© *Proc. Indian natn. Sci. Acad.*, **47**. A, No. 3, 1981, pp. 324-330.
Printed in India.

Inorganic Chemistry

METAL DERIVATIVES OF ORGANO-PHOSPHORUS COMPOUNDS PART VII : ANTIMONY(V) DERIVATIVES

SORAN SINGH, HEMANT K. SHARMA *and* D. M. PURI*

Department of Chemistry, Kurukshetra University, Kurukshetra 132 119, India

(*Received 24 July 1980; after revision 22 October 1980*)

Interactions between antimony(V) chloride and dialkyl/diaryl (Et-, Pr^i-, Bu^n-, Ph-) phosphites have been carried out in different molar ratios of reactants and under different conditions of temperature and solvent media. The products of the stoichiometry Sb [OP(O) (OR) (R)] Cl_4 (I), Sb [O_2P(O) (R)] Cl_3 (II), Sb [OP(O) (OR) (R)]$_2Cl_3$ (III), Sb [O_2P(O) (R)] [OP(O) (OR) (R)] Cl_2 (IV), Sb [OP(O) (OR)]$_2Cl$ (V), Sb [OP(O) (OR) (R)]$_3Cl_2$ (VI), Sb [O_2P(O) (R)] [OP(O) (OR) (R)]$_2Cl$ (VII), Sb [OP(O) (OR) (R)]$_4Cl$ (VIII), Sb [O_2P(O) (R)] [OP(O) (OR) (R)]$_3$ (IX) and Sb [OP(O) (OR) (R)]$_5$ (X) have been isolated and characterized by infrared spectral studies, and molecular weight data, and elemental analyses. Polymeric six coordinated structures involving —O—P—O— bridges have been assigned to these complexes.

Keywords: Antimony (V) Alkyl/Aryl Phosphonates

INTRODUCTION

ROSENHEIM *et al.* (1903) reported the formation of adducts of antimony(V) chloride with acetyl acetone. Malhotra *et al.* (1979) synthesised similar adducts of antimony(V) chloride with benzoyl acetone and triphenylphosphine sulphide. The complexes of tetrachloroantimony(V) alkoxides with oxygen and nitrogen donor ligands have been reported by Paul *et al.* (1976) and Chadha *et al.* (1979). However, very little work seems to have been carried out on the organo-phosphorus compounds of antimony(V) so far. With this interest in view, we thought it proper to extend our earlier work, i.e., Puri and Attam Parkash (1972*a*, *b*), (1975), (1978) and Puri and Singh (1980*a*, *b*, *c*, *d*, *e*, *f*) to the reactions of antimony pentachloride with dialkyl/aryl phosphites.

MATERIALS AND METHODS

Chemicals

Antimony(V) chloride (Fluka) was used as such. Diethyl phosphite (Fluka) and diphenyl phosphite (Aldrich) were used after distillation under reduced pressure. Di-isopropyl phosphite and di-n-butyl phosphite were prepared by the methods reported by Mandel'baum *et al.* (1967). These dialkyl phosphites were distilled under reduced pressure and their purity was determined by TLC and elemental analyses. Benzene was dried over sodium wire and distilled azeotropically. Due

*For correspondence

to highly hygroscopic nature of the reactants and products, all manipulations were carried out in dry glass apparatus with standard joints.

Analyses and Instruments

Chlorine and phosphorus were estimated gravimetrically. To estimate phosphorus, the compounds were oxidized with nitric acid and potassium permanganate solution (2 per cent), precipitated as phosphomolybdate, dissolved in dilute ammonia and precipitated as magnesium ammonium phosphate.

The infrared spectra of the complexes were recorded on Beckman Spectrophotometer (IR-20 model) in nujol mull or neat as required. The molecular weights were determined on Gallenkamp Semi-micro ebulliometer.

Reactions of Anhydrous Antimony(V) Chloride with Dialkyl/Diaryl Phosphites in different Molar Ratios

1. *In Benzene Solvent*: To an ice cooled known amount of anhydrous antimony(V) chloride in benzene was added a calculated amount of the respective dialkyl/diaryl phosphite in benzene dropwise and under anhydrous conditions. Hydrogen chloride and heat were evolved in the reaction mixture and orange solution turned yellow towards the end of mixing of phosphite. The reaction mixture on refluxing at 110–120° and under reduced pressure (~ 20mm) formed some white to brownish solid mass after 10–12 hours. It was refluxed for 30–40 hours and the reaction was completed in this period. Benzene was removed by distillation and the product was dried under reduced pressure at 80°. Solid and liquid parts were separated and analysed. The products were yellowish to brownish liquids and white to brownish solids.

