6. *The Infrared Spectra of Phosphorus and Antimony Pentachlorides and their Ionization in Acetonitrile.*

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The infrared spectra of phosphorus pentachloride and antimony pentachloride and several of their addition compounds have been examined. These show that phosphorus pentachloride in acetonitrile is effectively fully ionised to unsolvated PCl_4^+ and PCl_6^- (at concentrations of $\sim$1% w/v), also that antimony pentachloride in acetonitrile is ionised to $SbCl_6^-$ and, probably, *trans*-$[SbCl_4(MeCN)_2]^+$. Certain previous assignments for the PCl_4^+ ion and molecular PCl_5 are believed to have been due to the presence of phosphoryl chloride. The compound reported as $C_{14}H_{14}Cl_7P$ contains the PCl_6^- ion.

Many compounds of phosphorus(v) or antimony(v) display ionic or covalent character depending on their environment. Phosphorus pentachloride is known from *X*-ray data [1] to be present in the solid state in the fully ionised form $PCl_4^+PCl_6^-$. It is, however, readily soluble in carbon disulphide being then molecular PCl_5,[2] whereas for solutions of it in ionising solvents the equilibrium $2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$ has been suggested.[3] Similarly the 1 : 1 addition compound formed between phosphorus pentachloride and iodine monochloride is ionic in the solid state [4] ($PCl_4^+ICl_2^-$). In solution in carbon tetrachloride the main reaction appears to be [5] $PCl_6I \rightleftharpoons PCl_5 + ICl$, although in acetonitrile ionisation occurs: [5] $PCl_6I \rightleftharpoons PCl_4^+ + ICl_2^-$. Volatile $PCl_2(CF_3)_3$ is a conductor in acetonitrile [6]

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[1] Clark and Powell, and (independently) Wells, *J.*, 1942, 642.
[2] Wilmshurst and Bernstein, *J. Chem. Phys.*, 1957, **27**, 661.
[3] Payne, *J.*, 1953, 1052.
[4] Zelezny and Baenziger, *J. Amer. Chem. Soc.*, 1952, **74**, 6151.
[5] Popov and Schmorr, *J. Amer. Chem. Soc.*, 1952, **74**, 4672.
[6] Emeléus and Harris, *J.*, 1959, 1494.

" with the probable occurrence of solvation of the ions," but the closely related $PCl_3(CF_3)_2$ is effectively a non-conductor. Dichlorotrifluorophosphorane (m. p. ~ —130°) is slowly transformed[7] into the ionic compound tetrachlorophosphorus(V) hexafluorophosphate[8] (sublimes with decomposition at 135°). Antimony pentachloride shows a very high conductivity in acetonitrile[9] although the solid is molecular.[10] Dichlorotrifluoroantimony(V), a powerful fluorinating agent, has recently been prepared[11] in the ionic form $SbCl_4^+SbF_6^-$.

Emeléus and Harris[6] quote Λ_0 values (in acetonitrile) for $PCl_2(CF_3)_3$, PBr_5, PCl_5, and $(PhO)_3PCl_2$ of 66, 20 (data from ref. 12), 35 (from unpublished work by Payne), and 105 (data from ref. 13) ohm^{-1} cm.^{2} mole^{-1}. It is doubtful whether these are significantly different. To avoid greater than pairwise ionic interactions it has been suggested[14] that the concentration of a uni-univalent electrolyte should be $<3{\cdot}2 \times 10^{-7} D^3$ mole l.$^{-1}$ (*i.e.*, less than 0·015 mole l.$^{-1}$ in the case of acetonitrile). Most of the results for phosphorus compounds lie in a concentration range well above this figure, so that extrapolations based on a Λ–$\sqrt{c}$ plot must be treated with caution. From Walden's rule and previous work on conductance phenomena in acetonitrile[15] we might expect a Λ_0 value for PCl_5 in the region of 200 ohm^{-1} cm.^{2} mole^{-1}. If the PCl_5 values are treated on the basis of the ion pair $PCl_4^+PCl_6^-$, with no molecular PCl_5, an (unjustified) extrapolation of Payne's figures leads to a Λ_0 value of 70 ohm^{-1} cm.^{2} mole^{-1}. Kolditz and Preiss[9] worked at concentrations as low as 0·0004M (10 p.p.m. of water is 0·0005M in *water*) to obtain the extraordinarily high value of 368 ohm^{-1} cm.^{2} mole^{-1} for Λ_0, based on the uni-univalent electrolyte $SbCl_4^+SbCl_6^-$. The molecular weight of antimony pentachloride in acetonitrile corresponds to a monomer, while removal of the solvent leaves a solvate formulated[9] $[SbCl_4][SbCl_6]$,2MeCN. By contrast, phosphorus pentachloride may be recrystallised quantitatively unsolvated from the solvent.[3] Similarly silicon tetrachloride forms no adduct with acetonitrile,[16] although tin tetrachloride yields the 1 : 2 addition compound[17] $SnCl_4$,2MeCN. It appeared to us that a study of the ionisation of phosphorus and antimony pentachloride in acetonitrile and of the solvation of the ions produced, might conveniently be made by infrared spectroscopy in the cæsium bromide region.

