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# DESORPTION IONIZATION MASS SPECTROMETRY

## SECONDARY ION MASS SPECTRA OF PHOSPHONIUM SALTS

A. BA-ISA, K. L. BUSCH and R. G. COOKS*
Department of Chemistry, Purdue University, West Lafayette, IN 47907, U.S.A.

and

A. VINCZE and I. GRANOTH†
Israel Institute for Biological Research, P.O. Box 19, Ness Ziona, Israel

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**Abstract**—Secondary ion mass spectra are obtained for involatile phosphonium salts not analyzable by conventional ionization methods. The spectra typically exhibit an abundant intact cation and fragment ions which result from predictable losses of stable neutral species from the cation. A systematic pattern of fragmentation occurs in simple salts which serve as model compounds, and also more complex structures which are of pharmaceutical interest. Close parallels with the behavior of related volatile compounds in electron and chemical ionization mass spectrometry are observed in the presence of characteristic fragment ions and a tendency for rearrangement with elimination of stable molecules. Doubly charged salts undergo loss of a charged fragment such as a proton to give stable singly charged species. Sensitivity is such that a few nanograms of phosphonium salt suffices to provide a spectrum observable for ten to twenty minutes. The preferential desorption of precharged species makes possible the direct analysis of these salts in chromatographic media, including electrophoresis membranes, and also the direct desorption of these salts from vacuum compatible solutions.

Field desorption (FD),[1] laser desorption (LD),[2] plasma desorption (PD),[3] secondary ion mass spectrometry (SIMS),[4] fast atom bombardment (FAB),[5] and electrohydrodynamic ionization (EHD),[6] known collectively as desorption ionization (DI) mass spectrometry, are particularly useful in the analysis of thermally fragile and nonvolatile samples.[7] In producing ions directly from a condensed phase, DI methods avoid thermal decomposition of the sample by circumventing the requirement for vaporization. Organic "onium" salts amost invariably produce excellent DI mass spectra which contain not only abundant intact cations $C^+$ and anions $A^-$, but frequently fragment ions which can be used to elucidate structure,[8] and in some cases cluster ions such as $CAC^+$ and $ACA^-$. FD has been applied to the analysis of onium salts,[1] including ammonium, phosphonium, sulfonium and arsonium compounds, but suffers from a reputation for poor reproducibility. Possessing greater promise is SIMS, for which direct analysis of complex mixtures,[9] picogram sensitivity,[10] and the metastable origin of fragment ions[11] have all been demonstrated for ammonium salts. In addition, SIMS spectra usually persist for many minutes. Existing mass spectrometers are easily retrofitted with DI sources, particularly ion or neutral beam guns. The analysis of previously intractable salts should therefore become straightforward. This SIMS study of phosphonium salts represents an effort to develop spectrum/structure correlations necessary for the full interpretation of the spectra. Developments of methodology to include direct examination of electrophoresis membranes and of solutions are also introduced.

Phosphonium salts are versatile intermediates in organic synthesis,[12,13] but until the advent of DI techniques, could not be analyzed directly by mass spectrometry. The FD mass spectra of various phosphonium salts have been reported,[14–18] often in conjunction with reports on their preparation. Thermal evaporation mass spectrometry has also been used in the analyses of such compounds.[19] Typically, these spectra contain abundant ions corresponding to the intact cation. A reasonable expectation was that SIMS would also produce such ions, and structurally informative fragments as well. Some phosphonium salts show biological activity, for example, as antiarrhythmic drugs.[20] These latter compounds are structurally interesting in that they contain positive charge centers on both phosphorus and nitrogen. SIMS has been applied to the study of diquaternary ammonium salts;[21] to further that interest, SIMS spectra have now been obtained for these phosphonium/ammonium salts.