2. *Without Solvent*: The conditions of the reactions were essentially the same as above, with the difference that solvent benzene was not used in the beginning. At the end of the reactions the solid products were washed with dry benzene and dried in vacuo at 80°. The products were white to brown solids and colourless to brownish liquids.

The analytical results have been reported in Table I.

Results and Discussion

The reactions between antimony(V) chloride and dialkyl/diaryl phosphites were studied in different molar ratios in refluxing benzene as well as without solvent. The reactions without using any solvent were faster than the reactions in benzene. Hydrogen chloride was evolved in both the reactions but alkyl/aryl chloride was also liberated at higher temperatures.

The reactions in benzene resulted in the formation of 1:1, 1:2 and 1:3 ratio products indicating the replacement of upto three chlorine atoms from antimony(V) chloride in solvent systems. In the reactions where no solvent has been used, the successive replacement of all the five chlorine atoms of antimony(V) chloride by phosphite units yielded 1:1 to 1:5 ratio products. However, the reactions of $SbCl_5$

TABLE I

Preparation and analytical data of antimony(V) chloride with dialkyl/diaryl phosphites

S. No.	Reactants		Yield (g)	Compound	Colour state	Ratio	Analysis % Found (Cal.)		
	$SbCl_5$ (g)	Dialkyl/diaryl phosphites (g)					Cl	P	Molecular weight
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1*	2.55	1.20	2.83	$SbCl_4$ [OP(O) $(OC_2H_5)_2$]	Brown viscous liquid	1:1	35.06 (35.37)	7.86 (7.73)	1370 (401)
2**	1.85	0.89	1.29	$SbCl_3$ [OP(O) (OC_2H_5)]	Brownish solid	1:1	32.51 (31.70)	8.75 (9.73)	—
3*	3.38	3.15	5.60	$SbCl_3$ [P(O) $(OC_2H_5)_2]_2$	Brownish viscous liquid	1:2	22.18 (21.13)	11.87 (12.36)	—
4**	2.39	2.26	2.53	$SbCl_2$ [P(O) $(OC_2H_5)_2$] [OP(O) (OC_2H_5)]	Brownish solid	1:2	15.89 (16.21)	14.67 (14.16)	—
5*	2.95	4.10	7.07	$SbCl_2$ [P(O) $(OC_2H_5)_2]_3$	Brown viscous liquid	1:3	11.85 (11.75)	14.05 (15.35)	—
6**	1.80	2.51	2.88	$SbCl_2$ [P(O) $(OC_2H_5)_2]_3$	Brown sticky solid	1:3	11.80 (11.75)	15.21 (15.38)	-
7*	1.55	2.17	3.15	$SbCl_2$ [P(O) $(OC_2H_5)_2$] [OP(O) (OC_2H_5)]	Yellowish viscous liquid	1:4	16.50 (16.21)	14.95 (14.16)	643 (438)
8**	2.23	3.08	3.39	SbCl [P(O) $(OC_2H_5)_2]_4$	White	1:4	4.69 (5.03)	17.12 (17.58)	—
9*	3.29	7.62	9.20	$SbCl_2$ [P(O) $(OC_2H_5)_2]_3$	Yellow viscous liquid	1:5	11.19 (11.75)	14.92 (15.38)	—
10**	2.36	5.45	5.22	Sb [P(O) $(OC_2H_5)_2]_5$	Yellowish viscous liquid	1:5	nil (nil)	18.75 (19.22)	—
11*	3.47	1.93	3.90	$SbCl_4$ [P(O) $(OC_3H_7)_2$]	Brownish viscous liquid	1:1	34.04 (33.13)	7.15 (7.22)	—
12**	2.11	1.17	2.47	$SbCl_3$ [OP(O) (OC_3H_7)]	Brown viscous liquid	1:1	29.71 (30.41)	7.99 (8.85)	—

(*continued*)

