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Electrospray Mass Spectrometric Studies of Some Phosphonium Cations

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A series of methylphosphonium cations derived from mono- and polyphosphines were generated by interaction of the phosphine with methyl iodide. Electrospray mass spectra of the cations were obtained directly from dichloromethane–methanol solutions. In all cases the intact phosphonium cations were observed, often as the base peak, emphasizing the 'soft' nature of this type of ionization. Some of the polyphosphines showed additional peaks at *m/z* 16 and 32 units higher than the molecular ions due to oxidation of the non-methylated phosphine groups. Collisionally activated dissociation mass spectra show a consistent mode of fragmentation with the formation of alkene ions being dominant. Where comparisons are possible, there is a close correlation with the electron impact mass spectra of the neutral phosphines.

INTRODUCTION

Electrospray mass spectrometry (ESMS) is a technique which has been widely used in the structural analysis of large biomolecules.[1,2] After dissolution in a suitable solvent, the compound is protonated with an organic acid and the solution is then passed directly into the ion source, where the solvent is evaporated to produce gas-phase ions. The ionization is very 'soft', causing minimum fragmentation which, together with the ability to produce multiply charged ions, has led to its wide application to the study of biological samples.

Our approach has been to use ESMS to investigate solutions of ionic inorganic and organometallic compounds for which the protonation step is unnecessary, and we have shown that the method is applicable to a wide range of species.[3] In a previous study[4] we investigated the electron impact mass spectra of a number of diphosphine and diarsine compounds such as $(C_6H_5)_2PCH_2P(C_6H_5)_2$, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and their arsenic analogues. Being uncharged, these phosphines cannot be studied directly by ESMS. However, conversion to the corresponding methylphosphonium salts by reaction with methyl iodide, a process which is analogous to the protonation of proteins in solution, produces cations which are readily observed. Fenn *et al.*[1] have reported that the molecular ion $[P(C_4H_{10})_4]^+$ may be observed in its ES mass spectrum. In this paper we report the ES and collisionally activated dissociation (CA) mass spectra of a number of phosphonium cations derived from mono- and polyphosphines.

RESULTS AND DISCUSSION

Monophosphine cations

Mass spectral data for all compounds are given in Table 1. The positive-ion ES mass spectrum of methyltriphenylphosphonium iodide in dichloromethane–methanol solution gives the intact phosphonium cation (*m/z* 277) and its associated ^{13}C isotopes peaks as the only significant peaks in the mass spectrum (Fig. 1). No metastable decompositions of these cations were observed in the absence of collision gas, showing the cation to be stable in the gas phase on the time-scale of this experiment (~100 μs). In the presence of argon as a collision gas, considerable fragmentation occurred at laboratory collision energies of 200 eV. Daughter ions corresponding to $[P(C_6H_5)_3]^{+\bullet}$ (*m/z* 262) and $[P(C_6H_5)_2Me]^{+\bullet}$ (*m/z* 200) were observed, with all other peaks in the CA mass spectrum being assigned to the products of further fragmentation of $[P(C_6H_5)_3]^{+\bullet}$, as previously identified by electron impact studies.[4,5] Triphenylbenzylphosphonium chloride also gives the intact phosphonium cation (*m/z* 353) in the positive-ion mass spectrum, but in this case collisional activation gives only $[P(C_6H_5)_3]^{+\bullet}$ and its further fragmentation products, with no evidence for the formation of $[P(C_6H_5)_2Bz]^{+\bullet}$. Hence in this case it appears most

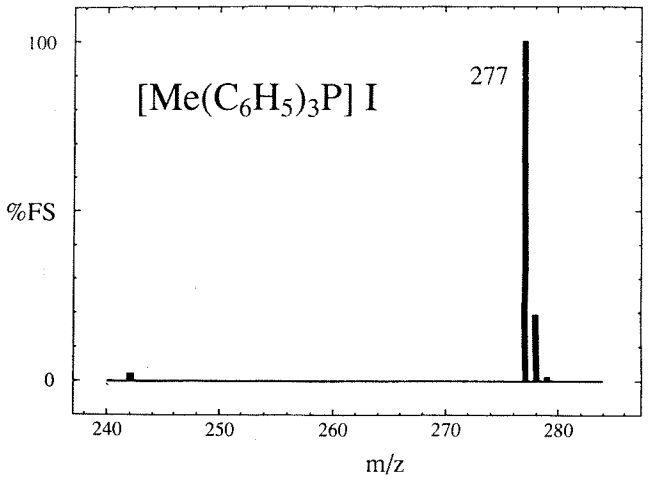

Figure 1. Positive-ion ES mass spectrum of $[Me(C_6H_5)_3P]I$.