A concurrent study in this laboratory has used SIMS as a method of identification of phosphonium ions and neutral phosphine ligands in complexes containing molybdenum and rhenium.[22] Differentiation of charged and neutral moieties has been achieved, paralleling results from field desorption.[23] This capability is predicted by the fact that direct desorption of preformed ions from a surface is a highly favored process, and in fact, derivatization reactions can be devised to take advantage of this phenomenon.[24]

### EXPERIMENTAL

Positive ion SIMS spectra were obtained with a commercial Riber instrument (Model SQ 156L) utilizing an energy selector, a quadrupole mass filter, a channeltron electron multiplier, and pulse counting electronics. A 4 keV argon ion beam was used to bombard the sample. Ion currents were held at $1 \times 10^{-9}$ A/cm$^2$ or below to minimize beam damage and produce static SIMS spectra.[25] Operating pressure in the main chamber of the instrument

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†Deceased.

was typically $1 \times 10^{-8}$ torr or less. Adsorbed gases contribute to a background signal below m/z 60, but do not interfere with the analysis of these organic compounds. The quadrupole was scanned at a rate of 3 s/amu, and the scan and the analog rate meter output voltages sent to an XY recorder.

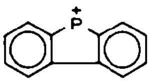
Samples were burnished onto silver foils of 1 $cm^2$ area (0.125 mm thick) which had been abrasively cleaned. Alternatively, solutions were syringed onto the planchette with the solvent subsequently being removed. Samples were introduced through a separately pumped preparation chamber into the main analysis chamber. Under static SIMS conditions, stable spectra of these precharged compounds could be obtained for several hr. Even after such extensive bombardment, samples could be removed from the instrument, and reanalyzed at a later time with no change in the spectra. Despite thick sample layers on the silver foil, no charging problems were encountered. To establish the mass scale, the organic material and the silver foil were simultaneously irradiated, the latter giving the silver doublet at m/z 107 and 109.

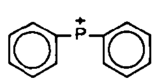
## RESULTS AND DISCUSSION

Results are presented for some simple salts first. The positive ion SIMS spectrum of tetra-n-butylphosphonium bromide contains the intact cation at m/z 259 as the base peak. An ion occurs at m/z 257, formally due to loss of $H_2$ from the cation; with a relative abundance (RA) of 20%; this is the most abundant fragment in the spectrum. This process has been noted in the SIMS spectra of other organic compounds,[26,27] but not with as great an abundance; it is probably the result of a distinct ionization process at the surface, *viz*, a hydride abstraction. The next most abundant ion appears at m/z 229 (10% RA) representing loss of 30 daltons (the elements of $C_2H_6$) from the cation. A series of ions corresponding to losses of alkane molecules from the alkyl side chains can be distinguished down to m/z 62. An ion at m/z 76 is the most abundant of these (10% RA), and is probably $[HP(C_2H_5)_2]^{+\cdot}$.

The SIMS spectrum of methyltriphenylphosphonium iodide (Fig. 1) contain as its base peak the intact cation ($C^+$) at m/z 277, and a fragment ion at m/z 183 (believed to be structure **a**[28]) of about 10% relative abundance. The FD mass spectrum of this compound contains a base peak at m/z 277, and a fragment ion at m/z 262 ($Ph_3P^+$), as well as a $(C + 14)^+$ ion at m/z 291.[15] Such adduct ions are not observed in the SIMS spectrum, although $(C + 14)^+$ peaks have been observed in the SIMS and FD spectra of quaternary ammonium salts,[26] where they have been shown to result from intermolecular methylation. The positive ion spectrum of a similar salt, tetraphenylphosphonium bromide, also contains the intact cation (m/z 339) as the base peak. Here the most abundant fragment ion is again m/z 183 (structure **a**) with a relative abundance of 70%. Fragment ions $Ph_2P^+$ (20% RA) and $Ph_3P^+$ (10% RA) are also observed in this spectrum.

Recently, cyclic phosphonium ylides have been used in a synthesis of insect pheromones[29] which involved synthetic elaboration of the salt 1,1-diphenylphospholanium bromide. The intact cation at m/z 241 is observed as the base peak in this SIMS spectrum. Virtually the only other fragment ion in the spectrum is the ion at m/z 183 (5% RA) which corresponds to the diphenylphosphenium ion **a**. This fragment ion is almost ubiquitous in the FD mass spectra of aryl phosphonium salts, and in these SIMS spectra as well; it is also a common ion in the electron ionization mass spectra of these compounds. A much less abundant ion is observed at m/z 185, **b**. Bracketed by the signal for the two isotopes of silver (the metal foil upon which the organic was burnished) is an additional fragment ion of about 5% RA at m/z 108, $PhP^+$. The S/N for the intact cation at m/z 241 is observed to be about 150. This contrasts markedly with the quality of spectra obtained by EHD, PD and FAB, where the S/N is typically lower, but compares well with spectra obtained by LD and FD.