TABLE I (*continued*)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
13*	2.89	3.28	4.30	$SbCl_3$ $[P(O)(OC_3H_7)_2]_3$	Brown viscous liquid	1:2	19.36 (19.07)	10.74 (11.11)	—
				$SbCl_2$ $[OP(O)(OC_3H_7)]$ $[P(O)(OC_3H_7)_2]$	Brownish solid	1:2	14.16 (14.79)	13.08 (12.93)	—
14**	1.34	1.62	1.51	$SbCl_2$ $[OP(O)(OC_3H_7)]$ $[P(O)(OC_3H_7)_2]$	Brownish solid	1:2	13.99 (14.79)	13.17 (12.93)	—
15*	2.92	4.89	5.52	$SbCl_2$ $[OP(O)(OC_3H_7)]$ $[P(O)(OC_3H_7)_2]$	Yellowish viscous liquid	1:3	14.24 (14.79)	11.99 (12.93)	—
			0.41	$SbCl_2$ $[P(O)(OC_3H_7)_2]_3$	Yellowish solid	1:3	9.89 (10.32)	13.02 (13.52)	—
16**	1.45	2.45	2.29	$SbCl_2$ $[P(O)(OC_3H_7)_2]_3$	Brownish solid	1:3	10.32 (10.32)	13.06 (13.52)	—
17*	1.07	2.42	3.24	$SbCl_2$ $[P(O)(OC_3H_7)_2]_3$	Yellowish viscous liquid	1:4	10.08 (10.32)	13.64 (13.52)	1687 (687)
18**	1.69	3.77	1.15	$Sb(OP(O)(OC_3H_7)$ $[P(O)(OC_3H_7)_2]_3$	Brown sticky solid	1:4	nil (nil)	15.86 (16.79)	—
19*	1.61	4.47	5.35	$SbCl_2$ $[P(O)(OC_3H_7)_2]_3$	Yellowish viscous liquid	1:5	9.98 (10.32)	12.89 (13.52)	—
20**	0.87	2.45	1.57	Sb $[P(O)(OC_3H_7)_2]_5$	White solid	1:5	nil (nil)	15.78 (16.37)	—
21*	1.89	1.27	2.90	$SbCl_4$ $[P(O(OC_4H_9)_2]$	Brownish liquid	1:1	30.74 (31.09)	6.22 (6.78)	—
22**	1.25	0.84	1.63	$SbCl_4$ $[P(O)(OC_4H_9)_2]$	Brown liquid	1:1	32.19 (31.09)	7.40 (6.78)	—
23*	2.13	2.77	2.88	$SbCl_3$ $[P(O)(OC_4H_9)_2]_2$	Yellowish liquid	1:2	18.61 (17.34)	10.74 (10.09)	—
24**	1.78	2.34	1.08	$SbCl$ $[OP(O)(OC_4H_9)]_2$	Yellowish solid	1:2	8.06 (8.27)	14.13 (14.44)	—

(*continued*)

TABLE I (*continued*)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
25*	1.15	2.26	3.19	$SbCl_2$ [P(O) $(OC_4H_9)_2]_3$	Yellowish liquid	1:3	10.05 (9.20)	13.02 (12.05)	—
26**	1.91	3.73	1.955	SbCl [OP(O) (OC_4H_9)] [P(O) $(OC_4H_9)_2]_2$	White solid	1:3	4.89 (5.20)	13.79 (13.68)	—
27*	0.51	1.39	1.52	Sb [OP(O) (OC_4H_9)] [P(O) $(OC_4H_9)_2]_3$	White solid	1:4	nil (nil)	14.54 (14.84)	—
28**	1.19	3.92	2.54	Sb [P(O) $(OC_4H_9)_2]_5$	White solid	1:5	nil (nil)	14.81 (14.28)	—
29*	2.78	2.19	4.68	$SbCl_4$ [P(O) $(OC_6H_5)_2$]	Orange viscous liquid	1:1	28.05 (28.58)	6.32 (6.25)	—
30**	2.98	2.34	4.45	$SbCl_3$ [OP(O) $(OC_6H_5]$	Orange viscous liquid	1:1	27.50 (27.67)	7.15 (8.05)	—
31*	2.49	3.92	6.02	$SbCl_3$ [P(O) $(OC_6H_5)_2]_2$	Orange viscous liquid	1:2	14.85 (15.34)	8.57 (8.90)	—
32**	0.98	1.55	2.08	$SbCl_3$ [P(O) $(OC_6H_5)_2]_2$	Orange viscous liquid	1:2	16.14 (15.34)	7.86 (8.90)	—
33*	2.32	5.51	7.61	$SbCl_3$ [P(O) $(OC_6H_5)_2]_2$	Orange viscous liquid	1:3	14.12 (15.34)	9.19 (8.90)	—
34**	2.34	5.52	6.72	$SbCl_3$ [P(O) $(OC_6H_5)_2]_2$	Orange viscous liquid	1:3	14.21 (15.34)	9.67 (8.90)	—
35*	2.34	7.37	9.24	$SbCl_2$ [P(O) $(OC_6H_5)_2]_3$	Orange viscous liquid	1:4	8.23 (7.96)	10.81 (10.42)	—
36**	1.85	5.84	6.94	$SbCl_2$ [P(O) $(OC_6H_5)_2]_3$	Orange viscous liquid	1:4	8.66 (7.96)	9.82 (10.42)	—
37*	2.50	9.73	11.82	$SbCl_2$ [P(O) $(OC_6H_5)_2]_3$	Orange viscous liquid	1:5	8.24 (7.96)	10.91 (10.42)	1665 (892)
38**	2.63	10.35	12.24	$SbCl_2$ [P(O) $(OC_6H_5)_2]_3$	Orange viscous liquid	1:5	7.62 (7.96)	10.48 (10.42)	—