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Table 1. Electrospray mass spectra

Compound	Molecular ions (*m/z*)	CA daughter ions (200 eV argon) (*m/z*)[a]
$[Me(C_6H_5)_3P]I$	$[Me(C_6H_5)_3P]^+$ (277)	$[P(C_6H_5)_3]^{+\cdot}$ (262), $[(C_6H_5)_2P{-}CH_3]^{+\cdot}$ (200), $[(C_6H_5)_2P]^+$ (185), $[(C_6H_4)_2P]^+$ (183), $[(C_6H_5)P{\equiv}CH]^+$ (121), $[(C_6H_5)P]^{+\cdot}$ (108), $[C_7H_7]^+$ (91), $[C_6H_5]^+$ (77)
$[(C_6H_5)_3BzP]Cl$	$[(C_6H_5)_3BzP]^+$ (353)	(262), (185), (183), (108), (91)
$[MeBu_3P]I$	$[MeBu_3P]^+$ (217)	
[dpmMe]I	$[dpmMe]^+$ (399)	(199), (121), (91), (77)
$[dpmMe_2]I_2$	$[dpmMe_2]^{2+}$ (207)	$[Me(C_6H_5)_2PCHPMe(C_6H_5)_2]^+$ (413)
[dpeMe]I	$[dpeMe]^+$ (413)	$[Me(C_6H_5)_2PCH{=}CH_2]^+$ (227), $[Me(C_6H_5)_2P]^{+\cdot}$ (200), (185)
[dpe(O)Me]I	$[dpe(O)Me]^+$ (429)	
$[dpeMe_2]^{2+}$	$[dpeMe_2]^{2+}$	(200), (185)
[bppMe]I	$[bppMe]^+$ (549)	$[Me(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH{=}CH_2]^+$ (363), $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)]^+$ (321), (227), $[Me(C_6H_5)_2P{\equiv}CH]^+$ (213), (200), (185)
[bpp(O)Me]I	$[bpp(O)Me]^+$ (565)	(363), $[(C_6H_5)_2P(O)CH_2CH_2P(C_6H_5)]^+$ (337), (227), (185)
$[bpp(O)_2Me]I$	$[bpp(O)_2Me]^+$ (581)	$[Me(C_6H_5)_2PCH_2CH_2P(O)(C_6H_5)CH{=}CH_2]^+$ (379), (227), $[Me(C_6H_5)P(CH{=}CH_2)_2]^+$ (177)
$[bppMe_2]I_2$	$[bppMe_2]^{2+}$ (282)	
$[bpp(O)Me_2]I_2$	$[bpp(O)Me_2]^{2+}$ (290)	
$[bppMe_3]I_3$		$[Me(C_6H_5)_2PCH_2CH_2P(C_6H_5)(Me)CH{=}CH_2]^{2+}$ (189)

[a] Structures of ions are given only when first mentioned, thereafter only *m/z* given.

likely that the phosphorus—arene bond is significantly stronger than the phosphorus—alkyl bond, although a possible explanation of the observed spectrum would be instability of the $[P(C_6H_5)_2Bz]^{+\cdot}$ ion. Methyltributylphosphonium iodide gives its intact phosphonium ion (*m/z* 217) but collisional activation gave only very weak peaks in the tandem mass spectrum.

Polyphosphine cations

When $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (dpm) is reacted with 1 mol equiv. of MeI, an almost quantitative conversion to $[dpmMe]^+$ is indicated by phosphorus-31 NMR spectroscopy. The ES mass spectrum of [dpmMe]I gives the intact phosphonium cation (*m/z* 399). The CA mass spectrum derived from the intact cation shows strong peaks at *m/z* 199 and 121, which are due to $[(C_6H_5)_2P{=}CH_2]^+$ and $[(C_6H_5)P{\equiv}CH]^+$. These ions were observed in the electron impact mass spectrum of dpm itself,[4] and the observation of metastable peaks in those spectra showed that they were formed both directly from $[dpm]^+$ and from $[P(C_6H_5)_3]^{+\cdot}$. The $[P(C_6H_5)_3]^{+\cdot}$ was formed from $[dpm]^+$ by a phenyl migration reaction. It is interesting that in the electrospray mass spectrum there is no evidence for the formation of $[P(C_6H_5)_3]^{+\cdot}$ from $[dpmMe]^+$, so in this case the ions at *m/z* 199 and 121 are formed directly from $[dpmMe]^+$. The loss of a $P(C_6H_5)_2$ group and a hydrogen atom to give an alkene ion will be seen to be a common mode of decomposition in collisionally activated dissociation tandem mass spectra for all the polyphosphine compounds.