**a**, m/z 183


**b**, m/z 185

These fragmentations of phosphonium salts in DI spectra parallel those observed in conventional electron

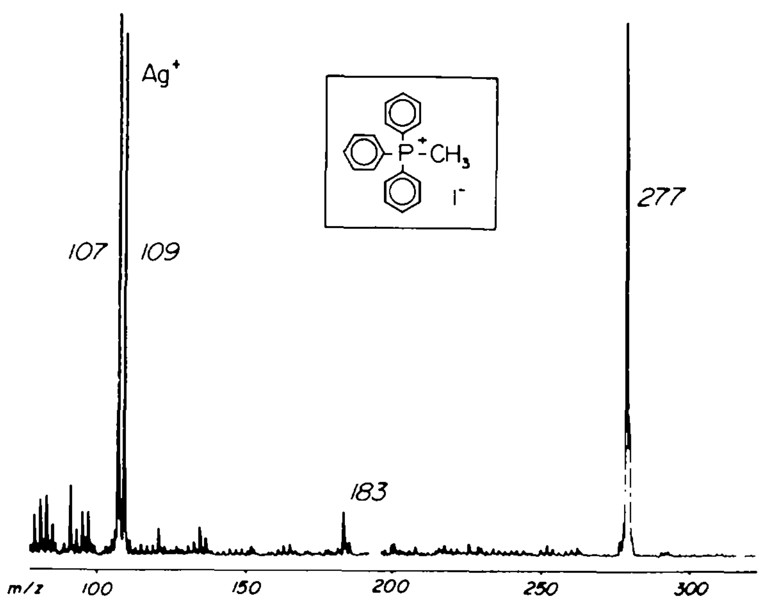
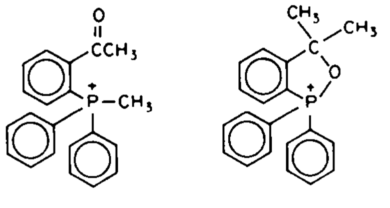


Fig. 1. The positive ion SIMS spectrum of methyltriphenylphosphonium iodide contains as its base peak the intact cation at m/z 277. The sample was burnished onto silver foil.

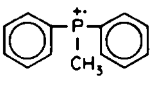
and chemical ionization masss spectrometry, even though the latter are limited to the examination of volatile samples. An example of this is the ion pair at *m/z* 183 and 185, which is a hallmark of the group $(C_6H_5)_2P$- in both techniques, and in a wide variety of compounds containing this moiety.[29-33]

These simple model compounds confirm that SIMS can be used to characterize phosphonium salts directly from the solid phase. In organic synthesis, the preparation of these versatile intermediate salts is on occasion complicated by rearrangement reactions to give products with ambiguous structures, and thus their characterization is of practical interest. The high sensitivity of the DI techniques for such precharged compounds can become a telling advantage when only a small amount of material is available for analysis. As shown in FD for these compounds,[17] MS/MS techniques[34,35] can provide valuable additional information which can be used to resolve structural ambiguities.

