

Secondary Ion Mass Spectrometry. Cationization of Organic Molecules with Metals

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Abstract: Attachment of metal ions to organic molecules in secondary ion mass spectrometry (SIMS) represents a new ionization technique. The phenomenon is general with regard to both the metal (alkali, transition, and noble metals) and the organic (polar and nonpolar compounds). Metals may be present in the free form or as their salts. The process allows for multiple checks on molecular weights and has the advantage that the quasi-molecular ions can be shifted out of regions of the spectrum which are subject to interferences. Fragmentation patterns are obtained and as in other mass spectrometric techniques they can be interpreted to provide molecular structures. The extent of fragmentation varies with the cationizing agent and conditions. The ability to attach a distinctive metal atom, rather than the ubiquitous H atom, as is done when ionizing by protonation, represents an important analytical advantage. Competition studies show that completed d-shell ions such as Cu^+ and Ag^+ are more effective at cationization than are Pd^+ and Pt^+ , for example. The fragmentation reactions which occur in SIMS correspond to those observed when protonated molecules are mass analyzed and subjected to collision-induced dissociation. These data, together with correspondences between SIMS and electron impact mass spectra, provide strong evidence that the SIMS spectrum arises in large measure from the fragmentation of a single precursor cationized molecule. Some information on the site of cationization is available and there is evidence for σ bonding in some cases and π bonding or simple electrostatic interactions in others. The phenomena observed in SIMS show marked phenomenological parallels with other ionization methods, specifically, field desorption, plasma desorption, laser desorption, and electrohydrodynamic ionization. The unique feature of SIMS is the attachment of metals other than the alkalis. As an indication of the types of studies now possible, results are presented in which a binary alloy is analyzed by examination of organometallic adducts.

Introduction

In this paper a new ionization method for organic compounds is presented.¹ In this procedure metal ions are attached to organic molecules under the influence of a bombarding primary ion beam and the mass spectrum of the ejected secondary ions (the SIMS spectrum) is recorded. The scope of this method, the processes responsible for ion formation, the effects of experimental variables, and some of the applications of the technique in surface analysis and in a mass spectrometry are treated here.

Secondary ion mass spectrometry has been heralded as the most sensitive of all the surface techniques.² Up until now organic molecules have largely been encountered as interferences in the method,³ although there has been some effort made to study polymers⁴ by SIMS. The first observations of organic molecular ions in SIMS were reported recently⁵ as emphasis turned to the potential of the method as an ionization technique. Studies have been made on the fragmentation characteristics of organic compounds in SIMS by investigation of the collision-induced dissociation of the secondary ions.⁶ The SIMS method is also becoming of interest as a source of information on the adsorption of organic molecules onto metals.⁷ Of particular relevance to the present work is the reported observation of the $(\text{Ni} + \text{C}_2\text{H}_4)^+$ ion from ethylene adsorbed on nickel.^{7a}

The ideal ion source for mass spectrometry would be one based on the direct conversion of the molecule in the condensed phase to a gas-phase ion. The ions so formed should, even for fragile, involatile molecules, include molecular ions or their simple analogues. The traditional ionization method for organic molecules, electron impact (EI), does not fulfill these criteria nor do the more recently deployed chemical ionization (CI) and field ionization (FI) techniques. In response to this situation, there is now intense development of alternative methods. Interest centers on field desorption (FD),⁸ plasma desorption (PD),⁹ laser desorption (LD),¹⁰ and electrohydrodynamic ionization (EHD)¹¹ and on the use of field emitters in chemical ionization,¹² all of which procedures have registered some spectacular successes with thermally labile and

involatile compounds. However, even the best established of these techniques, field desorption, has a record of mixed success partially attributable to the lack of understanding of the physical basis of the technique.^{12,13} Nevertheless, progress is being made particularly with regard to methods for the attachment of alkali metal atoms to the sample molecules.¹⁴

In a preliminary communication we reported¹ the cationization of organic molecules (M) by metals Ag, Pt, and Li to give species of the type $(\text{C} + \text{M})^+$ where C is the cation. Recent experiments by Benninghoven and co-workers^{5c,15} have demonstrated the formation of $(\text{H} + \text{M})^+$ ions in organic SIMS. Both sets of experiments show that molecular weights can be determined and Benninghoven's results establish that this is so even for labile and involatile molecules. The spectra show fragmentation patterns from which molecular structural information can be sought. The ion chemistry underlying SIMS spectra is a topic which now merits detailed attention.

Organic compounds provide an excellent vehicle for investigating the fundamental processes occurring in SIMS. The measured spectrum represents the combined results of (1) the sputtering process and (2) fragmentation of the gas-phase ions after leaving the surface and before reaching the analyzer. Since the ion chemistry of organic compounds is well known, separation of these two factors is feasible. Organic compounds also provide particularly simple tests, including the use of specifically labeled substrates, for investigating any molecular reorganization which occurs during ion bombardment. Concern over the possibility of reactions accompanying ion impact has led to the evolution of the static SIMS method^{2b,16} which employs low ion fluxes to minimize surface damage but does so at large cost in terms of sensitivity. It is noteworthy that, while quantitative models have been developed for the sputter process^{2c} on which SIMS is based, a simple qualitative description of the process is yet to be agreed upon. The long-term objective of the work initiated here is the utilization of organic compounds as a vehicle for investigating the mechanism of secondary ion emission while also developing an analytically useful ionization protocol.

