

II. CHEMISTRY

Inorganic Chemistry

PHOSPHORUS CHLORIDE-ANTIMONY(V) CHLORIDE-ALKYL CHLORIDE COMPLEXES

SNEH LATA, M. S. SAINI, S. N. DUBEY and D. M. PURI*

Department of Chemistry, Kurukshetra University, Kurukshetra-132 119

(Received 26 December 1978)

The reactions of antimony (V) chloride with trichloro- and phenyldichlorophosphine have been studied in presence of alkylating agents such as tert butyl chloride, iso-butylchloride, tert-amyl chloride and cyclohexyl chloride. Solid products have been obtained. The structures of the complexes have been confirmed by infrared spectral study.

Keywords: Organophosphonium polychlorometallates

INTRODUCTION

REACTIONS of antimony pentachloride with different tertiary phosphines have been studied by Ruff (1963). Similar reactions of other metal chlorides with phosphorus trichloride and methyl/phenyl dichlorophosphine were reported by Bullock *et al.* (1972, 1973) and Puri *et al.* (1977, 1978a, b). However, little attempt seems to have been made to study such reactions with antimony pentachloride. The present authors report here the reaction systems $\text{R}(\text{P}(\text{Cl})_2)_2\text{-SbCl}_5\text{-R}'\text{Cl}$, where R is phenyl or chloride and R' is iso-butyl, tert-butyl, tert-amyl and cyclohexyl group.

EXPERIMENTAL

Anhydrous, pure antimony pentachloride (Koch-Light Lab. Ltd.) was used after analysis. Phenyl-dichlorophosphine was prepared by known method (Buchner & Lockhart Jr., 1951). Phosphorus trichloride (BDH) after analysis, was used as such. Alkyl chlorides were prepared from their respective alcohols using standard methods and dried over CaCl_2 and distilled before use. Solvent dichloromethylene was purified as usual (Puri *et al.*, 1977, 1978a,b) and the manipulations for syntheses and analyses of products were the same as used earlier (Puri *et al.*, 1977).

Syntheses of Complexes : A weighed quantity of SbCl_5 was dissolved in 20-30 ml. of dry deoxygenated solvent (CH_2Cl_2) and small excess of phosphorus chloride was added to the solution. Finally, alkyl chloride was added. After mixing the reactants, the reaction vessel was set aside till precipitation of the reaction product was complete. To avoid the formation of polymers, the order of adding the reagents was always kept the same. Further, the reagents were used in excess to minimise the formation of polymeric anions. The completion of the reaction depended upon the use of different alkylating agents. It took from few minutes to two days for complete precipitation. The solvent was decanted into

*To whom correspondence should be addressed.

another flask and precipitate was washed with solvent by decantation. The products (dirty white coloured solids) were dried in vacuum (1-2 mm) at room temperature for about one and a half hours. The amount of the reagents taken, the colour and the yield of the products have been given in Table I.

TABLE I

| S. No. | Amount (in gms) | | | Product colour, state and yield (in gms) | Cl | Analysis (%) | |
|--------|-------------------|-------|-------------------|--|------------------|----------------|------------------|
| | SbCl ₅ | R'Cl | RPCl ₂ | | | P | Sb |
| 1. | 2.20 | 0.68 | 1.0 | [Bu ^t PCl ₂] [SbCl ₅] Dirty white solid (3.5) | 61.09 (60.37) | 6.23 (5.66) | 24.29 (23.00) |
| 2. | 1.8 | 0.56 | 0.83 | [Bu ^{iso} PCl ₂] [SbCl ₅] Blackish solid (2.88) | 59.29 (60.37) | 5.45 (5.66) | 24.00 (23.00) |
| 3. | 2.5 | 1.0 | 1.15 | [C ₆ H ₁₁ PCl ₂] [SbCl ₅] Dirty white solid (4.20) | 56.30 (57.54) | 5.80 (5.57) | 20.00 (21.92) |
| 4. | 2.35 | 0.73 | 1.40 | [Bu ^t PhPCl ₂] [SbCl ₅] Dirty white solid (3.90) | 50.62 (49.49) | 6.02 (5.24) | 20.57 (21.32) |
| 5. | 2.82 | 0.875 | 1.70 | [Bu ^{iso} PhPCl ₂] [SbCl ₅] Light yellow solid (4.70) | 48.60 (49.49) | 4.93 (5.24) | 20.00 (21.32) |
| 6. | 1.93 | 0.775 | 1.15 | [C ₆ H ₁₁ PhPCl ₂] [SbCl ₅] Dirty white solid (3.20) | 48.73 (47.67) | 7.95 (8.55) | 21.07 (20.43) |
| 7. | 2.49 | 0.89 | 1.50 | [Am ^t PhPCl ₂] [SbCl ₅] White solid (4.00) | 48.24 (48.59) | 5.31 (5.60) | 19.00 (20.82) |