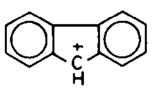
As part of a continuing study of the chemistry of organophosphorus compounds and their biological pathways,[36] a series of substituted phenyl phosphonium salts have been prepared. As expected from the spectra of the simple phosphonium salts, these compounds also produce SIMS spectra containing an abundant intact cation which is used to determine the weight of the cationic portion of the salt. In addition, and as shown also in FD for some very similar samples,[36] the fragmentation pattern can be used to confirm the molecular structure. Figure 2 shows the SIMS spectrum of the first of a series of related phenyl phosphonium salts (**1**–**6**), the structures of which are shown. For **1**, the intact cation at *m/z* 335 is the base peak in the spectrum, but a variety of fragments are also observed. The most abundant of these are again the phosphenium ions 183 and 185, structures **a** and **b** respectively. The cation undergoes loss of 16 daltons, probably $CH_4$, to give the ion at *m/z* 319, presumed on the basis of the spectra of related compounds (see below) to have two structures, **c**. Other losses of neutral molecules from the intact cation occur; loss of isopropanol produces a fragment ion at *m/z* 275; loss of benzene yields *m/z* 257. The structure of the ion at *m/z* 200 is most likely **d** (i.e. the result of loss of the substituted aromatic ring from the cation). The origin of the fragment ion at *m/z* 165 is plausibly given as **e** by analogy with electron ionization results,[29-33] although its formation requires considerable rearrangement. In these instances, the use of MS/MS or high resolution mass spectrometry to further characterize these fragments would be valuable.



**c**, *m/z* 319



**d**, *m/z* 200



**e**, *m/z* 165

The SIMS spectrum of the related salt **2**, in which the Me group has been replaced by a benzyl ring, contains as its highest mass ion the intact cation at *m/z* 411. Loss of 16 daltons gives the fragment ion at *m/z* 395, and this loss must originate in the alcohol side chain. The most abundant fragment ion is that at *m/z* 335, representing loss of 76 daltons from the cation. This produces a fragment ion with a structure that may be that of the intact cation of the previous sample. In fact, the remaining fragmentation processes parallel those already discussed; loss of 16 from 335 yields 319, and ions at *m/z* 257, 200, 185, 183 and 165 are observed.

The SIMS spectra of several phosphonium salts related to these first two compounds have been obtained. In addition to an alcohol substituent, compounds with both acid and ester functions were examined. In each case, the spectra of both Me and benzyl salts were

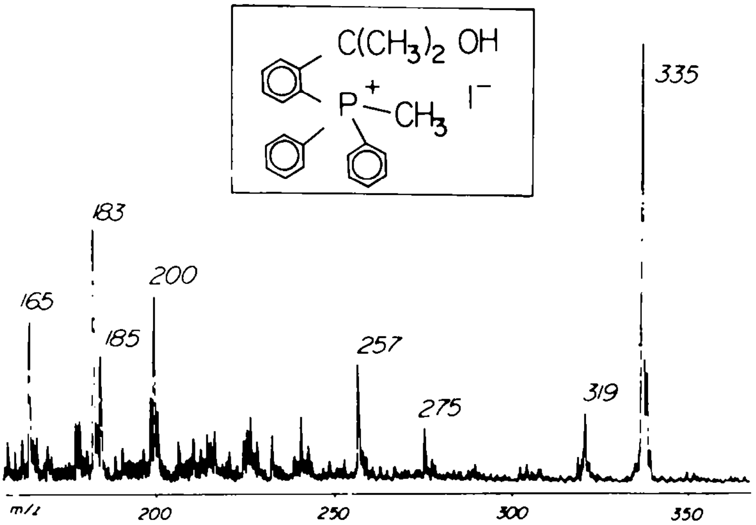


Fig. 2. The intact cation at *m/z* 335 is observed in the SIMS spectrum of this ring substituted triarylphosphonium salt.