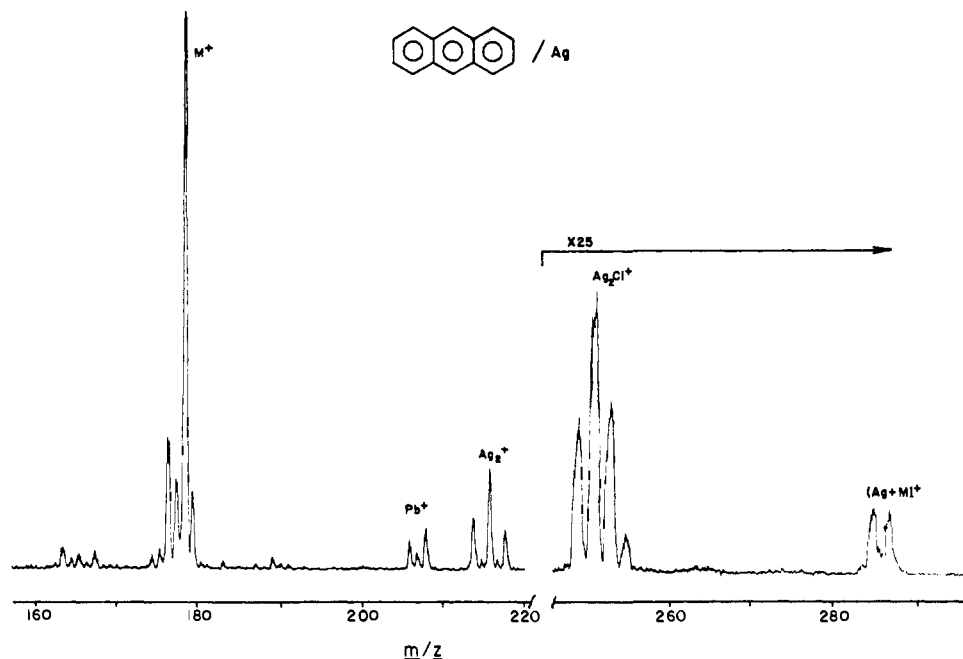


Figure 1. Cationization of anthracene by silver as evidenced by its SIMS spectrum.

Experimental Section

The mass-analyzed ion kinetic energy (MIKE)¹⁷ and SIMS spectrometers¹⁸ used have been described elsewhere. The samples were introduced into the chemical ionization (CI) source of the MIKES via the direct insertion probe. Isobutane was used as the reagent gas for chemical ionization. The ion accelerating voltage was 7 kV. Pressures of ca. 2×10^{-4} Torr of N_2 were used in the collision chamber between the two sectors to produce collision-induced dissociation of the protonated molecular ions. MIKE spectra were taken on selected ions by scanning the electric sector potential.

Samples were prepared and introduced into the SIMS instrument as described elsewhere.^{18b,19} The organic compounds or their mixtures with salts were supported on metal foils. All compounds were commercial samples and were used without purification. The metal foils were of >99.9% purity and were abrasively cleaned prior to use. The preparation of the 60:40 silver/palladium alloy is described elsewhere.¹⁹ Charging of the sample could be avoided in a number of different ways including (1) scratching a grid onto the samples with a razor blade so that the support metal was exposed and (2) admixing salts or graphite to the sample. Large (~ 0.5 mg) sample sizes were employed in these studies and this sufficed to allow spectra to be obtained for many hours. Spectra were scanned at 1–20 s/amu with 15 s/amu being representative.

The operating pressure for most of the SIMS experiments was 6×10^{-10} to 9×10^{-9} Torr. For experiments in which the pressure was raised to 4×10^{-8} Torr, the general features of the spectra did not change. A 5-keV beam of Ar^+ ions was used as the primary ion species, but in selected experiments 2.5-keV beams gave identical results. Static SIMS conditions were employed with primary ion current densities of 6×10^{-10} to 7×10^{-9} A cm^{-2} . Experiments at higher ion densities were also performed (see Results).

The electron impact (EI) mass spectra which were used for comparisons were either taken on a CEC-110B mass spectrometer or were obtained from the literature. The EI spectra which are discussed refer in all cases to 70-eV electron energies.

Results and Discussion

The results of secondary ion mass spectrometry experiments using metal foils onto which were adsorbed pure organic compounds or organic compounds mixed with metal salts will be described. The organic compounds that were used were *p*-aminobenzoic acid, 1,4-dicyanobenzene, anthracene, hexamethylbenzene, *o*-phenylenediamine, phenylalanine, and stilbene. These results are presented in conjunction with mass-analyzed ion kinetic energy spectra of the protonated

analogues in most cases and with electron impact mass spectra in some cases.

Cationization was observed for every combination of compound with metal which was examined, although the intensity of the peak due to the cationized molecule varied. Most commonly, the evidence for cationization consisted of the presence of the species $(C + M)^+$ in which C is the cationizing agent (the metal) and M is the intact organic molecule. The scope of the cationization reaction can be inferred by comparing the behavior of nonpolar compounds with that of highly polar compounds. Anthracene serves as an example of a nonpolar compound; its spectrum, taken from a sample deposited on silver, is shown in part in Figure 1. The cationized molecule, $(Ag + M)^+$, occurs at m/z 285 and 287. In forming the metal-molecular adduct this compound parallels the behavior of *p*-aminobenzoic acid, whose SIMS spectrum was reported in a preliminary communication.¹ While nonpolar compounds can be cationized, the extent to which they fragment by loss of the metal is expected and found to be much greater than is the case for more polar compounds. The $(Ag + M)^+/M^+$ ratio for *p*-dicyanobenzene, for example, is three orders of magnitude greater than that for anthracene, while stilbene gives intermediate results. Thus the major ion in the high mass region of the anthracene spectrum is the anthracene molecular ion, m/z 178.²⁰

Given that silver adducts could be formed from all the compounds examined—ranging from nonpolar through zwitterionic molecules—a simple polar molecule, *p*-dicyanobenzene, was chosen in order to examine effects due to the metal. On the assumption that cationization might be facilitated if the metal were supplied as a salt, the spectrum of a mixture (ca. 10:1) of $AgNO_3$ and *p*-dicyanobenzene on a platinum support was obtained (Figure 2). Abundant cationized molecule formation is observed. In an extension of this approach the dicyanobenzene was mixed intimately with $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, blue tungsten oxide, and $CuCl_2 \cdot 2H_2O$ and the mixture was examined on a silver support. Addition of each metal to the organic molecule was observed, the relative intensity order being $(Cu + M)^+ > (Ni + M)^+ > (Ag + M)^+ > (Co + M)^+ > (W + M)^+$. Figure 3 shows the region of the spectrum in which most of the cationized molecules fall. Clearly, transition metal salts can provide ions for cationization, a result which extends and generalizes the earlier results¹