*Reactions in benzene solvent. **Reactions without solvent.

with di-n-butyl/diphenyl phosphites without solvent could form the products only upto 1:3 ratio indicating slow nature of the reactions with di-n-butyl/aryl phosphites. The products were colourless to brownish or yellowish liquids and white to brownish solids. The products were highly susceptible to atmospheric moisture and became sticky on exposure to moist air due to hydrolysis. The liquid products were soluble in benzene and other common organic solvents. The solid products were insoluble in organic solvents. The liquid products on heating to a higher temperature or refluxing in benzene for a longer period became insoluble showing an increase in their molecularity.

The 1 : 1 molar ratio reaction under two different conditions and reduced pressure may be represented as follows:

$$SbCl_5 + (RO)_2P(O)H \xrightarrow{< 80^\circ \text{ in } C_6H_6} \underset{(I)}{Sb\,[OP(O)\,(OR)\,(R)]\,Cl_4} + HCl\uparrow$$

$$SbCl_5 + (RO)_2P(O)H \xrightarrow{120^\circ \text{ without solvent}} Sb\,[OP(O)\,(OR)\,(R)]\,Cl_4 + HCl\uparrow$$

$$\downarrow \Delta \mid -RCl$$

$$\underset{(II)}{Sb\,[O_2P(O)\,(R)]\,Cl_3}$$

(R = Et-, Pr^i-, Bu^n-, Ph-)

The reaction is exothermic in nature.

The reactions in molar ratios of 1:2, 1:3, 1:4 and 1:5 gave the products of compositions $SbCl_3\,[P(O)\,(OR)_2]_2$ (III), $SbCl_2\,[OP(O)\,(OR)]\,[P(O)\,(OR)_2]$ (IV), $SbCl\,[OP(O)\,(OR)]_2$ (V), $SbCl_2\,[P(O)\,(OR)_2]_3$ (VI), $SbCl\,[OP(O)\,OR)]\,[P(O)\,(OR)_2]_2$ (VII), $SbCl\,[P(O)\,(OR)_2]_4$ (VIII), $Sb\,[OP(O)\,(OR)]\,[P(O)\,(OR)_2]_3$ (IX) and $Sb\,[P(O)\,(OR)_2]_5$ (X). The amount of reactants, yields and analytical data have been reported in Table I.

The infrared spectra of these complexes showed very strong to medium intensity bands in the range of 1220–1120 cm^{-1} which could be assigned to $\nu P = 0$ vibrations. Bellamy and Beecher (1952) and Bellamy (1958) had reported infrared absorption frequency at 1265 cm^{-1} for free phosphoryl group. The lowering of this frequency in the compounds could be attributed to the coordination of phosphoryl oxygen to the antimony atom of the neighbouring molecules; this type of lowering was also reported by Cotton *et al.* (1960). Weak to broad and sharp intensity bands were observed in the range of 1080–1020 cm^{-1}, which could be assigned to (P)-O-C bonds. The bands falling in the region of 980–750 cm^{-1} could be due to P-O-(C) linkages. Broad and very sharp peaks, occurring around 730 cm^{-1} and 680 cm^{-1}, were assigned to P-C bands. In diphenyl phosphite derivatives, νP-Ph bands were observed around 1010 cm^{-1} and 540 cm^{-1}. The presence of νP-C and νP-Ph bands in the spectra of these complexes indicates intramolecular rearrangement in the molecules to acquire stable configuration. Very sharp absorption bands observed at 610–600 cm^{-1} indicated the presence of P-O-Ph bonds. Weak and broad bands in the region 600–550 cm^{-1} could be linked to νSb-O (Beauchamp *et al.*, 1969) and bands at $\sim$ 480 cm^{-1} were due to $\nu O \rightarrow Sb$ frequencies observed by

Paul *et al.* (1976). Weak bands, observed around 350 cm^{-1} could be assigned to νSb-Cl frequencies,

The molecular weights of benzene soluble complexes in boiling benzene ebullioscopically indicated the ratio of observed molecular to calculated value weight to be higher than unity which indicates a polymerising tendency of these complexes.