$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (dpe) reacts with 1 mol equiv. of MeI to give [dpeMe]I as indicated by NMR spectroscopy. A dilute solution of $[dpeMe]^+$ in dichloromethane–methanol gives the intact phosphonium cation $[dpeMe]^+$ as the base peak (*m/z* 413) together with other peaks at *m/z* 429 and 445. The ion with *m/z* 429 is $[dpe(O)Me]^+$ in which the non-methylated phosphorus is converted into the oxide. The intensity of the peak at *m/z* 445 varies between spectra and it is thought to be due to the methanol adduct $[dpeMe]^+ \cdot MeOH$. Collisional activation fragmentation of the intact phosphonium cation (*m/z* 413) gives peaks which may be assigned to $[(C_6H_5)_2P]^+$ (*m/z* 185), $[Me(C_6H_5)_2P]^{+\cdot}$ (*m/z* 200) and $[Me(C_6H_5)_2PCH{=}CH_2]^+$ (*m/z* 227). The observation of these fragments confirms the strength of the phosphorus—methyl bond.

On reaction of dpm and dpe with an excess of MeI, the compounds $[dpmMe_2]I_2$ and $[dpeMe_2]I_2$ are formed. The ES mass spectrum of $[dpmMe_2]I_2$ shows the doubly charged cation $[dpmMe_2]^{2+}$ (*m/z* 207), but the base peak in the spectrum is assigned to $[(dpmMe_2) - H]^+$ (*m/z* 413). In contrast, the positive-ion ES mass spectrum of $[dpeMe_2]I_2$ gives a base peak for the cation $[dpeMe_2]^{2+}$ (*m/z* 214), but also another peak at *m/z* 227, due to $[Me(C_6H_5)_2PCH{=}CH_2]^+$. Presumably these fragment ions are formed by collisional activation in the ion source during the volatilization process. Dpm itself may be deprotonated at the central carbon atom[6] to give $[(C_6H_5)_2PCHP(C_6H_5)_2]^-$, which is a resonance-stabilized ion, and the same mechanism operates in collisional activation to give $[Me(C_6H_5)_2PCHP(C_6H_5)_2Me]^+$ from $[dpeMe_2]^{2+}$. This mechanism cannot operate for dpe or $[dpeMe_2]^+$, so the result of collision-induced fragmentation is to cleave a phosphorus—carbon bond to give $[Me(C_6H_5)_2PCH{=}CH_2]^+$ (*m/z* 227), which is also observed in the deliberate collisionally activated dissociation tandem mass spectrum of $[dpeMe]^+$ (above) and of triphosphine derivatives described below.

Phosphorus-31 NMR spectroscopy shows that when $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (bpp) reacts with 1 mol equiv. of MeI, a mixture of products is formed including the two isomers of $[bppMe]^+$ and also $[bppMe_2]^{2+}$. Similar behaviour giving several products has been reported for the reaction of bpp with sulphur.[7] The ES mass spectrum of the methylated mixture gives the base peak for the molecular ion $[bppMe]^+$, *m/z* 549, with weaker peaks at *m/z* 565 and 581 assigned to $[bpp(O)Me]^+$ and $[bpp(O)_2Me]^+$,

respectively. There are also small peaks due to $[bppMe_2]^{2+}$ (*m/z* 282) and $[bpp(O)Me_2]^{2+}$ (*m/z* 290) and two small unidentified peaks at *m/z* 413 and 429. There is evidence that the oxidation of the non-methylated phosphorus groups to give $[bpp(O)Me]^+$ and $[bpp(O)_2Me]^+$ occurs in the dichloromethane–methanol solution before the samples are injected into the electrospray mass spectrometer, since on allowing the solution to stand for some time before sample injection the proportion of oxide species increases. The oxidation is not observed on the same time-scale with samples examined by phosphorus-31 NMR spectroscopy, but this is attributed to the different concentrations of sample employed in the two techniques, 0.2 mM for ESMS and about 0.1 M for NMR spectroscopy.

Tandem mass spectra with collision energies of 200 eV were observed for parent ions at *m/z* 549, 565 and 581. The cation $[bppMe]^+$ gave weak peaks for several daughter ions derived from breakdown of the ethylene chain between the phosphorus atoms, loss of phenyl groups or loss of the methyl group (Table 1), so that no clear indication is obtained for any preferred sequence of bond rupture. The ions of *m/z* 565 and 581 containing oxygen gave some of the same daughter ions on collisional activation, together with some fragments containing oxygen. They also gave an ion at *m/z* 177 which is identified as $[Me(C_6H_5)P(CH{=}CH_2)_2]^+$. This is derived from the central phosphorus atom of bpp with loss of $P(C_6H_5)_2$ and a hydrogen atom occurring in both arms of the compound to give the favoured alkene complex.