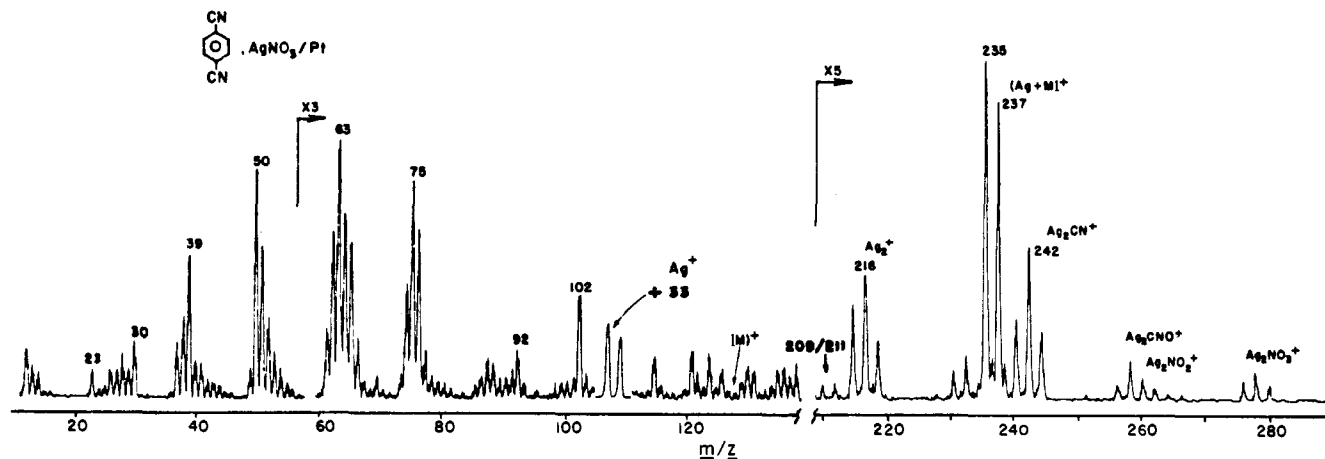


Figure 2. The SIMS spectrum of a mixture of 1,4-dicyanobenzene and silver nitrate supported on Pt.

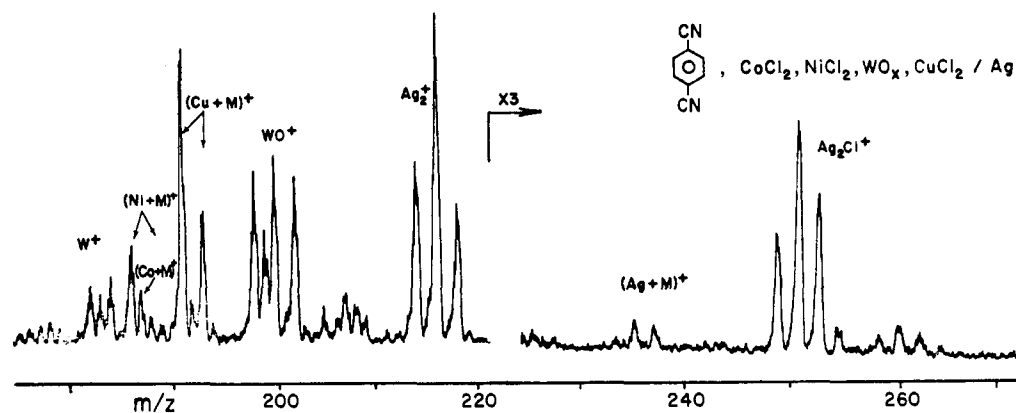


Figure 3. Cationization of 1,4-dicyanobenzene by a variety of metal ions in SIMS.

on Li^+ attachment by admixture of LiCl with *p*-aminobenzoic acid. The relative effectiveness of alkali metals and transition metals has not yet been determined. In some cases $(\text{K} + \text{M})^+$ and $(\text{Al} + \text{M})^+$ peaks associated with the inadvertent presence of particular cations are observed. Nevertheless, the large intensity of the Na^+ and K^+ peaks at m/z 23 and 39 observed in virtually all SIMS spectra does not translate into large intensities of $(\text{Na} + \text{M})^+$ and $(\text{K} + \text{M})^+$ ions.

The relative effectiveness of metal ions in cationization was further tested in experiments in which copper salts in different oxidation states were mixed with AgNO_3 and 1,4-dicyanobenzene and supported in Pt foil. Cu^{2+} derived from $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was found to be a significantly better cationizing agent than Ag^+ derived from AgNO_3 while the $\text{Cu}(\text{I})$ and $\text{Ag}(\text{I})$ salts, Cu_2O and AgNO_3 , give comparable results (Figure 4). The relative cationizing ability does not simply reflect the relative peak heights of Ag^+ and Cu^+ for the two spectra, as the Cu^+/Ag^+ ratio for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{AgNO}_3$ mixture was 10:1, and for the $\text{Cu}_2\text{O}/\text{AgNO}_3$ mixture it was 7.5:1. In contrast the $(\text{Cu} + \text{M})^+ / (\text{Ag} + \text{M})^+$ ratio is some 30 times greater for the $\text{Cu}(\text{II})$ - than for the $\text{Cu}(\text{I})$ -containing sample. Charge neutralization is an important process which is expected to reduce the ion current in SIMS, so the extra charge in Cu^{2+} might facilitate the ejection of an ionic species in this case.

