Tetrahedron, Vol. 37, pp. 1067 to 1073, 1981
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0040-4020/81/061067-07$02.00/0

NEGATIVE AND POSITIVE SECONDARY ION MASS SPECTRA OF ORGANIC ACIDS

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(*Received in USA* 27 *May* 1980)

Abstract—Organic compounds can be ionized by sputtering the solid sample. The resulting negative and positive secondary ions provide mass spectra which characterize both the molecular weights and the structures of the compounds. Ionization occurs either by direct ejection of charged species from the solid into vacuum or by electron or proton transfer. The sputtered secondary ions dissociate unimolecularly to give fragment ions. These reactions are identical to those which occur when the secondary ions are independently generated by chemical ionization, selected by mass and dissociated in a high energy gas phase collision. The negative ion SIMS spectra show molecular ions ($M^{-\cdot}$) or $(M-H)^-$ ions as the dominant high mass species together with fragments due to decarboxylation, dehydration and losses of other simple molecules. Stronger acids show larger $(M-H)^-/M^{-\cdot}$ abundance ratios. The positive ion spectra are complementary and also useful in characterizing molecular structures. Attachment of cations to organic molecules (cationization) occurs much more readily than anion attachment and this makes negative SIMS spectra simpler than these positive ion counterparts.

Procedures for obtaining mass spectra of involatile and thermally labile compounds scarcely existed a decade ago.[1] There are now several such ionization methods, although they are still in the process of being characterized and optimized. Field desorption[2] is perhaps best known, although plasma desorption has had even more striking successes.[3] Also successful are new "in-beam" techniques in which the sample is placed on a suitable substrate such as an organic polymer or carbon microneedles and introduced directly into the electron beam of an electron impact source or into the plasma in a chemical ionization source.[4] The advantage of simplicity and minimal instrumental modification with "in-beam" methods over field or plasma desorption techniques is apparent.

With the exception of field desorption,[5] all these methods, as well as others such as laser desorption,[6] give useful negative ion as well as positive ion spectra. The complementary nature of the analytical information obtained from negative ions, their high structural specificity, and the simplicity of their dissociation patterns are well-known,[7] especially from work on negative chemical ionization. This paper is a study of negative and positive ion mass spectra obtained with one of the newer methods for ionizing organic compounds, secondary ion mass spectrometry (SIMS). Most of the compounds studied are volatile and could have been ionized by other methods but spectra of involatile organic salts are also discussed. Some analytical characteristics of negative SIMS are treated, comparisons with the better known positive ion spectra are made, and the chemistry which yields the observed mass spectra is discussed. For the acidic compounds investigated, negative ion SIMS provides molecular weight and functional group information and demonstrates that certain positional isomers of aromatic compounds give distinguishable spectra.

In SIMS, a solid is bombarded by a kilovolt energy ion beam, often Ar^+, and the mass spectrum of the sputtered secondary ions is recorded. For more than two decades SIMS has been used in the analysis of metallic surfaces,[8] but only recently has it been applied in any systematic way to organic analysis.[9] Benninghoven[10] has recorded the SIMS spectra of many compounds of biological interest, observing both $M^{+\cdot}$ and $(M+H)^+$ species in positive SIMS and $(M-H)^-$ species in negative SIMS. Rabalais[11] and Michl[12] *et al.* have reported the positive SIMS spectra of frozen hydrocarbons prepared in an argon matrix or as a neat solid.

Reports from this laboratory have delineated three ionization processes in positive SIMS.[13] The first of these is cationization (1), an association reaction in which an adduct between a metal ion, C^+, and an organic molecule, M, is formed. The formation of metal adducts of organic molecules, $(C+M)^+$ in SIMS is reminiscent of protonation, to yield $(M+H)^+$, in chemical ionization and parallels alkali ion attachment to molecules in field and laser desorption. The other two ionization processes are electron detachment (2) and direct ejection of ions from the solid to the gas phase (3). The last mechanism is particularly important with regard to the analysis of ionic compounds as shown in its application to the identification of quaternary nitrogen salts such as choline esters.[14] The sensitivity of SIMS for cationic salts is good, allowing detection limits in the picogram range for certain organic compounds.[15] This characteristic, together with the fact that SIMS is a surface sensitive technique makes it a valuable method for detecting molecular species on surfaces. This capability distinguishes SIMS and laser desorption from the ionization methods mentioned above.