Acetonitrile has one weak band at 377 cm.$^{-1}$ in the region of interest for this work (this band is allocated to a C–C–N wag[18]). The infrared spectrum of phosphorus pentachloride in the solid state (14—40 μ) shows two main bands, one of medium intensity at 649 cm.$^{-1}$ [cf. the infrared spectrum of silicon tetrachloride vapour[19] with ν_3 (f_2) at 621 cm.$^{-1}$] which may be assigned to ν_3 (f_2) of the PCl_4^+ ion, and a strong one at 448 cm.$^{-1}$ (cf. the a_2'' fundamental associated with the P–axial Cl antisymmetric stretching frequency[2] of molecular PCl_5 at 465 cm.$^{-1}$) which we assign to the antisymmetric stretching frequency of the PCl_6^- ion ν_3 (f_{1u}). Waddington and Klanberg[20] mention a further strong band at 584 cm.$^{-1}$ which they attribute to $\nu_1 + \nu_4$ of PCl_4^+ (by analogy with $SiCl_4$, although the band in $SiCl_4$ is much less intense than that reported for PCl_4^+). However, using the Raman data[21] for PCl_4^+, we find that $\nu_1 + \nu_4 = 673$ cm.$^{-1}$, nearly 100 wavenumbers different from the value quoted by Waddington and Klanberg. Further, although we frequently observed a band

[7] Kennedy and Payne, *J.*, 1959, 1228.

[8] Kolditz, *Z. anorg. Chem.*, 1956, **284**, 144.

[9] Kolditz and Preiss, *Z. anorg. Chem.*, 1961, **310**, 242.

[10] Ohlberg, *J. Amer. Chem. Soc.*, 1959, **81**, 811.

[11] Kolditz and Lieth, *Z. anorg. Chem.*, 1961, **310**, 236.

[12] Harris and Payne, *J.*, 1956, 4617.

[13] Harris and Payne, *J.*, 1956, 3038.

[14] Fuoss, *J. Amer. Chem. Soc.*, 1935, **57**, 488.

[15] See Harned and Owen, " Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 1958.

[16] See, *e.g.*, Alikberov, Shklover, Syromyatnikova, and Belanovskii, *Russ. J. Inorg. Chem.*, 1960, **5** 1094.

[17] See, *e.g.*, Brown and Kubota, *J. Amer. Chem. Soc.*, 1961, **83**, 4175.

[18] Herzberg, " Infra-Red and Raman Spectra," Van Nostrand, New York, 1945.

[19] Smith, *J. Chem. Phys.*, 1953, **21**, 1997.

[20] Waddington and Klanberg, *J.*, 1960, 2339.

[21] Gerding and Houtgraaf, *Rec. Trav. chim.*, 1955, **74**, 5.

at 580 cm.$^{-1}$, the intensity varied greatly in relation to that of the fundamental at 649 cm.$^{-1}$ depending on the sample used. In one preparation where we took exceptional precautions to avoid hydrolysis, this band appeared only very weakly. As phosphoryl chloride has a very intense band near this frequency (581 cm.$^{-1}$ in benzene, 585 in acetonitrile, 588 in the pure liquid and 581 cm.$^{-1}$ from Raman data [22] on the pure liquid) we assume that the band is due to the hydrolysis product.