It is of interest to note the presence of inorganic ions, such as the mixed metal species AgCuCN^+ seen in Figure 4. Inorganic metal ion adducts of the type $(\text{CAC}')^+$ where A is an anion and C and C' are cations occur widely. The anions incorporated in these types of adducts were Cl, CN, O, OH, NO_2 , and NO_3 , depending on the types of anions present and their concentrations. Ions containing only the metal, such as

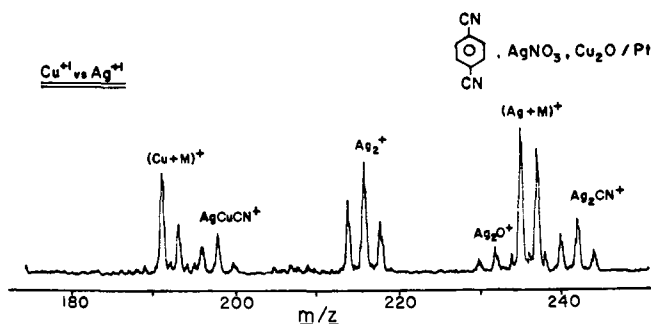


Figure 4. Relative cationization efficiency for a Ag^+ salt vs. a Cu^+ salt as determined by SIMS.

Ag^+ , Ag_2^+ , and Ag_3^+ , could always be observed. The cluster ions could thus be used as mass markers, as they give both absolute mass references and a mass scale.

Experiments were generally done under conditions of low primary ion current so as to minimize any possible damage to the sample resulting from the ion bombardment. It is anticipated that such effects may be of less concern in experiments directed toward molecular structure elucidation than they are in other SIMS work. Thus, the strong intramolecular bonds of organic compounds should mitigate against structural reorganizations involving neighboring molecules (although they would not of course prevent intramolecular rearrangement or fragmentation). To further this enquiry the effect of increasing the primary ion current was studied. An order of magnitude increase (giving conditions definitely not characterizable as corresponding to static SIMS) produced no de-

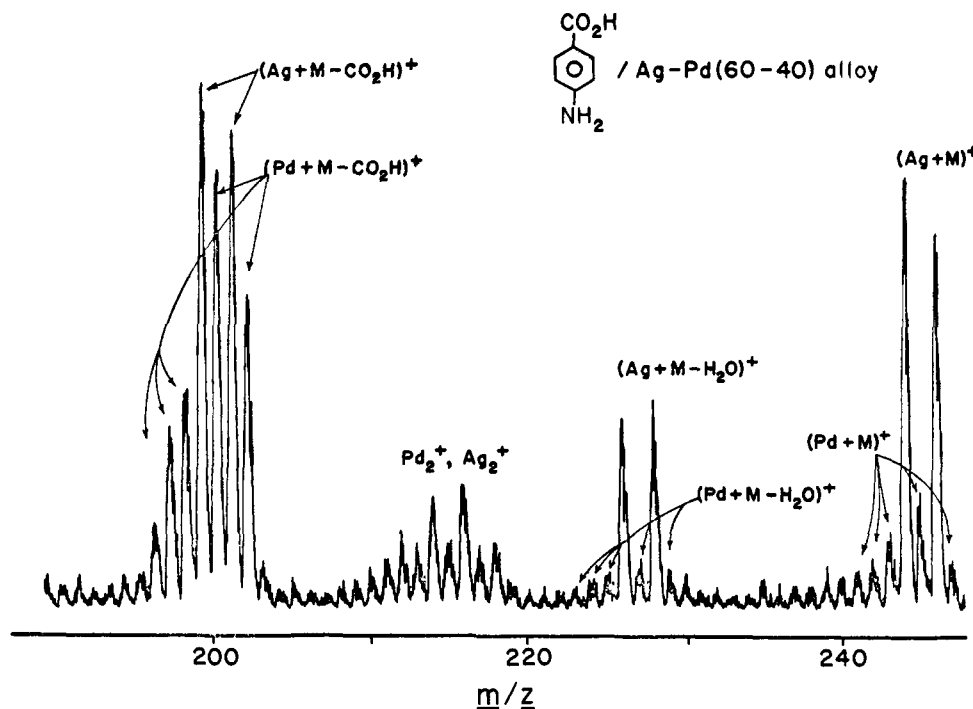


Figure 5. SIMS spectrum of *p*-aminobenzoic acid supported on a Ag-Pd (60:40) alloy.

tectable effect on the dicyanobenzene spectrum except that the total secondary ion yield increased by a factor of about 5.

Attention is now turned to the organic and organometallic ions which occur below $(C + M)^+$ in the SIMS spectra. These ions appear to be related to $(C + M)^+$ by loss of neutral fragments. The particular processes which occur are predictable from a knowledge of unimolecular ionic fragmentations as will now be shown. Detailed arguments supporting the view that the cationized molecule is the precursor of most lower mass ions are given below.

In general the major fragmentations of the cationized molecules involve losses of simple stable neutral molecules such as H_2O and HCN or radicals such as the metal atom, $CN\cdot$, and $HCO_2\cdot$. While the types of fragmentations of a given organic compound do not vary, the extent of fragmentation as judged by the relative abundances of fragment ions and cationized molecules depends upon (1) the nature of the cation and (2) the state of the metal. Thus, in an experiment in which *p*-aminobenzoic acid was examined on a silver/palladium alloy, the $(Ag + M)^+ / (Ag + M - CO_2H)^+$ ratio was ~ 1 while the $(Pd + M)^+ / (Pd + M - CO_2H)^+$ ratio was $\sim 1/7$ (Figure 5).²¹ The greater extent of fragmentation of the palladium adduct also shows up in the presence of $(Pd + 65)^+$ and $(Pd + 39)^+$ ions which do not have silver analogues. Platinum adducts correspond to those of palladium in showing extensive fragmentation.

In order to obtain reproducible spectra, standard sample preparation methods and metal support cleaning procedures have been used.¹⁹ This is necessary since the extent of fragmentation of a given adduct does depend on the metal support. For example, the usual $(Ag + M)^+ / (Ag + M - CO_2H)^+$ ratio for *p*-aminobenzoic acid upon silver is $\sim 1/3$ but the ratio observed for an oxidized silver support (treated briefly with nitric acid) was 10. The ability to selectively control the degree of fragmentation, especially by cationizing with different metals, is analogous to the control exerted in electron impact mass spectrometry by varying the electron energy and in chemical ionization mass spectrometry by varying, for example, the acidity of the reagent ion. This feature should therefore be of advantage in analysis.