When bpp is reacted with an excess of MeI the product is $[bppMe_3]^{3+}$, but under the normal conditions of spectrometer operation the intact phosphonium cation is not observed. Instead, the base peak is due to a doubly charged ion $[Me(C_6H_5)_2PCH_2CH_2P(C_6H_5)(Me)CH{=}CH_2]^{2+}$ at *m/z* 189 generated by loss of $MeP(C_6H_5)_2$ and a hydrogen atom to yield the alkene ion. In this case it is thought that collisional activation occurs with solvent molecules in the vicinity of the sampling orifice of the ion source. Attempts to observe the cation $[bppMe_3]^{3+}$ by varying the collision energies in the ion source were unsuccessful.

When $CH_3C[CH_2P(C_6H_5)_2]_3$ (tde) was reacted with 1 mol equiv. of MeI and the ES mass spectrum observed on a freshly prepared solution, the base peak in the mass spectrum corresponds to the cation $[tdeMe]^+$ (*m/z* 639). There are other peaks due to $[tde(O)Me]^+$ (*m/z* 655) and $[tde(O)_2Me]^+$ (*m/z* 671) and a small peak assigned to $[tdeMe_2]^{2+}$ (*m/z* 327). If the dilute solution of [tdeMe]I is allowed to stand for some days before observation of the mass spectrum, then only $[tde(O)_2Me]^+$ is observed in the higher *m/z* region. This is hardly surprising since tde itself is susceptible to oxidation, even in the solid state.

$P[CH_2CH_2P(C_6H_5)_2]_3$ (tpp) reacts with 1 mol equiv. of MeI to give predominantly [tppMe]I together with some $[tppMe_2]I_2$, as shown by phosphorus-31 NMR spectroscopy. A freshly prepared solution of [tppMe]I gives the intact phosphonium ion at *m/z* 685, but other peaks of similar intensity are also observed due to $[tpp(O)Me]^+$ (*m/z* 701), $[tpp(O)_2Me]^+$ (*m/z* 717) and $[tpp(O)_3Me]^+$ (*m/z* 733). In addition, a strong peak was observed due to $[tpp(O)_2Me_2]^{2+}$ (*m/z* 366) and a weak peak assigned to $[tpp(O)Me_2]^{2+}$ (*m/z* 358). A sample allowed to stand in dilute solution for some days showed a base peak due to $[tppMe(O)_3]^+$ and other peaks of decreasing intensity due to $[tpp(O)_2Me]^+$, $[tpp(O)Me]^+$ and $[tppMe]^+$ (very weak). The observation of all these species in solution is consistent with the known ease of oxidation of the polyphosphine.

CONCLUSION

The results show that electrospray mass spectrometry is applicable to phosphonium cations and, in principle, to the study of any inorganic or organometallic cations in organic solvents. In all cases, except for $[bppMe_3]^{3+}$, the intact phosphonium cations of the salts were observed, and in the case of polyphosphine derivatives other ions formed by oxidation of remaining phosphorus(III) atoms were also detected. The collisionally activated dissociation tandem mass spectra of the polyphosphine derivatives showed a common fragmentation scheme involving loss of $P(C_6H_5)_2$ and a hydrogen atom to give alkene ions. In those cases where a comparison is possible, the fragmentation scheme is similar to that observed in electron impact mass spectra of the neutral phosphines.

EXPERIMENTAL

The polyphosphines were all commercial samples (Strem). The phosphonium salts were prepared by the method of Grim and Walton[8] by the interaction of the appropriate amount of MeI with the phosphine in refluxing toluene for 3 h under a nitrogen atmosphere. The white crystals were collected and washed with cold methanol.

Electrospray mass spectra were recorded by using a VG Bio-Q triple quadrupole mass spectrometer (VG Bio-Tech, Altrincham, UK). The compounds were dissolved in dichloromethane solution (2 mM) and this solution was then diluted 1:10 with either dichloromethane or methanol. The dilute solution was injected directly via a Rheodyne injector with a 10 μl loop using a Phoenix 20 micro LC syringe pump to deliver the solution to the vaporization nozzle of the electrospray ion source at a flow rate of 2 μl min^{-1}. CA mass spectra were determined by admitting argon into the collision cell to a pressure that gave a 50% reduction in the parent ion abundance.

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