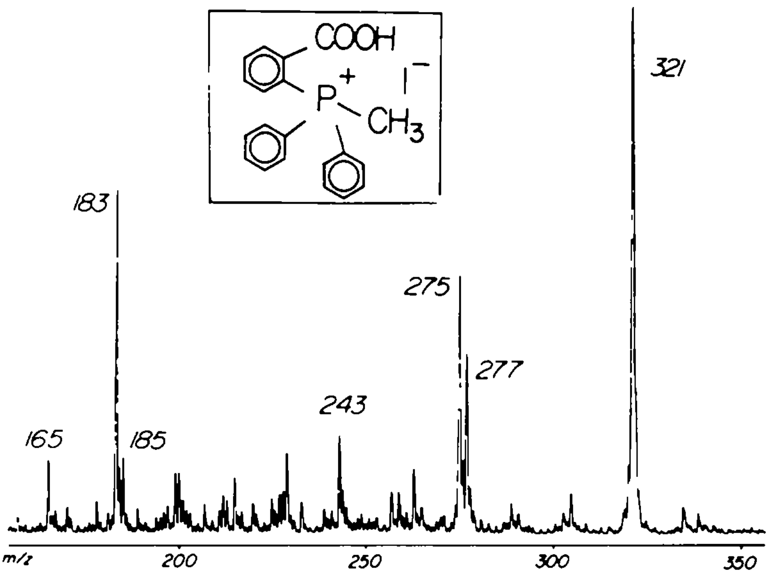
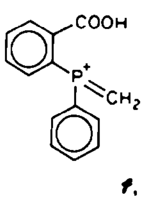
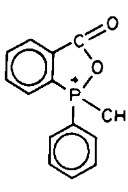


Fig. 3. Loss of small neutral molecules ($CO_2$ and formic acid) form stable phosphorus-containing cations in the SIMS spectrum of this salt.

compared. Figure 3 exhibits the SIMS spectrum of the acid substituted methyl phosphonium salt **3**. From the intact cation at *m/z* 321, loss of $CO_2$ forms 277 and loss of formic acid yields 275. Loss of benzene, a process noted before, yields the fragment ion at *m/z* 243, **f**. The ions at *m/z* 165, 183 and 185 are again observed. The SIMS spectrum of the analogous acid substituted benzyl phosphonium salt **4** contains the intact cation at *m/z* 397 as the base peak. Fragment ions are observed at *m/z* 351 and 353 (losses of carbon dioxide and formic acid, respectively), *m/z* 305 (loss of toluene), and the characteristic ions at *m/z* 183 and 165.



**f**, *m/z* 243



The SIMS spectra of the phosphonium salts with ester substituents, **5** and **6**, were also obtained. These compounds are of the same integral mass as the alcohol substituted salts (**1** and **2**), but the isomers can be differentiated via their distinctive fragmentation patterns. The intact cations appear at *m/z* 335 and 411, respectively, for the Me and benzyl salts. In Fig. 4, as compared to Fig. 2, loss of 30 (ethane) rather than 16 daltons from the cation occurs, so that the ions at 305 and 319 serve to distinguish these isomers. Again, a series of ions at *m/z* 165, 183, and 243 serve to characterize this aryl phosphonium salt. The fragment ion at *m/z* 243 results from loss of toluene from the cation. As before, an excellent signal to noise ratio (125) is observed for the peak corresponding to the intact cation.

For the benzyl analogue **6**, both an abundant intact cation (*m/z* 411) and many fragments are observed. Neutral molecule losses form fragment ions at *m/z* 367 (assignable to loss of carbon dioxide), *m/z* 351 (loss of acetic acid), and *m/z* 319 (loss of toluene). An ion at *m/z*

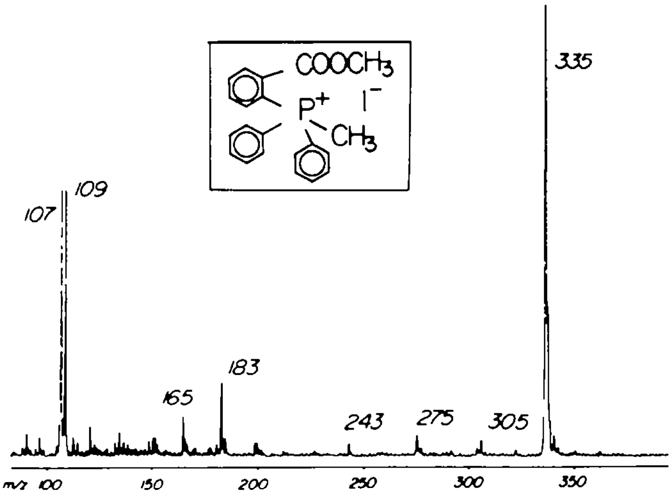
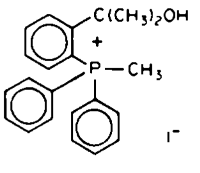


Fig. 4. The SIMS spectrum of this ester substituted phosphonium salt differs from that of the alcohol substituted salt at the same integral mass.