We now turn to a detailed discussion of fragmentation behavior and in doing so comparisons are made between the behavior of $(C + M)^+$ ions in SIMS, $(H + M)^+$ ions in CI/MIKES,²² and $M^+\cdot$ ions in EI. It will be shown that for most of the systems studied, the SIMS and MIKE spectra are closely parallel. When the silver is weakly bonded to the organic molecule, as in nonpolar compounds, the resemblance to the EI spectrum is striking. These facts are interpreted to mean that corresponding reactions occur in the cationized species, $(C + M)^+$ and $(H + M)^+$, but loss of the metal regenerates $M^+\cdot$ and hence when this latter process is the dominant primary reaction the spectrum must resemble that observed on electron impact.

A comparison of the behavior of argentated and protonated *p*-aminobenzoic acid is made in Table I. Interest here is limited to the types of reactions undergone by these ions; the differences in composition and associated thermochemistry do not lead one to expect quantitative similarities even for exactly analogous ion structures nor would the entirely different experimental procedures permit such congruence in any event. The qualitative agreement seen in Table I, however, is remarkable. This result supports the empirical interpretation of the SIMS spectra in terms of unimolecular fragmentation sequences from the cationized molecule.²³ This interpretation is also supported by a comparison of the SIMS spectrum of *p*-dicyanobenzene (Figure 2) with the MIKE spectrum of the protonated molecule (Figure 6) where analogous reactions are again observed. This latter example also provides explicit evidence that fragment ions are derived from $(C + M)^+$, not from $M^+\cdot$, as a primary precursor. In the electron impact spectrum, the most intense ion is the molecular ion (100%) which fragments by loss of $CN\cdot$ (5%), HCN (50%), and $H_2CN\cdot$ (3%) to give m/z 102, 101, and 100, respectively. The MIKE spectrum of the protonated molecule shows loss of $H\cdot$ (100%), $CN\cdot$ (5%), HCN (65%), and $H_2CN\cdot$ (18%) to give m/z 128, 103, 102, and 101, respectively. The loss of HCN , the major fragmentation pathway in both spectra, gives m/z 101 from $M^+\cdot$ and m/z 102 from $(H + M)^+$. As seen in Figure 2, the argentated molecule in SIMS $(Ag + M)^+$ shows loss of $CN\cdot$ at m/z 209 and 211 and $AgCN$ at m/z 102. The peak at m/z 101 is almost completely absent in the SIMS spectrum, so an $M^+\cdot$ precursor for the

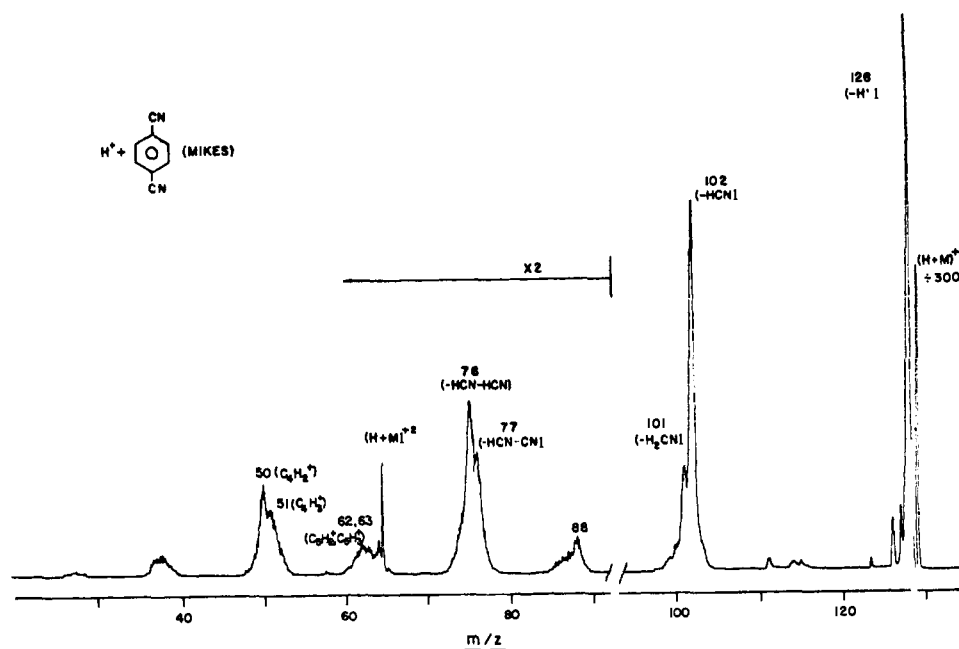


Figure 6. MIKE spectrum showing the collision-induced dissociation of protonated *p*-dicyanobenzene.

fragments in SIMS is unlikely. The loss of AgCN from the cationized molecule is, on the other hand, exactly analogous to the loss of HCN seen for the protonated molecule.

