosphorus such as hexafluorodisiloxane or phosphorus pentafluoride were detected. The reaction mixture was further heated for another four hours at 400°C, but reaction did not go to completion. The examination of the solid products indicated the presence of silica and unreacted phosphorus pentoxide. This silica produced probably forms a coating on phosphorus pentoxide and prevents further reaction. So fresh samples of phosphorus pentoxide are introduced and the reactants heated to 400°C for 4 hours. Now the reaction goes to completion as observed from the disappearance

of the absorption bands due to silicon tetrafluoride in the infrared spectrum. The phosphoryl fluoride formed is condensed out and estimated [6]. The percentage is found to be of the order of 91-98% based on the amount of silicon tetrafluoride taken indicating that it is the major fluoride formed.

b) Reaction of silicon tetrachloride with phosphorus pentoxide

In a similar manner, to an excess of phosphorus pentoxide (~1.2g, ~4.2mmol) is condensed a known amount of silicon tetrachloride (~0.400g, ~2-3mmol) and heated for 6 hours at 500°C. The gas-phase infrared spectrum shows the formation of phosphoryl chloride [7] as one of the products of reaction. The nonvolatile product is silica. In this case also, fresh samples of phosphorus pentoxide are needed to drive the reaction to completion. The phosphoryl chloride formed is condensed out and estimated and the percentage is found to lie in the range 96-98% based on the amount of silicon tetrachloride taken.

c) Reaction of silicon tetrabromide with phosphorus pentoxide

The reaction of silicon tetrabromide (~1.0g, ~2.9mmol) with phosphorus pentoxide (~1.5g, ~5.3 mmol) occured only above 550°C and brown fumes of bromine due to decomposition of silicon tetrabromide were also formed along with the phosphoryl bromide [7]. The other product of the reaction is found to be silica. In a separate experiment, silicon tetrabromide alone is heated to 550°C but no decomposition is observed indicating that the solids (P_4O_{10} and SiO_2) promoted the decomposition. On this account no quantitative data is possible.

2 Reactions of alkali metal (Na and K) fluorosilicates with phosphorus pentoxide

Into a quartz reaction vessel the solids in the ratio 3:1,(Na_2SiF_6/P_4O_{10}=2·925/1.021 ; K_2SiF_6/P_4O_{10}=2.850/0.995 in mmol) are taken and heated for 1 hour at 400°C. The infrared spectrum of the gas phase indicated the presence of silicon tetrafluoride only and complete absence of any other volatile fluorinated products. The solid product left in the reaction vessel was highly soluble in water in contrast to the sparingly soluble nature of M_2SiF_6 (M=Na or K). The infrared spectrum of the solid showed the characteristic absorption bands of monofluoro phosphate and difluoro phosphate by comparison with reported values [8]. The results are given in Table 1.

In separate experiments the amount of silicon tetrafluoride liberated during the reaction is estimated and found to be quantitative on the basis of alkali metal fluorosilicate taken.

When the reactant ratio was varied to 3:5 (Na_2SiF_6/P_4O_{10}= 3.248/5·511, K_2SiF_6/P_4O_{10}=3·150/5·459 in mmol) in addition to the above solid products, the gas phase infrared spectrum indicated the presence of phosphoryl fluoride along with silicon tetrafluoride.

3 Reaction of metal (Na and K) fluorosilicates with sulphur trioxide

Into a glass reaction vessel containing the metal fluorosilicate (Na_2SiF_6, 6·995 mmol or K_2SiF_6, 7.053 mmol) is introduced an excess of sulphur trioxide ($\sim$ 17.0 mmol). The solid is wetted with the sulphur trioxide. The solids are then stirred for 12 hours at room temperature. The gas phase infrared spectrum indicated the presence of silicon tetrafluoride as one of the products of reaction. The solid products were found to be the corresponding metal fluoro sulphate [9,10]. The results are presented in Table 2.

Table 1

Infrared spectral data of the solid compounds obtained in the reactions of Na_2SiF_6 (A) and K_2SiF_6 (B) with P_4O_{10}

Observed frequency for A	Observed frequency for B	Reported frequency for PO_3F_2	Reported frequency for PO_2F_2	Assignment
530 s	530 s	530 s		ν_{as} (PO_3)
690 s	700 m	705 s		ν_s (PF)
1000 vs	1000 s,br	1008 s		ν_s (PO_3)
1170 s	1160 m	1170 vs		ν_{as} (PO_3)
480 m	480 m,br		481 s	δ (OPF)
520 s	520 m,br		512 m	
			535 w	δ (PO_2)
830-860 s,br	830-860 s,br		834 s	ν_s (PF_2)
			857 vs	ν_{as} (PF_2)
1150 m	1150 m		1145 s	ν_s (PO_2)
1300 vs	1300 vs,br		1311 vs	ν_{as} (PO_2)
			1330 w	Combination

