The Characterisation of the Ions $[PCl_nBr_{4-n}]^+$ $(0 \leqslant n \leqslant 4)$ by means of Solid State ^{31}P Nuclear Magnetic Resonance

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Summary The characterisation of the complete series of ions $[PCl_nBr_{4-n}]^+$, $(0 \leqslant n \leqslant 4)$, including the previously unknown species $[PCl_2Br_2]^+$ and $[PBr_3Cl]^+$, has been accomplished in the solid state using ^{31}P n.m.r. spectroscopy.

IN the series of possible tetrahalogenophosphonium ions $[PCl_nBr_{4-n}]^+$, only the species $[PCl_4]^+$ and $[PBr_4]^+$ are well known. The trichlorobromophosphonium ion was first reported by Salthouse and Waddington[1] in the compound $[PCl_3Br]^+[BCl_4]^-$, and its presence in other complex series suggested. A detailed vibrational characterisation of the $[PCl_3Br]^+$ ion in this compound and in the hexafluorophosphate $[PCl_3Br]^+[PF_6]^-$ has recently been published from one of our laboratories.[2] The other mixed species have not been positively identified.[3] Antimony(V) chloride when treated with phosphorus(III) bromide gave an unstable solid of composition $PSbBr_3Cl_7$, for which various ionic formulations such as $[PBr_3Cl]^+[SbCl_6]^-$ are possible.[4] On the basis of the vibrational spectra,[5] however, there is some doubt as to whether this structure is found.

We report here the characterisation of the complete series of ions, including the hitherto unknown $[PCl_2Br_2]^+$ and $[PClBr_3]^+$, by means of solid state ^{31}P n.m.r., using a high resolution spectrometer.[6] The chemical shift of the tetrachlorophosphonium ion has been determined in solid compounds by Andrew's rotating sample method,[7–9] by broad line measurements,[10–13] and by a high resolution technique.[6] Values between -96 and -73 p.p.m. relative to 85% phosphoric acid were obtained, depending on the counter-ion and also the method used; only the high resolution method gives results of high accuracy, however.[6,9] Shifts for the tetrabromophosphonium ion of between $+68$ and $+104$ p.p.m. have been similarly obtained.[6,10,11]

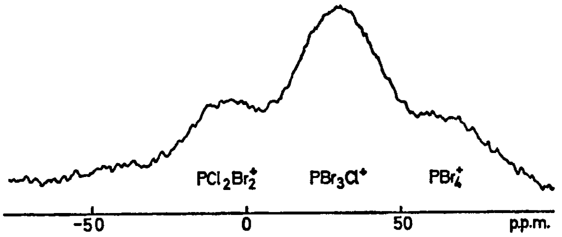
The ^{31}P resonance of the $[PCl_3Br]^+$ ion occurs at -49 ± 1 p.p.m. in the solid tetrachloroborate. Spectra were also recorded for a number of solid mixtures obtained from reaction of a phosphorus trihalide PX_3, a halogen Y_2, and a boron trihalide BZ_3 (X, Y, Z = Cl or Br). Peaks corresponding to $[PCl_4]^+$ or $[PBr_4]^+$ could be readily characterised if present. Variations of shift between -50 and -38 p.p.m. were found for the $[PCl_3Br]^+$ ion in different mixtures (Table), but an unambiguous assignment is possible in each case because of the large shift differences with respect to other species. Two other signals may be observed between $[PCl_3Br]^+$ and $[PBr_4]^+$ for some samples, in the ranges $-8{\cdot}1$ to $-3{\cdot}5$ p.p.m. and $+29$ to $+30$ p.p.m. (Table).

Range of chemical shifts for tetrahalogenophosphonium ions in the solid state

Ion	$\delta^{31}P$ (p.p.m. rel. to 85% H_3PO_4)
PCl_4^+	-96 — -73[a]
PCl_3Br^+	-50 — -38
$PCl_2Br_2^+$	$-8{\cdot}1$ — $-3{\cdot}5$
$PClBr_3^+$	$+29$ — $+30$
Br_4^+	$+66$ — $+104$[b]

[a] Refs 6—13. [b] Refs. 6, 10, and 11.

These are therefore assigned to the $[PCl_2Br_2]^+$ ion and the $[PBr_3Cl]^+$ ion respectively. The spectrum (1024 scans; speed $25{\cdot}6$ p.p.m. min^{-1}; T.C. $0{\cdot}1$s) of a typical mixture with $[PBr_3Cl]^+$ as the main constituent is shown in the Figure. Chemical shift differences between adjacent members of the series are entirely consistent with successive replacement of chlorine by bromine in a phosphorus(v) compound. Similar shift differences are observed in phosphoryl halides, phosphonitrilic compounds and pyrocatechyl derivatives.[14] Characteristic shift values are thus extremely useful as an aid to structural determination in phosphorus(v)-mixed halide systems. Vibrational spectroscopic measurements are completely in agreement with these conclusions.[5] Attempts to prepare pure compounds containing $[PCl_2Br_2]^+$ and $[PBr_3Cl]^+$ ions are continuing.



FIGURE

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