Wilmshurst and Bernstein [2] made a complete vibrational assignment for molecular phosphorus pentachloride on the basis of D_{3h} symmetry. We have examined the spectrum of phosphorus pentachloride in carbon disulphide and in benzene in the range 14—40 μ (see Table). Our results are generally in good agreement with those of the earlier workers in the overlapping spectral regions. However, we find only a weak band in the region of 338 cm.$^{-1}$, which we attribute to hydrolysis. Thus it is probable that the *e′* fundamental assignment for phosphorus pentachloride in benzene solution is incorrect and that the band observed is due to phosphoryl chloride. (Phosphoryl chloride has a medium strength band at 336 cm.$^{-1}$ in benzene, 338 in acetonitrile, 336 in the pure liquid and at 337 cm.$^{-1}$ from Raman work [22] on the pure liquid.) It is probable that the band at 301 cm.$^{-1}$ found in the infrared spectra of phosphorus pentachloride in benzene and carbon disulphide is the *e′* fundamental, in agreement with that found by Raman work on the benzene solution but assigned to a combination band. We do not question the assignment in the vapour, as examination of the spectrum given in ref. 2 shows clearly that the band centred at

Infrared spectra in the CsBr region of antimony and phosphorus pentachlorides and related compounds under various conditions.

Compound	State	Window material	Range (μ)	Absorption bands (cm.$^{-1}$)					
$SbCl_5$	In C_6H_6	*a*	17—40	397s	372s		339m *		
	In CCl_4	CsBr	14—40	398s	374s				
$CH_3CN,SbCl_5$	In C_6H_6	*a*	17—40	398vw	371s		341w *		
	Mull	CsBr	14—40	400w	369s	351s	340w *		
	In CH_3CN	*a*	16—25·5, 28—40			348m($SbCl_6^-$)			
$C_5H_5N,SbCl_5$	In C_6H_6	CsBr	17—40			435vw †	358s	328vw	
	Mull	*b*	14·5—40	673m †	643w †	438m †	353vs, br	344vs, br	
$C_5H_6N,SbCl_6$	Mull	CsBr	14—40	662m($C_6H_6N^+$)		383vw	336vvs, br($SbCl_6^-$)		
	In CH_3CN	*a*	16—25·5, 28—40			348m($SbCl_6^-$)			
PCl_5	In C_6H_6	CsBr	16—40	578vs	485w ‡	441vs	336w ‡	301m	274m
	In CS_2	CsBr	14—24, 27—40	575vs	488w ‡	441vs	334w ‡	300m	274m
	Mull	CsBr	14—40	649s(PCl_4^+)	580m ‡	488w ‡	448vs(PCl_6^-)	333w ‡	
	In CH_3CN	NaCl + *a*	14—25·5, 28—40	658s(PCl_4^+)	588m ‡	488w, sh ‡	452s(PCl_6^-)	339w ‡	
$C_{14}H_{14}Cl_7P$	Mull	CsBr	14—40	654w($C_7H_7^+$)	630w($C_7H_7^+$)	435s(PCl_6^-)			
	In CH_3CN	*a*	16—25·5, 28—40	654w($C_7H_7^+$)	632w($C_7H_7^+$)	516w(?)	451vs(PCl_6^-)		
$PCl_5,SbCl_5$	Mull	CsBr (*b*)	14—40	650s(PCl_4^+)	585w ‡		336vs, br($SbCl_6^-$)		
	In CH_3CN	NaCl + *a*	14—25·5, 28—40	658s(PCl_4^+)	586m ‡		347s($SbCl_6^-$)		
C_5H_5N,PCl_5 §	In C_6H_6	CsBr	16·5—40	585m *	495s	483s	~448s, br	337vw *	
	Mull	*b*	14—40	676m †	641vw †	606vw	584w	484s, br	432s, br
	In CH_3CN	*a*	16—25·5, 28—40	597w	493s	448s	339vw		
$POCl_3$	Smear	CsBr	14—40	588vvs	483m	336m			
	In C_6H_6	*a*	16·5—40	581vs	481m	336m			
	In CH_3CN	*a*	16—25·5, 28—40	585s, br	485m	338m			

a = 0·8-mm. thick Polythene windows. *b* = 0·25-mm. thick Polythene windows. * Impurity due to hydrolysis. † Peak due to co-ordinated pyridine. ‡ $POCl_3$ impurity. § The two forms of PCl_5 (solid state and CS_2 solution) apparently gave the same 1 : 1 addn. compound when treated with pyridine.