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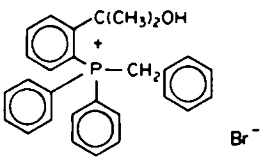

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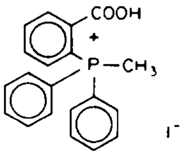

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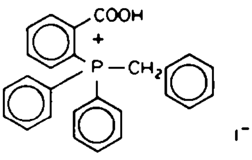

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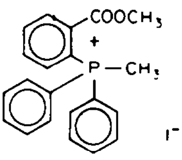

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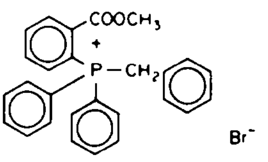

6

335 presumably forms by loss of benzyne to form a methyl phosphonium ion. An ion at *m/z* 305 may arise by loss of xylene from the *m/z* 411 cation, or a loss of ethane from the fragment at *m/z* 335. A greater abundance relative to 335 here than in the related Me salt suggests the former. Other ions common to both spectra are those at *m/z* 243, 185, 183 and 165, all of which have been discussed previously.

Boranato-bis-alkylphosphonium salts have been used in the synthesis of new coordination compounds of metals,[37,38] new boron containing P heterocycles,[39] and are also of interest because of their potential pharmacological activity.[40] The SIMS spectrum of a simple example of this class of compounds, $(CH_3)_3P{-}BH_2{-}P(CH_3)_3$, is shown in Fig. 5. It contains as its base peak the intact cation at *m/z* 165, and a single fragment ion which corresponds to loss of trimethylphosphine (again a stable neutral molecule) from the cation to give the fragment ion at *m/z* 89. The spectrum is shown for the mass range 20–200. The silver foil substrate and Na and K impurities give rise to peaks at *m/z* 107 and 109, and *m/z* 23 and 39. Some small amount of $(C+14)^+$ is also noted. The spectrum shown was taken at a very low primary ion current (less than $1\times10^{-12}$ A/cm$^2$). At slightly higher ion currents, increased fragmentation of the cation could be observed, *m/z* 89 becomes the base peak in the spectrum, and new fragmentation processes form an ion at *m/z* 41 $[(CH_3)_2B^+]$. Thus the primary ion flux in SIMS is shown to be a factor controlling the extent of fragmentation of desorbed organic molecules.

Finally, SIMS spectra were obtained for several compounds which have been investigated specifically for their biological activity. These ketophosphonium salts have demonstrated substantial antiarrhythmic action, and levels of this activity have been correlated with the structure of these molecules.[20] These are doubly-charged salts, carrying charges on both N and P, and thus study of this compound class also extends earlier work on the SIMS spectra of doubly charged ammonium salts.[21] The positive ion spectrum of (2-exo-4-morpholino)-butyltriphenylphosphonium bromide hydrobromide is shown in Fig. 6. As observed in previous work on other doubly charged ions,[21,41] charge separation is a dominant process. The highest mass ion observed is *m/z* 418, formed by loss of $H^+$ from the doubly-charged intact cation. Successive losses of neutral molecules occur from this ion. Thus, loss of neutral morpholine yields the fragment ion at *m/z* 333. Loss of 2,3-dihydro-4-methyl-p-isoxazine produces the *m/z* 319 ion, and loss of ethylmorpholine forms the fragment at *m/z* 303. The methyl triphenylphosphonium cation appears at *m/z* 277; loss of $H_2$ to form a bridged analogue forms the ion at *m/z* 275. The triphenylphosphine ion is seen at *m/z* 262. The base peak in the spectrum is the *m/z* 183 ion, with its satellite ion at *m/z* 185. In that these losses form a singly-charged phosphonium cation, the similarity between the subsequent fragmentations and previously noted processes (shown in this work and a previous study of double-charged ammonium salts[21]) is gratifying. The SIMS spectrum affords both molecular weight information and fragmentation patterns interpretable in terms of known ion chemistry.