EXPERIMENTAL

The SIMS instrument and sample preparation procedures are described in detail elsewhere.[13] Approximately 0.1 mg of the organic compound was burnished onto a silver foil and bombarded with an argon primary ion beam (10^{-10}–10^{-8} A; 10^{-8}–10^{-6} A/cm^2; 5 keV). Negative and positive ion SIMS spectra were recorded using a quadrupole mass analyzer. Scan times were typically 10 min. The conditions employed were such that spectra did not change significantly over a period of several hours. Spectra are reproducible from day to day to within 10% relative ion abundance, providing instrumental parameters such as primary ion flux are reproduced accurately. Corrections of background ions are not made. Ubiquitous ions in the lower mass

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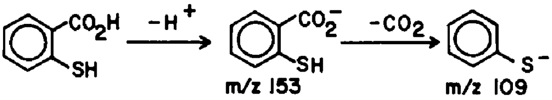
region include m/z 12, 13, 16, 17, 24, 25, 26, 35, and 37 all of which can be attributed to residual hydrocarbons, oxygen, and chloride on the surface. The intensity of 0^- at m/z 16 varies somewhat with sample preparation and instrumental parameters. Typical anion and cation signals are 10^3–10^4 counts/sec for primary ion currents of 10^{-8} A/cm^2.

With the exception of *p*-mercaptobenzoic acid, which was prepared by a procedure similar to that of Allen and MacKay,[16] all compounds were commercial samples and were used without further purification. Electron impact mass spectra were recorded with a CEC-110B mass spectrometer to establish compound purity. The mass-analyzed ion kinetic energy spectra (MIKES) were recorded on a MIKE spectrometer which has been described previously.[17]

RESULTS AND DISCUSSION

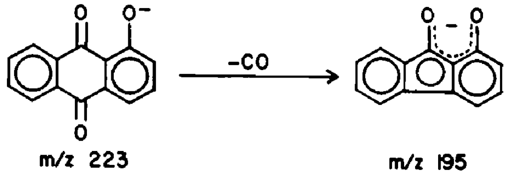
A representative negative ion SIMS spectrum, that of *o*-mercaptobenzoic acid, is shown in Fig. 1. Besides the anion $(M-H)^-$, m/z 153, the only high mass ion of large abundance is m/z 109 which is associated with loss of 44 mass units from the quasi-molecular ion $(M-H)^-$. This type of decarboxylation has been encountered in other forms of mass spectrometry.[18] Specifically it has been shown that decarboxylation can occur as a gas phase dissociation by generating the $(M-H)^-$ ion via chemical ionization, mass-selecting this ion and then recording its dissociation spectrum. This spectrum, a mass-analyzed ion kinetic energy (MIKE) spectrum of $(M-H)^-$, m/z 153, of *o*-mercaptobenzoic acid is also shown in Fig. 1.



Scheme 1.

The experiments described here also address the mechanism of dissociation in SIMS. If negative ion reactions parallel those of positive ions, direct ejection of $(M-H)^-$ followed by spontaneous dissociation during transit from the sample to the analyzer must be a contributing process. This is supported by the fact that sodium salts of organic acids such as benzoic and barbituric acid gave similar spectra to those of the free acids.[19] The proposed fragmentation pattern associated with ortho mercaptobenzoic acid is given in Scheme 1 (ion structures not independently proven). Related possibilities for generating $(M-H)^-$ are loss of H$^\cdot$ from the $M^{-\cdot}$ ion (not observed) and sputtering of the neutral acid followed by proton abstraction.

The spectrum of a weaker acid, 1-hydroxyanthraquinone, is shown in Fig. 2. Again, the $(M-H)^-$ ion at m/z 223 and a single fragment ion at m/z 195 are dominant, illustrating the simplicity of these spectra. Those fragment ions which are observed, however, typically have high structural information content. In this example loss of 28 mass units indicates the presence of a carbonyl group which is readily lost as CO. This spectral feature is rationalized in Scheme 2.



Scheme 2.