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[22] Ziomek and Piotrowski, *J. Chem. Phys.*, 1961, **34**, 1087.

335 cm.$^{-1}$ increases in intensity with increasing temperature, unlike the impurity peaks. The shift of about 35 cm.$^{-1}$ in this band between vapour and solution does not seem to be anomalously high.

The infrared spectrum of phosphorus pentachloride in acetonitrile (14—40 μ) shows two main peaks, together with other peaks which we attribute to phosphoryl chloride. The peak at 658 cm.$^{-1}$ may be assigned to PCl_4^+ with confidence, while that at 452 cm.$^{-1}$ could reasonably be assigned to PCl_6^-, although the solvated ion *trans*-$[PCl_4(MeCN)_2]^+$ would also be expected to have a single peak in this region. It was, therefore, necessary to examine a compound containing PCl_4^+ ions but having no band likely to occur near to 450 cm.$^{-1}$. We selected the well-established compound $PCl_5,SbCl_5$, which has been studied conductometrically in acetonitrile.[23] In the solid state this gives two main bands, at 650 [$\nu_3(f_2)$ of PCl_4^+] and 336 cm.$^{-1}$; the latter we assign to $\nu_3(f_{1u})$ of the $SbCl_6^-$ ion. The observed spectrum suggests that this compound is ionic in the solid state. In solution in acetonitrile we observed two main bands, one due to PCl_4^+ at 658 cm.$^{-1}$ and one due to $SbCl_6^-$ at 347 cm.$^{-1}$. There was no band observable at 452 cm.$^{-1}$, proving that the PCl_4^+ ion is effectively unsolvated in acetonitrile. An additional point of interest is that the $SbCl_6^-$ ion must be quite stable (as expected) in acetonitrile solution, as free chloride ion would lead to a PCl_6^- peak. Two factors of importance remain, the possibility that solvated phosphorus pentachloride is present (presumably as the 1 : 1 adduct $MeCN,PCl_5$) and the stability of the PCl_6^- ion. The compound py,PCl_5 [24] shows two main bands associated with P–Cl stretching vibrations in the cæsium bromide region in solution in benzene, where it is undissociated. These bands * occur at about 490 and 448 cm.$^{-1}$. As we observe only one peak around 450 cm.$^{-1}$ for acetonitrile solutions of phosphorus pentachloride (assigned to the PCl_6^- ion) it appears that there is no solvated phosphorus pentachloride present in such solutions. Finally, an equimolar mixture of phosphorus pentachloride and tetramethylammonium chloride in acetonitrile showed no evidence for a PCl_4^+ peak at 658 cm.$^{-1}$. Our results prove that when phosphorus pentachloride is dissolved in acetonitrile at concentrations of the order of 1% (w/v) the ionisation to PCl_4^+ and PCl_6^- is complete and that no solvation of the PCl_4^+ ion occurs. The assignment of the vibration at 336 cm.$^{-1}$ in $PCl_4^+SbCl_6^-$ to ν_3 (f_{1u}) of the $SbCl_6^-$ ion was confirmed by preparing pyridinium hexachloroantimonate(v), which showed one strong main peak at 348 cm.$^{-1}$ in acetonitrile and one at 336 cm.$^{-1}$ in the solid state, apart from those due to the pyridinium ion. The compound reported as $C_{14}H_{14}Cl_7P$ shows a strong band at 435 cm.$^{-1}$ in the solid state, shifted to 451 cm.$^{-1}$ in acetonitrile solution and attributable to the PCl_6^- ion.