Table 2

Infrared spectral data of the solid compounds obtained in the reactions of Na_2SiF_6(A) and K_2SiF_6 (B) with SO_3

Observed frequency for A	Reported frequency for $NaSO_3F$	Observed frequency for B	Reported frequency for KSO_3F	Assignment
			408 vw	
570 sh	Not investigated	575 sh	570 sh	δ_s (SO_3)
590 s		590 s	590 s	δ_{as}(SO_3)
745 vs	740 m	740 vs	750 s	ν(S-F)
795 vs	785 s			
1085 s	1095 s	1070 m	1080 s	ν_s (SO_3)
	1275 s			combination
1250-1300 vs,br	1290 s	1230 vs,br	1280 s	ν_{as}(SO_3)
	2370 w			combination

This was confirmed by elemental analysis [11](calc. for $NaSO_3F$ (%) S, 26.25, F, 15.57, found (%) S, 26.53, F, 15.35; Calcd. KSO_3F (%), S, 23.19, F,13.75; found : S, 23.37, F, 13.45). The silicon tetrafluoride formed during the reaction was estimated and found to be quantitative on the basis of the metal fluorosilicate taken.

RESULTS AND DISCUSSION

From the experimental observations it is evident that all the three silicon halides react with phosphorus pentoxide at elevated temperatures in a similar way giving rise to their respective phosphoryl halides and silica. In the case of silicon tetrabromide excessive decomposition occurs resulting in the liberation of bromine along with phosphoryl bromide and silica as expected from the reaction. The overall reaction in the three cases could be represented as follows:

$$3\ SiF_4 + P_4O_{10} \xrightarrow{300°C\text{-}600°C} 4\ POF_3 + 3\ SiO_2 \qquad \text{(i)}$$

$$3\ SiCl_4 + P_4O_{10} \xrightarrow{500°C} 4\ POCl_3 + 3\ SiO_2 \qquad \text{(ii)}$$

$$3\ SiBr_4 + P_4O_{10} \xrightarrow{550°C} 4\ POBr_3 + 3\ SiO_2 + \text{decomposition-products.}$$

The reactions with silicon tetrafluoride and silicon tetrachloride go to completion only on introduction of fresh samples of phosphorus pentoxide and reheating the mixture to the desired temperatures. The possible reason could be that the silica formed coats the phosphorus pentoxide and hinders further reaction or there is a structural change of the phosphorus pentoxide from the normal H-form to the O'form, when heated. It has been reported that such a change occurs when it is heated at 450°C for 24 hours [12]. The O'form being polymeric could be less reactive.

The results of the reactions of sodium and potassium fluorosilica with phosphorus pentoxide indicate that the reaction products vary with the molar ratio of the reactants. When the metal fluorosilicate is in excess of phosphorus pentoxide, only silicon tetrafluoride is found to be the volatile product. On increasing the concentration of phosphorus pentoxide, phosphoryl fluoride is also formed along with silicon tetrafluoride. In both the cases the nonvolatile solids are the respective metal fluorophosphates and difluorophosphates. It is possible that the initial reaction is the decomposition of metal fluorosilicate to the metal fluoride and silicon tetrafluoride. The metal fluoride formed immediately reacts with phosphorus pentoxide to give the fluoro phosphates. When excess of phosphorus pentoxide is taken, the silicon tetrafluoride formed also reacts with phosphorus pentoxide as enumerated above to give phosphoryl fluoride. The overall reaction may be represented as follows:

$$3\ M_2SiF_6 + P_4O_{10} \longrightarrow 3\ SiF_4 + 2\ M_2PO_3F + 2\ MPO_2F_2 \quad \ldots\ (i)$$

$$3\ SiF_4 + P_4O_{10} \longrightarrow 4\ POF_3 + SiO_2 \quad \ldots\ (ii)$$

As reaction (ii) is not quantitative without fresh surface of phosphorus pentoxide, silicon tetrafluoride formed does not undergo complete reaction.

In contrast to the above reactions occuring at high temperatures, the reaction of sulphur trioxide with metal fluorosilicates occurs at room temperature giving rise to metal fluorosulphates and silicon tetrafluoride. The overall reaction may be represented as follows:

$$M_2SiF_6 + 2\ SO_3 \longrightarrow 2\ MSO_3F + SiF_4.$$

M = Na, K

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