Analyses : The chloride and phosphorus were estimated by the methods already described (Puri *et al.*, 1977, 1978a, b). Antimony was estimated as antimony trisulphide (Vogel, 1961). The elemental analyses of the compounds have been given in Table I.

Physical Measurements : The infrared spectra were taken in the region 250-4000 cm⁻¹ by using Beckman IR-20 infrared spectrophotometer. The samples were prepared in nujol-mull between potassium bromide plates for examining 600-4000 cm⁻¹ spectral region and polythene sheets were used to examine the 250-600 cm⁻¹ spectral region.

RESULTS AND DISCUSSION

The reaction between trichloro- or phenyl dichloro-phosphine, antimony (V) chloride and alkylating agent was carried out at room temperature/in dichloromethylene solvent. The solid product separated and it took from few minutes to two days for

the complete precipitation of the product. The time taken for the completion of the reaction depended upon the use of alkyl chloride in a particular reaction. Depending upon this the order of reactivity of alkyl chlorides can be given as: tert. Amylchloride > Tert-Butyl chloride > Cyclohexyl chloride > isobutylchloride.

The products were fairly moisture sensitive and became sticky upon exposure to the atmosphere.

From the elemental analysis of the complexes and their infrared spectral study the complexes were considered to be univalent ionic species $[\text{RPCl}_4]^+ [\text{SbCl}_6]^-$. This was in agreement with the results obtained earlier by Beattie *et al.* (1967) and Reich and Preiss (1967).

The infrared spectra of alkyl trichlorophosphonium $[\text{RPCl}_3]^+$ and alkylphenyldichloro-phosphonium $[\text{RPhPCl}_2]^+$ cations (Table II), in all complexes, showed a weak absorption between $740\text{--}770\text{ cm}^{-1}$ which could be assigned to P-C (alkyl) vibrations (Puri *et al.*, 1977). Very strong absorptions at 998 cm^{-1} and 1440 cm^{-1} could be assigned to P-Ph vibrations in comparison with similar bands observed by Seel *et al.* (1961). P-Cl vibrations were observed in the form of very strong and shoulder absorptions between $600\text{--}630\text{ cm}^{-1}$ and between $480\text{--}500\text{ cm}^{-1}$ respectively. As suggested earlier (Puri *et al.*, 1977) the alkyl trichlorophosphonium ions and alkyl phenyldichloro-phosphonium ions could have C_{3v} and C_6 symmetries respectively.

TABLE II
Vibrational spectra

| S. No. | Complex | ν P-Cl | ν P-Cl (In cm^{-1}) | ν P-Ph | ν Sb-Cl |
|--------|---|------------|--------------------------------------|------------|-------------|
| 1. | $[\text{Bu}^t \text{PCl}_3] [\text{SbCl}_6]$ | 750 | 630,485 | — | 330,280 |
| 2. | $[\text{Bu}^{iso} \text{PCl}_3] [\text{SbCl}_6]$ | 770 | 625,490 | — | 330,280 |
| 3. | $[\text{C}_6 \text{H}_{11} \text{PCl}_3] [\text{SbCl}_6]$ | 760 | 610,500 | — | 335,275 |
| 4. | $[\text{Bu}^t \text{PhPCl}_2] [\text{SbCl}_6]$ | 740 | 620,495 | 998,1440 | 330,270 |
| 5. | $[\text{Bu}^{iso} \text{PhPCl}_2] [\text{SbCl}_6]$ | 740 | 600,490 | 1000,1435 | 325,280 |
| 6. | $[\text{C}_6 \text{H}_{11} \text{PhPCl}_2] [\text{SbCl}_6]$ | 750 | 610,490 | 1000,1440 | 325,275 |
| 7. | $[\text{Am}^t \text{PhPCl}_2] [\text{SbCl}_6]$ | 765 | 600,480 | 995,1440 | 325,280 |