In the case of antimony pentachloride our spectra of solutions in carbon tetrachloride and in benzene are generally in accord with earlier work.[25] Antimony pentachloride in solution in acetonitrile shows only one observable strong peak, at 348 cm.$^{-1}$, identical with the position previously found for $pyH^+SbCl_6^-$ in acetonitrile. By analogy with tin tetrachloride [18] [ν_3 (f_2) = 403 cm.$^{-1}$] and the $InCl_4^-$ ion [26] [ν_3 (f_2) = 337 cm.$^{-1}$] we should expect one strong band for the $SbCl_4^+$ ion, well above 400 cm.$^{-1}$. Our spectra thus exclude the discrete $SbCl_4^+$ ion. For *trans*-$[(MeCN)_2SbCl_4]^+$ we should expect a single peak at a frequency rather higher than that for the $SbCl_6^-$ ion (348 cm.$^{-1}$) and therefore lying under the fairly broad acetonitrile band centred at 377 cm.$^{-1}$. Similarly we cannot establish in this case the absence of the 1 : 1 adduct molecular $MeCN,SbCl_5$, as this compound on dissolution in benzene shows a main single peak associated with the Sb–Cl stretching vibrations at 371 cm.$^{-1}$, again lying under the acetonitrile absorption. The addition compound $py,SbCl_5$ shows one main peak at 358 cm.$^{-1}$, when dissolved in benzene.

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* It is unlikely that the band at 448 cm.$^{-1}$ is due solely to liganded pyridine.

[23] Kolditz, *Z. anorg. Chem.*, 1957, **289**, 128.

[24] Beattie and Webster, *J.*, 1961, 1730.

[25] Wilmshurst, *J. Mol. Spectroscopy*, 1960, **5**, 343.

[26] Woodward and Taylor, *J.*, 1960, 4473.

The 1 : 1 addition compound of antimony pentachloride with acetonitrile shows, in the solid state, two main bands, one at 369 cm.$^{-1}$ which could reasonably be attributed to *trans*-$[(MeCN)_2SbCl_4]^+$ and one at 351 cm.$^{-1}$ which may be attributed to $SbCl_6^-$. It is, however, possible that the compound is molecular and the two bands arise from crystal-field resolution of the single peak at 371 cm.$^{-1}$ found for a solution in benzene.

EXPERIMENTAL

Preparation of Reagents and Compounds.—Solvents were fractionally distilled from calcium hydride and then distilled from calcium hydride *in vacuo* into ampoules which were then sealed. Phosphorus pentachloride was sublimed *in vacuo* into ampoules. Antimony pentachloride was treated with chlorine, distilled under reduced pressure, and distilled *in vacuo* into ampoules. The compound $PCl_5,SbCl_5$ was prepared by mixing the reagents in carbon disulphide solution. Pyridinium hexachloroantimonate was prepared from chloroform solutions of pyridinium chloride and antimony pentachloride.

Analyses and Characterisation.—The adduct py,PCl_5, as described previously;[24] $PCl_5,SbCl_5$ by titration until no more precipitation of adduct occurred (mole ratio 1 : 1·1); py,$SbCl_5$ (Found: Cl, 47·1. Calc. for $C_5H_5Cl_5NSb$: Cl, 46·9%). $pyH^+SbCl_6^-$ (Found: C, 14·6; H, 1·6; Cl, 51·4. Calc. for $C_5H_6Cl_6NSb$: C, 14·5; H, 1·5; Cl, 51·3%); MeCN,$SbCl_5$, m. p. 172—177° (uncorr.) (lit.,[9] 175°).

Infrared Spectra.—Handling of reagents and solvents was carried out in a dry-box or a vacuum sytem. The infrared cells for the chloro-compounds in solution were made of Teflon. Cæsium bromide is not a suitable window material for use with acetonitrile, and usually Polythene or occasionally rock-salt windows were used. Nujol mulls were measured through cæsium bromide windows. The Nujol was heated carefully with molten sodium to ensure that it was anhydrous (it picks up water very rapidly while stored over sodium and may be considered to be anhydrous only if the sodium is bright). The spectrum of the adduct py,PCl_5 in solution in benzene was also run in a vacuum-cell. All spectra were run on a Perkin-Elmer model 221 instrument equipped with grating and rock-salt and cæsium bromide optics.

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[27] Bryce-Smith and Perkins, *J.*, 1962, 1339.