The selective desorption of precharged species[24] has made possible the coupling of SIMS with static chromatography, such as paper and TLC.[4,9] In these off-line techniques, the samples are encapsulated within the medium until sampled by the primary ion beam; *time is*

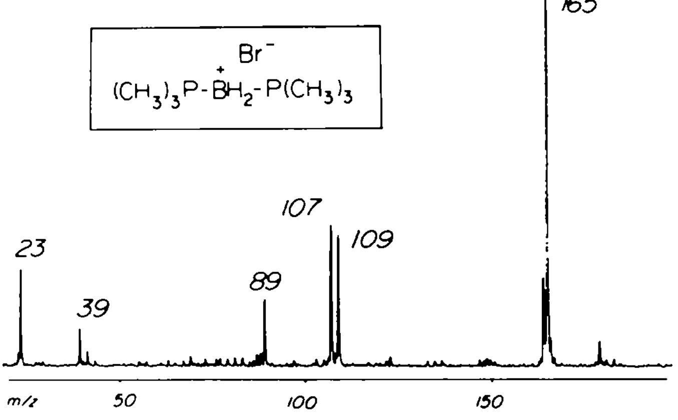

Fig. 5. The abundance of the cation of this organic salt decreases relative to the abundance of the fragment ions when the flux of primary ions is increased.

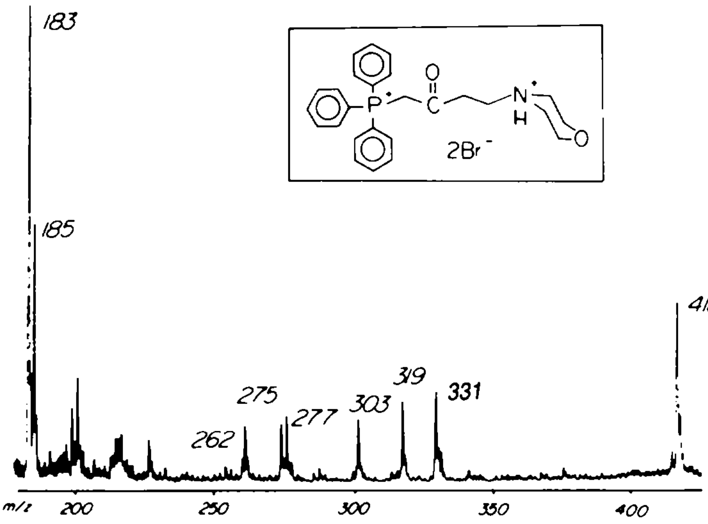

Fig. 6. Complex salts of biological significance produce SIMS spectra containing ions which can be used to gauge the mass of the molecule, and also abundant fragment ions which can be related to structure.

*not a factor in the spectroscopy as it is in the chromatography.* It is logical to also consider combining with desorption ionization a form of chromatography designed for the separation of compounds on the basis of their charge, *viz* electrophoresis. Using a cellulose acetate membrane, phosphonium salts can be directly desorbed from the chromatogram, and the spectra obtained are similar to those of the compounds supported on metal substrates. Figure 7 exhibits the SIMS spectrum of 1,1-diphenylphospholanium bromide desorbed directly from the electrophoresis membrane. The description of this spectrum follows that given for the spectrum of the neat compound (*vide supra*), although the fragment ion at *m/z* 109 was obscured in the spectrum obtained from the silver support. The ion at *m/z* 43 corresponds to $CH_3CO^+$ from the acetate membrane. The excellent S/N at the mass of the cation is preserved in this spectrum despite the presence of the chromatographic matrix. These experiments represent a successful integration of chromatography and spectroscopy where each technique has a special selectivity for precharged organic compounds.[42]