In contrast to the behavior displayed by *p*-aminobenzoic acid and *p*-dicyanobenzene, the nonpolar compounds anthracene and hexamethylbenzene give SIMS spectra which show close resemblances to EI mass spectra (M^+ fragmentations) rather than to CI mass spectra ($(H + M)^+$ fragmentations). The molecular ion region in the anthracene SIMS spectrum includes m/z 179 (15%), 178 (100%), 177 (14%), 176 (24%), and 175 (4%). The electron impact mass spectrum showed peaks at m/z 179 (16%), 178 (100%), 177 (10%), 176 (17%), and 175 (4%). The similarity of the two spectra is striking. The MIKE spectrum of the protonated species shows somewhat greater differences: 178 (100%), 177 (20%), 176 (15%), and 175 (5%). The low mass organic peaks in the SIMS spectrum also more closely resemble EI results than MIKE results. Another fact to be considered is that no peaks occur in the SIMS spectrum which represent fragments from the cationized molecule in which the Ag atom is retained. The interpretation of these data is that the silver forms a weak bond with the molecule. The adduct fragments very readily by losing the silver atom, and the ion which results is the molecular ion M^+ of anthracene which fragments just as it does in EI.

o-Phenylenediamine shows SIMS behavior (Table II) which is intermediate between that of anthracene and that of the polar dicyanobenzene. It shows both an intense $(Ag + M)^+$ adduct ion and an intense molecular ion. The fact that the peak due to the cationized molecule is intense suggests a fairly strong Ag-organic bond. However, the lowest energy fragmentation reaction is apparently Ag loss; no silver-containing fragment ions are observed and the SIMS spectrum corresponds closely with the EI mass spectrum (Table II) and also shows similarities to the MIKE spectrum.²⁴ These observations are consistent with the expectation that Ag^+ -amino bonding will be weak compared, for example, to Ag^+ -nitrile σ bonding where $d-\pi$ back-bonding can occur; hence the much smaller $(Ag + M)^+/(M^+)$ ratio in *o*-phenylenediamine as compared to *o*-dicyanobenzene.

A final and particularly interesting case where cationized molecules can be compared with other quasi-molecular ions is provided by hexamethylbenzene. The relevant data are summarized in Figure 7, which compares the MIKE spectrum

Table I. Comparison of the SIMS and MIKE Spectra of Ions Derived from *p*-Aminobenzoic Acid^a

MIKES	$(H + M)^+$		SIMS	$(Ag + M)^+$	
m/z	intensity	loss	m/z	intensity	loss
137	<i>b</i>	H	137	0.62	Ag
120	78	HOH	120, 226- 228	65, 0.4	AgOH, HOH
94	53	H + 43	150-152	0.25	Ag + 43 ^c
93	45	HCO ₂	199-201	1.0	HCO ₂
92	65	HCO- H	92	40	AgCO ₂ H
77	15	HCO ₂ - NH ₂	77	20	AgCO ₂ NH ₂
65	100	H + 72	65	100	Ag + 72
63	30	H + 74	63	40	Ag + 74
39	30	H + 98	145-147	0.18	H + 98

^a Intensity relative to the most abundant fragment ion. ^b Present but of uncertain intensity. ^c Charged fragment.

with the SIMS spectrum. The protonated molecule behaves as if it had the σ -bonded structure as seen by the losses of H or CH₃ to give ionized hexamethyl- and pentamethylbenzene, respectively. The expected facile loss of CH₃ from these molecular ions to give m/z 147 and 133 accounts for the other two major ions in the MIKE spectrum. By contrast the SIMS spectrum, while it shows Cu loss to give M^+ , shows no trace of CH₃ loss as might occur for a σ -bonded structure. While this result is by no means unexpected, it does represent attainment of considerable detail in understanding the ion chemistry which underlies SIMS spectra.

Information on ion structures is also accessible from the behavior of a given molecule cationized with different metals. The Li⁺ adduct of *p*-aminobenzoic acid behaved differently from the Ag⁺ adduct. The loss of H₂O and CO₂H in the latter adduct (Table I) constitutes evidence against a silver-carboxyl bond. The lithium adduct does not show H₂O and CO₂H losses. This could be due to differences in internal energies and ease of fragmentation or the ion may be the lithium carboxylate.

In addition to ions of lower mass than the cationized molecule, ions of higher mass were observed under certain circumstances. While such ions are undesirable from the ana-

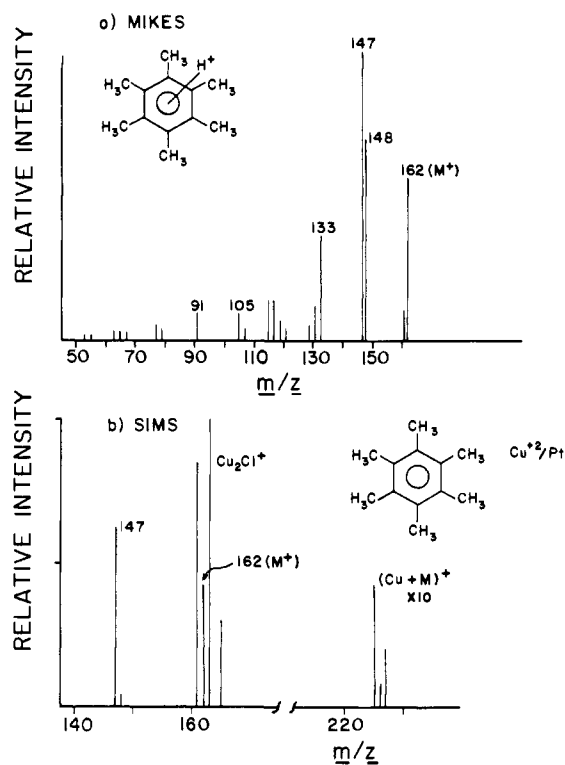


Figure 7. Comparison of the MIKE spectrum of protonated hexamethylbenzene with the SIMS spectrum of hexamethylbenzene mixed with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and supported on Pt. The $(M + H)^+$ ion is not shown in the MIKE spectrum.

lytical viewpoint, their occurrence can be controlled. Two types of ions, both containing more than one metal atom, were observed. Firstly, ions in which one or more hydrogen atoms were substituted by alkali atoms were generated; thus deliberate addition of an alkali salt (LiCl) to *p*-aminobenzoic acid gave $(M + 2\text{Li} - \text{H})^+$ and $(M + 3\text{Li} - 2\text{H})^+$.²⁵ The second type of ion occurred in significant intensity only for Pt for which the entire series of monoplated ions is repeated with two platinum atoms per ion. Platinum and palladium are relatively ineffective at producing simple cation adducts. For example, when *p*-aminobenzoic acid was adsorbed onto a platinum foil, three adduct species of the type observed for silver were observed as well as ions of the type $(\text{Pt} + \text{C}_n\text{H}_m)^+$, where m is not exactly known and $n = 3-6$. For the ions which do parallel those for silver, the intensities are very low as compared to the lower mass fragments. Platinum also showed contrasting behavior to silver in that it was retained in lower mass ionic adducts which are not related to the ions seen in MIKES. The inclusion of Pt or Pd in the molecular ion apparently results in a more reactive system.