Acknowledgement

The authors are thankful to the authorities of the Kurukshetra University for providing necessary facilities and one of us (S.S.) is thankful to U.G.C., New Delhi for financial assistance. He is also grateful to the authorities Ganjdundwara College, Ganjdundwara (Etah) for sanctioning study leave.

References

Beauchamp, A. L., Bennett, M. J., and Cotton, F. A. (1969) Molecular structure of tetraphenylantimony hyroxide. *J. Am. chem. Soc.*, **91**, 297.

Bellamy, L. J., and Beecher, L. (1952) The infrared spectra of some organophosphorus esters. *J. Chem. Soc.*, **Part I**, 475.

Bellamy, L. J. (1958) *The Infrared Spectra of Complex Molecules.* Methuen, London.

Chadha, S. L., Chander, Mohini and Gupta, P. K. (1979) Complexes of tetrachloroantimony(V) alkoxides with oxygen and nitrogen donor ligands. *Indian J. Chem.*, **17A**, 309.

Cotton, F. A , Barnes, R. D., and Bannister, E. (1960) Effect of complex-formation by phosphine oxides on their P-O stretching frequencies. *J. chem. Soc.*, **Part II**, 2199.

Malhotra, K. C., Mehrotra, Geeta and Chaudhary, S. C. (1979) Complexes of triphenylphosphine sulphide with some Lewis acids. *Indian J. Chem.*, **17A**, 421.

Mandel'baum, Ya. A., Itskova, A. L., and Mel'nikov, N. N. (1967) A new method for synthesis of dialkyl phosphites. *Khim. Org. Soedin. Fosfora, Akad. Nauk. SSSR*, Otd. *Obsch. Tekh. Khim.*, 288 (Russ.); *Chem. Abstr.*, **69**, (1968) 43338h.

Paul, R. C., Airon, Dev Kumar and Chadha, S. L. (1976) Complexes of 2,2,2-trichloroethoxytetrachloroantimony(V) with nitrogen and oxygen donors. *Indian J. Chem.*, **14A**, 51.

Puri, D. M., and Attam Parkash (1972*a*) Metal derivatives of dialkyl phosphites : Part I. *J. Indian Chem. Soc.*, **49**. 77.

——— (1972*b*) Metal derivatives of dialkylphosphites : Part II. *J. Indian Chem. Soc.*, **49**, 833.

——— (1975) Organic derivatives of zirconium : Part II. *Indian J. Chem.*, **13**, 384.

——— (1978) Metal derivatives of dialkylphosphites. Reactions with stannic chloride. *Acta Ciencia Indica*, **4**, 224.

Puri, D. M., and Singh, Soran (1980*a*) Metal derivatives of organophosphorus compounds : Part I. Tungsten(V) derivatives. *Indian J. Chem.* (*Accepted*).

——— (1980*b*) Metal derivatives of organophosphorus compounds : Part II. Nb(V) and Ta(V) derivatives. *J. Indian Chem. Soc.* (*accepted*).

——— (1980*c*) Metal derivatives of organophosphorus compounds : Part III. Vanadium(III) derivatives. *Proc. natn. Acad. Sci.* (*Allahabad*). (*Communicated*).

——— (1980*d*) Metal derivatives of organophosphorus compounds : Part IV. Oxovanadium(V) derivatives. *Indian J. Chem.* (*accepted*).

——— (1980*e*) Metal derivatives of organophosphorus compounds : Part V. Germanium(IV) derivatives. *Acta Ciencia Indica* (communicated).

——— (1980*f*) Metal derivatives of organophosphorus compounds. Part VI. Antimony(III) derivatives. *J. Indian chem. Soc.* (*accepted*).

Rosenheim, A., Lolwenstamm, W., and Singer, L. (1903) *Ber.*, **36**, 1833.