Some attention has been turned lately to the desorption of ions from solutions. Glycerol, with a long tenure as the solvent of choice in electrohydrodynamic ionization mass spectrometry,[6] suffers from the disadvantage that its persistence in moderate vacuum is generally shorter than the lifetime of the sample. We have reported success with the desorption of ions from lower vapor pressure solvents such as diffusion pump fluids and gas chromatographic stationary phases.[43] Such matrices reduce cluster ion abundances, concentrating ion current in the most significant ions. Following an example from field desorption mass spectrometry,[44] we report here that phosphonium salts can also be directly desorbed from polar solvents such as the long chain esters known commercially as Tweens. The advantages of desorbing ions from solutions have been discussed more fully elsewhere.[45]

The sensitivity of the SIMS method is such that full spectra can be obtained from as little as 2 ng of the salt supported directly on a metal substrate. Selected ion monitoring lowers the detection limit into the picogram range with some loss of selectivity. Micrograms of material can typically be analyzed from the various chromatographic media, or from solutions.[9] Sensitivity enhancement for bulk samples may be implicit in DI

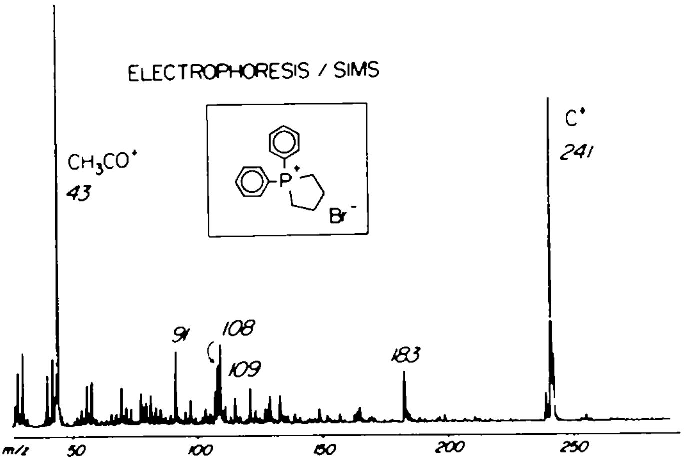

Fig. 7. This simple phosphonium salt can be desorbed directly from a cellulose acetate electrophoresis membrane to produce a spectrum quite similar to that of the neat salt.

analysis of solutions, in spite of the lowered surface concentration, as a greater proportion of the sample can be brought via diffusion under primary beam irradiation. This advantage is offset somewhat by the increased level of chemical noise observed in the spectrum.

## CONCLUSIONS

The study is significant in that it demonstrates an analytical method which is both sensitive and structure-specific and applicable to a class of compounds of intrinsic importance. Moreover, the close relationships[8,46] between the various methods of desorption ionization are buttressed with these further examples. With the rapidly increasing availability of ion sources for SIMS, widespread use in organic chemistry is expected. The characteristic behavior of precharged (ionic) compounds in SIMS is further generalized by observation of the close correspondence between the spectra of the phosphonium salts and their sulfonium and ammonium[47] analogs discussed earlier. Similarly, too, the doubly-charged ions mentioned here are observed to undergo charge separation reactions which also occur in the diquaternary ammonium dications.[21,41] Perhaps the most striking aspect of this work is the simple nature of the fragmentations observed. Covering a wide range of compounds, these examples emphasize the well-controlled nature of unimolecular fragmentation in DI, a point which follows from demonstrations of parallels between these fragmentations and those induced by collision in MS/MS, and between the fragmentation patterns of protonated, argentated, and cupriated molecules.[48] One must also note that SIMS spectra, under the conditions employed here, are not subject to deleterious thermal or transient effects.

Finally, SIMS analyses of these phosphonium salts provide further evidence for an underlying similarity among all DI methods in their ability to desorb organic salts from surfaces. Only a small amount of energy is needed for desorption of such species, and very fragile molecules can be lifted off the surface without excessive cleavage of bonds within the structure. Thus, the intact cation is invariably observed, but in contrast to typical FD results, the pattern of fragmentation yields additional details of structure. The ubiquity of the $183^+$ ion is a testament to its stability, and suggests its use in a selective ion monitoring scheme to detect arylphosphonium salts at very low levels. Moreover, the use of chromatography techniques in conjunction with SIMS, and the integration of the MS/MS method with DI sources, emphasize the possibility of obtaining abundant high mass ions unambigously related to structure.

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