The Preparation and Characterization by Raman Spectroscopy of $PI_4^+AsF_6^-$ containing the Tetraiodophosphonium Cation

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The thermodynamically unstable $PI_4^+AsF_6^-$ containing the first and only example of a tetrahedral PI_4^+ cation, formally a derivative of the unknown PI_5, was prepared by the reaction of PI_3 and $I_3^+AsF_6^-$ at low temperatures and characterized by Raman spectroscopy.

While the phosphorus pentahalides PF_5, PCl_5, and PBr_5 are well known and fully characterized compounds[1,2] the pentaiodide PI_5 is unknown. Although in 1978 the synthesis of PI_5 (postulated as $PI_4^+I^-$) was reported,[3] it is more than likely that only an equimolar mixture of PI_3 and I_2 was analysed. On the basis of a simple thermodynamic cycle using a similar approach as described previously,[4] we estimated a heat of formation from the elements for solid $PI_4^+I^-$ of $\Delta H^\circ_f = +43$ kcal mol^{-1}† [*cf.* ΔH°_f, $PBr_4^+Br^-$ (s) estimated as -10 kcal mol^{-1} (1 cal = 4.184 J)].† On the other hand a compound of the composition $PI_4^+AlI_4^-$ was prepared and its crystal structure determined.[5] In the black PI_4AlI_4 there are strong I · · · I cation · · · anion interactions ($d_{I\cdots I} = 3.39$—3.45 Å; sum of covalent radii: 2.66 Å,[6] sum of van der Waals radii: 4.40 Å[7]) and the PI_4 and AlI_4 units are connected to a three-dimensional structure by weak iodine–iodine bonds (the black colour is due to electron transitions in the remaining I_2 units). In the solid state the polymeric compound might be regarded as an intermediate between $PI_3/I_2/AlI_3$ and $PI_4^+AlI_4^-$. We were interested to synthesize a PI_4^+ salt containing an iodine free anion to establish the existence of a binary phosphorus(v) iodine species. This is important because the conjugated base (the neutral PI_5) is still unknown and PI_4^+ would represent the first example of a binary phosphorus iodine species containing the phosphorus in its highest oxidation state.

On the basis of a simple Born–Haber cycle (Scheme 1) we showed that the reaction of $I_3^+AsF_6^-$ with PI_3, leading to $PI_4^+AsF_6^-$ and I_2, is thermodynamically favourable (equation 1). Subsequently we identified $PI_4^+AsF_6^-$ from its Raman

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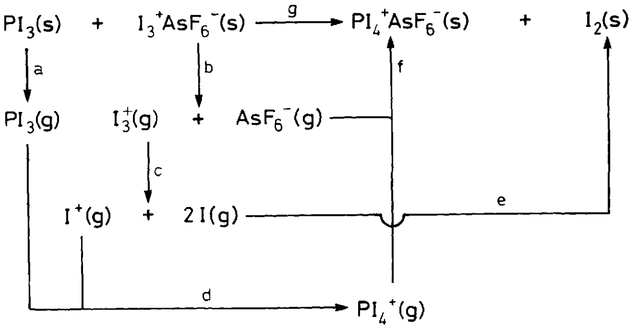
† ΔH(1/4 P_4, s → P, g) = +75.3 kcal mol^{-1},[9] IP (P, g) = +242.1 kcal mol^{-1},[9] $\Delta H(I_2$, s → 2 I, g) = +51.1 kcal mol^{-1},[9] $\Delta H(Br_2$, l → 2 Br, g) = +53.5 kcal mol^{-1},[1] ΔH(I, g → I^-, g) = −76.6 kcal mol^{-1},[9] ΔH(Br, g → Br^-, g) = −82.7 kcal mol^{-1},[9] BE(P^+ − I in PI_4^+) = −215.2 kcal mol^{-1} (see Scheme 1), BE (P^+ − Br in PBr_4^+) = −264 kcal mol^{-1} (see Scheme 1), $U_L(PI_4^+I^-)$ = −114 kcal mol^{-1} (see Scheme 1), $U_L(PBr_4^+Br^-)$ = −115 kcal mol^{-1} (see Scheme 1). [BE = bond energy, IP = ionization potential.]