The types of ions observed in this SIMS study have analogues in those observed in several other ionization methods in which the organic compound is ionized directly from the solid state. The cationization observed in SIMS is much more general than in the other techniques with the metals Li, K, Co, Ni, Ca, Pd, Ag, W, and Pt (all those tried) being used successfully to cationize organic molecules. In the other techniques the chief cationizing species have up to now been the alkali metals, although there have been isolated cases of Fe addition in electrohydrodynamic ionization^{11b} and possible cases of FeCl and CoCl addition in field ionization.²⁶

Parallels between SIMS and FD extend to the alkali metal substitution process. Contrasts with the other methods, particularly with EHD, are to be found in the absence in SIMS of ions in which clusters of organic molecules are cationized by a single metal atom. Since this type of ion is most undesir-

Table II. Comparison of the Electron Impact Mass Spectrum and the SIMS Spectrum of *o*-Phenylenediamine

m/z	SIMS ^a		SIMS		EI rel intensity
	rel intensity	EI rel intensity	m/z	rel intensity	
108	40	100	55	5	4
107	<i>b</i>	35	54	14	32
92	1	2	53	12	47
91	2	10	52	22	43
90	1	5	51	7	23
81	6	31	50	5	15
80	22	90	49		4
79	1	5	46	1	
78	3	7	45	4	
77	2	2	44	3	
76	1	4	43	8	4
75	3	3	42	12	7
69	4	1	41	100	18
68	1	1	40	<i>b</i>	8
67	4	9	39	<i>b</i>	24
66	5	4	38	11	15
65	16	12	37	2	7
64	5	14	35	1	
63	16	15	31	2	
62	2	4	30	10	5
61		2	29	13	5
60	3		28	41	40
59	7		27	31	17
57	2		26	5	5
56	12	3	25	2	
24	11				
23	<i>b</i>				

^a SIMS intensities are expressed relative to m/e 41 and encompass all ions up to m/z 108. ^b Obscured by $^{107}\text{Ag}^+$, $^{40}\text{Ar}^+$, $^{39}\text{K}^+$, or $^{23}\text{Na}^+$.

able in analytical studies, the metal-rich as opposed to organic-rich nature of the SIMS spectra is an advantage. Given that all these ionization procedures involve deposition of energy into organic solids in contact with metal supports, mechanistic similarities are evidently implied by the parallels between the spectra.

Conclusion

Cationization of organic molecules using transition and noble metals is a general procedure which can be applied to both polar and nonpolar organic molecules for which it yields the molecular weight and structural information. The metal can be supplied in pure form or as an added salt with only qualitative effects on the nature of the mass spectrum. Nevertheless, both the nature of the cation itself and that of the substrate (pure, oxidized, alloy) can affect the degree of fragmentation observed. Copper and silver adducts are associated with less fragmentation than are the platinum or palladium species.²⁷ The former species appear to be more suitable for organic structural analysis. Ions containing more than one metal atom are observed for Pt and are prominent for the alkali metals Li and K. Parallels exist between metal attachment observed here and the alkali metal adducts observed in plasma desorption, field desorption, and electrohydrodynamic ionization.

While the relative merits of the various procedures for directly ionizing organic solids are yet to be established there are clear advantages in cationizing with metals rather than with hydrogen. They are (1) multiple isotope cluster peaks can be used to characterize the molecular weight, (2) fragmentation patterns are easier to interpret because the cation is distinguishable from the atoms in the organic molecule, (3) by altering the cation the degree of fragmentation can be altered and the ions characterizing the molecular weight can be moved

away from background or interfering ions, and finally, (4) different metals may bond to different sites (cf. Ag^+ vs. Li^+ on *p*-aminobenzoic acid) and thus yield complementary fragmentation patterns.

The present data strongly point to a mechanism for cationization in which the cationized molecule is the precursor for all the major organic peaks observed in the SIMS spectra. Some of the adduct ions are sufficiently energized to fragment spontaneously in the gas phase. The similarities of the fragmentation observed in electron impact and collision-induced dissociation of $(\text{H} + \text{M})^+$ ions in MIKES point to the unimolecular fragmentations of the energized ions in all three techniques. The process in which the actual cationized molecule is formed is not yet known. By combining information from SIMS with that from FD, PD, LD, and EHD, significant progress should now be imminent in locating and controlling those factors which will optimize the efficiency, sensitivity, and specificity with which ions can be generated directly from the solid.