$[\text{SbCl}_6]^-$ anion exists in many organic solvents as well as in solid state. In the i.r. spectra of these compounds the absorption at $325\text{--}335\text{ cm}^{-1}$ was observed and is comparable to the one observed at 348 cm^{-1} by Beattie *et al.* (1963, 1967) for $\text{PyH}^+ \text{SbCl}_6^-$. Very weak absorption at $270\text{--}280\text{ cm}^{-1}$ was also observed in these compounds and is comparable to 283 cm^{-1} vw (impurity) (Beattie *et al.*, 1963, 1967).

ACKNOWLEDGEMENTS

Thanks are due to the authorities of the university for providing facilities for this work. Two of us (M.S.S. & S.L.) are thankful to C.S.I.R for the financial help.

REFERENCES

- Beattie, I. R., Gilson, T., Lingston, K., Fawcett, V., and Ozin, G. A. (1967) The Vibrational spectra of some chloro-complexes of germanium, tin, phosphorus, arsenic and antimony. *J. chem. Soc., A*, 712-718.
- Beattie, I. R., and Webster, M. (1963) The infrared spectra of phosphorus and antimony pentachlorides and their ionization in acetonitrile. *J. chem. Soc.*, 38-42.
- Buchner, B., and Lockhart, L. B., Jr., (1951). An improved method of synthesis of aromatic dichlorophosphines. *J. Am. chem. Soc.*, **73**, 755-756.
- Bullock, J. I., Parrett, F. W., and Taylor, N. J. (1972) Some metal halide-phosphorus halide-alkyl halide complexes, Part I : Reactions with boron, aluminium, silicon, germanium and tin halides. *J. chem. Soc. Dalton*, **17**, 1843-1846.
- (1973) Some metal halide-phosphorus halide-alkyl halide complexes, Part II : Reactions with niobium and tantalum pentachlorides and tungsten hexachloride. *J. chem. Soc.*, **5**, 522-524.
- Puri, D. M., Dubey, S. N., Saini, M. S., and Gupta, D. C. (1979) Metal chloride-phosphorus halide-alkyl chloride complexes : Reactions with ferric chloride. *J. Indian chem. Soc.*, **56**, 201-202.
- Puri, D. M., and Saini, M. S. (1977) Reactions of BCl_3 , AlCl_3 , SnCl_4 and FeCl_3 with phenyldichlorophosphine and *t*-Butyl chloride : Isolation of solid complexes. *Indian J. Chem.*, **15 A**, 362-363.
- (1978) Metal chloride-phosphorus chloride-alkyl chloride complexes : Reactions with niobium and tantalum pentachlorides. *Proc. J. Indian natn. Sci. Acad.*, **44A**, 271-275.
- Reich, P., and Preiss, M. (1967) Molecular spectra of some solid halides of group V elements. *Z. Chem.*, **7** (3), 115 (Ger.) ; (1967) *Chem. Abstr.*, **V 66**, 109803C.
- Ruff, J. K. (1963) A simple preparation of substituted chlorophosphonium salts; the salt $\text{FPCl}_2\text{SbCl}_5$. *Inorg. Chem.*, **2**, 813-817.
- Steel, F., Ballreich, K., and Schmutzler, R. (1961) Über Fluorophosphin-Komplexe des Nickels. *Chem. Ber.*, **94**, 1173-1184.
- Vogel, A. I. (1961) *Quantitative Inorganic Analysis*. Longmans Green and Co. Ltd., 3rd Edn., 502.