Scheme 1. Energy cycle for the formation of $PI_4^+AsF_6^-$ from PI_3 and $I_3^+AsF_6^-$ (all values in kcal mol^{-1}). (a) Calibrated on $\Delta H_{\mathrm{vap.}}$:AsF_3, 8.5; PF_3, 3.9; $\Delta H_{\mathrm{sub.}}$: AsI_3, 22.7.[1] (b) The P^+–I bond energy in PI_4^+, estimated as P–I bond energy in PI_3 (51.2)[8] + 5% (2.6) (calibrated on 2 AsF_3 + 2 Cl_2, $AsCl_4^+AsF_6^-$ with $\Delta H = -25$; thus giving As^+–Cl bond energy in $AsCl_4^+$: −77.6, 5% greater than in $AsCl_3$). This gives P^+–I: −53.8 in PI_4^+. $\Delta H_d = -53.8 - 3\ (2.6) = -61.6$. (c) Crystal lattice energy (U_L) calculated from the molecular volume (V_M in Å^3) using the linear relationship: $U_L = 556.3\ (V_M)^{-0.33} + 26.3$;[10,11] $V_M(PI_4^+)$ was taken to be equal to $V_M(SiI_4)$ = 212 Å;[3]‡ $V_M(AsF_6^-)$ = 105 Å.[7,12] This gives $U_L(PI_4^+AsF_6^-) = -107.9$ kcal mol^{-1}.

spectrum.§ Although $PI_4^+AsF_6^-$ has sufficient stability to be isolated for a short time as a pure yellowish compound, it decomposes slowly to the thermodynamically more stable products, PF_3 (MS), AsF_3 (MS) and I_2 (Raman) (equation 2).

$$I_3^+AsF_6^-(s) + PI_3(s) \rightarrow PI_4^+AsF_6^-(s) + I_2(s) \qquad (1)$$

$$PI_4^+AsF_6^-(s) \rightarrow PF_3(g) + AsF_3(l) + 2\ I_2(s) \qquad (2)$$

Thus we have prepared and characterized a salt of PI_4^+, formally a derivative of the unknown PI_5 and the first example of a salt containing the tetrahedral PI_4^+ cation. The decomposition of $PI_4^+AsF_6^-$ may also be described in terms of a simple thermodynamic model. The heat of formation of $PI_4^+AsF_6^-$(s) was estimated, using an energy cycle in analogy as described previously,[4] to be −376 kcal mol^{-1},[19] and it follows that the enthalpy change of reaction (2) is −73 kcal mol^{-1}.¶ Both the formation and the decomposition of $PI_4^+AsF_6^-$ are therefore seen to be thermodynamically allowed.

In a typical reaction, $I_3^+AsF_6^-$ (1.0000 g, 1.755 mmol) was dissolved in $CFCl_3$. The solution was cooled to −95 °C and a cold suspension of PI_3 (0.7227 g, 1.755 mmol) in $CFCl_3$ was added slowly. Iodine and yellowish solid formed after the reaction mixture had been held at 0 °C for 10 min. The product was washed with cold $CFCl_3$ and traces of remaining iodine were removed under dynamic vacuum, leaving a light yellowish solid, the Raman spectrum of which showed PI_4^+ to be present.§ The part of the spectrum assigned to PI_4^+ consists of three strong bands (the low intensity ν_3 mode was not observed) which are very similar in intensity and relative position to those observed for PBr_4^+ (ν_1, 254; ν_2, 116; ν_4, 148 cm^{-1}),[15—17] PCl_4^+ (ν_1, 458; ν_2, 178; ν_4, 255 cm^{-1}),[18] and (the isoelectronic) SiI_4 (ν_1, 168; ν_2, 62; ν_4, 91 cm^{-1}),[14] and is consistent with its possessing T_d geometry. The totally symmetric ν_1 stretching mode was expected to appear as the strongest line at 192 cm^{-1} [estimated according to; $\nu_1(MI) = 0.42\ \nu_1(MCl)$][13] and observed at 193.5 cm^{-1} (100%).

Unfortunately, despite several experiments we were not able to find a solvent for $PI_4^+AsF_6^-$ and therefore no single crystals for a low temperature *X*-ray structure determination could be obtained. $PI_4^+SbF_6^-$ was synthesized from IF, SbF_5, and PI_3 but it is less stable than $PI_4^+AsF_6^-$.

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19 See ref. 6 and Scheme 1. ΔH°_f (AsF_6^-, g) = −471.4 kcal mol^{-1}.[9,10,20]
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‡ Calculated from $d_{(\mathrm{SiI_4,\ xtl.})}$ = 4.198 g cm^{-3}.

§ *Raman spectrum* of $PI_4^+AsF_6^-$. Spex 1403, Spectra Physics krypton laser, exciting line: 647 nm, 20 mW, 20 °C. 28.0, 44.0 (lattice vibrations); 71.0 (ν_2, PI_4^+); 89.0 (ν_4, PI_4^+); 108.5 (ν_2, PI_3); 193.5 (ν_1, PI_4^+); 212.0 (ν, I_2); 309.0 (ν_3, PI_3). The intensity of all peaks due to impurities (PI_3) is less than 10%.

¶ $\Delta H^\circ_f(PF_3, g) = -219.8$ kcal mol^{-1},[10] $\Delta H^\circ_f(AsF_3, l) = -228.8$ kcal mol^{-1}.[12]