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References and Notes

- (1) For a preliminary communication, see H. Grade, N. Winograd, and R. G. Cooks, *J. Am. Chem. Soc.*, **99**, 7725 (1977).
- (2) For reviews see (a) J. A. McHugh in "Methods of Surface Analysis", A. W. Czanderna, Ed., American Elsevier, New York, N.Y., 1975; (b) A. Benninghoven, *Surf. Sci.*, **53**, 596 (1975); (c) K. F. I. Heinrich and D. E. Newbury, Ed., "Secondary Ion Mass Spectrometry", NBS Special Publication 427, U.S. Department of Commerce, Washington, D.C., 1975; (d) H. Liebl, *J. Phys. E*, **8**, 797 (1975); (e) C. A. Hofmann, *Vacuum*, **24**, 65 (1974).
- (3) See, for example, (a) R. E. Honig, *J. Appl. Phys.*, **29**, 549 (1958); (b) A. Benninghoven, *Z. Phys.*, **199**, 141 (1967).
- (4) (a) A. F. Dillon, R. S. Lowe, J. C. Robb, and D. W. Thomas, *Adv. Mass Spectrom.*, **4** (1968); (b) G. Müller, *Appl. Phys.*, **10**, 317 (1976); (c) G. D. Tantsyrev and N. A. Kleinov, *Dokl. Akad. Nauk SSR*, **213**, 649 (1973); (d) W. M. Riggs, *Conf. Fed. Anal. Chem. Spectrosc. Soc.*, No. 201 (1976).
- (5) (a) A. P. Duhamel, *Pittsburgh Conf. Anal. Chem. Appl. Spectrosc.*, No. 352 (1974); (b) F. W. Karasek, *Res./Dev.*, **25**, 42 (1976); (c) A. Benninghoven, D. Jaspers, and W. Sichtermann, *Appl. Phys.*, **11**, 35 (1976).
- (6) F. M. Devienne and J. Giroud, *Symp. Int. Jets. Mol.*, **5th**, No. B7 (1975).
- (7) (a) M. Barber, J. C. Vickerman, and J. Wolstenholme, *J. Catal.*, **42**, 48 (1976); (b) P. H. Dawson, *J. Vac. Sci. Technol.*, **14**, 786 (1977); (c) R. J. Colton, J. Murday, J. R. Wyatt, and J. J. DeCorpo, *Anal. Conf. Mass Spectrom. Allied Top.*, No. B8 (1977).
- (8) (a) H. D. Beckey and H. R. Schulten, *Angew. Chem., Int. Ed. Engl.*, **14**, 403 (1975); (b) H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 500 (1969); (c) H. U. Winkler and H. D. Beckey, *Org. Mass Spectrom.*, **6**, 655 (1972); (d) H.-R. Schulten, H. S. Beckey, G. Eckhardt, and S. H. Doss, *Tetrahedron*, **29**, 3861 (1973); (e) H. Budzikiewicz and M. Linscheid, *Biomed. Mass Spectrom.*, **4**, 103 (1977).
- (9) (a) D. F. Torgerson, R. P. Skowronski, and R. D. Macfarlane, *Biochem. Biophys. Res. Commun.*, **60**, 616 (1974); (b) R. D. Macfarlane and D. F. Torgerson, *Int. J. Mass Spectrom. Ion Phys.*, **21**, 81 (1976); (c) R. S. Macfarlane and D. F. Torgerson, *Science*, **191**, 920 (1976); (d) O. Becker, N. Fürstenau, F. R. Krueger, G. Weiss, and K. Wien, *Nucl. Instrum. Methods*, **139**, 195 (1976).
- (10) M. A. Posthumus, P. G. Kistemaker, and H. L. C. Meuzelaar, *Anal. Chem.*, **50**, 985 (1978).
- (11) (a) D. J. Simons, B. N. Colby, and C. A. Evans, Jr., *Int. J. Mass Spectrom. Ion Phys.*, **15**, 29 (1974); (b) R. P. Stimpson and C. A. Evans, Jr., *Biomed. Mass Spectrom.*, in press.
- (12) D. F. Hunt, J. Shabanowitz, and F. K. Botz, *Anal. Chem.*, **49**, 1160 (1977).
- (13) J. F. Holland, B. Soltmann, and C. C. Sweeley, *Biomed. Mass Spectrom.*, **3**, 340 (1976).
- (14) (a) O. Becker, N. Fürstenau, W. Knippelberg, and F. R. Krueger, *Org. Mass Spectrom.*, **12**, 461 (1977); (b) F. W. Rollgen and H.-R. Schulten, *ibid.*, **10**, 660 (1975).
- (15) A. Benninghoven and W. Sichtermann, *Org. Mass Spectrom.*, **12**, 595 (1977).
- (16) A. Benninghoven, *Surf. Sci.*, **39**, 427 (1973).
- (17) J. H. Beynon, R. G. Cooks, J. W. Amy, W. E. Baitinger, and T. Y. Ridley, *Anal. Chem.*, **45**, 1023A (1973).
- (18) (a) A. Shepard, R. W. Hewitt, G. J. Slusser, W. E. Baitinger, R. G. Cooks, N. Winograd, W. N. Delgass, A. Varon, and G. Devant, *Chem. Phys. Lett.*, **44**, 371 (1976); (b) N. Winograd, A. Shepard, R. Hewitt, W. Baitinger, and N. Delgass, *Proc. 7th Int. Vac. Congr. 3rd Int. Conf. Solid Surf. (Vienna)*, **1** (1977).
- (19) H. Grade, M.S. Thesis, Purdue University, 1977.
- (20) This result provides a striking contrast with the studies of Benninghoven which almost invariably led to $(\text{H} + \text{M})^+$ ions even though similar techniques were used.
- (21) Note that differences in the sputtering yields of the metal ions in the binary alloy can be moderated by comparing the corresponding organometallic ions. Thus the alloy was found to yield an order of magnitude more Ag^+ than Pd^+ under static SIMS conditions and also when covered with *p*-aminobenzoic acid. By contrast the total abundances of the organometallic ions are much more similar.
- (22) The protonated species is generated by chemical ionization, selected by mass analysis, and then its fragmentation pattern is recorded in the presence of collision gas.
- (23) It also indicates specific (covalent) metal ligand bonds rather than electrostatic interactions.
- (24) The peaks observed in the MIKE spectra are centered on m/e 92, 80, 65, 63, 52, 41, 38, and 28.
- (25) Related potassium-containing ions, $(\text{K} + \text{M})^+$ and $(2\text{K} + \text{M} - \text{H})^+$, due presumably to potassium chloride impurity in LiCl were also observed. These ions were not recognized as such in the preliminary communication.¹
- (26) See comments in ref 14b regarding J. R. Hass, M. C. Sammons, M. M. Bursey, B. J. Kukuch, and R. P. Buck, *Org. Mass Spectrom.*, **9**, 952 (1974).
- (27) This result, if it proves to be general, can be ascribed to the greater coordinating ability of the closed shell Ag^+ and Cu^+ (d^{10}) ions. The behavior of Zn as a cationizing metal in SIMS will be of particular interest.