The negative SIMS spectrum of 1,5-dihydroxynaphthalene shows two ions, m/z 159 (100%), $(M-H)^-$, and m/z 160 (50%, $M^{-\cdot}$). Two contrasts with the 1-hydroxyanthraquinone spectrum can be noted. First, the low energy dissociation pathway (CO loss) has been removed so the only observed ions occur in the molecular ion region. It is striking that, in addition to the $(M-H)^-$ ion, m/z 159, the molecular anion $M^{-\cdot}$, m/z 160, occurs with substantial relative intensity. Both ions, of course, provide the desired molecular weight information. The tendency for stronger acids to yield $(M-H)^-$ rather than $M^{-\cdot}$ ions is evidenced from results for another phenol. Pentachlorophenol shows an extremely simple spectrum confined to the $(M-H)^-$ ion.[20]

It is instructive to compare the positive and negative SIMS spectra of 1,5-dihydroxynaphthalene. The positive ion spectrum recorded on Ag foil (Fig. 3) has comparable signal to noise characteristics to the negative ion spec-

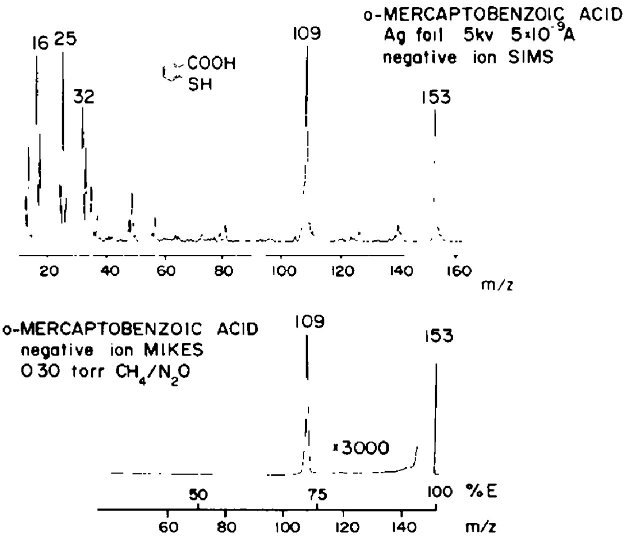


Fig. 1. Negative ion SIMS spectrum of *o*-mercaptobenzoic acid, M = 154 compared to the MIKE spectrum of its $(M-H)^-$ ion, m/z 153.

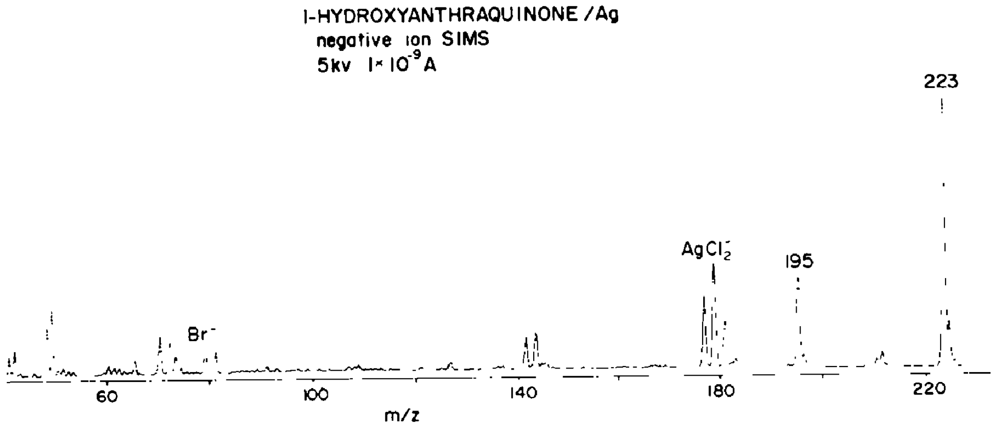


Fig. 2. Negative ion SIMS spectrum of 1-hydroxyanthraquinone, M = 224. Note the inorganic cluster ions, $AgCl_2^-$ and $AgCl^-$.

trum and provides analogous structural data. The molecular weight is again evident from the ions at m/z 159 and 160, as well as from the silver monomer and silver dimer adduct ions. The formation of the stable phenoxy cation 159^+ is predictable in view of the mounting evidence that ions in SIMS are formed by fragmentations which parallel those occurring in other forms of mass spectrometry.[13,21] On the other hand, the presence of intense $(Ag_2 + M - H)^+$ ions was somewhat unexpected, yet quite general for these types of compounds.[22] The $(Ag + M - H)^+$ ions may arise by attachment of neutral Ag to the phenoxy cation or by fragmentation of the $(Ag + M)^+$ or $(Ag_2 + M - H)^+$ ions. These features make positive SIMS data more complex than negative ion results, yet all the

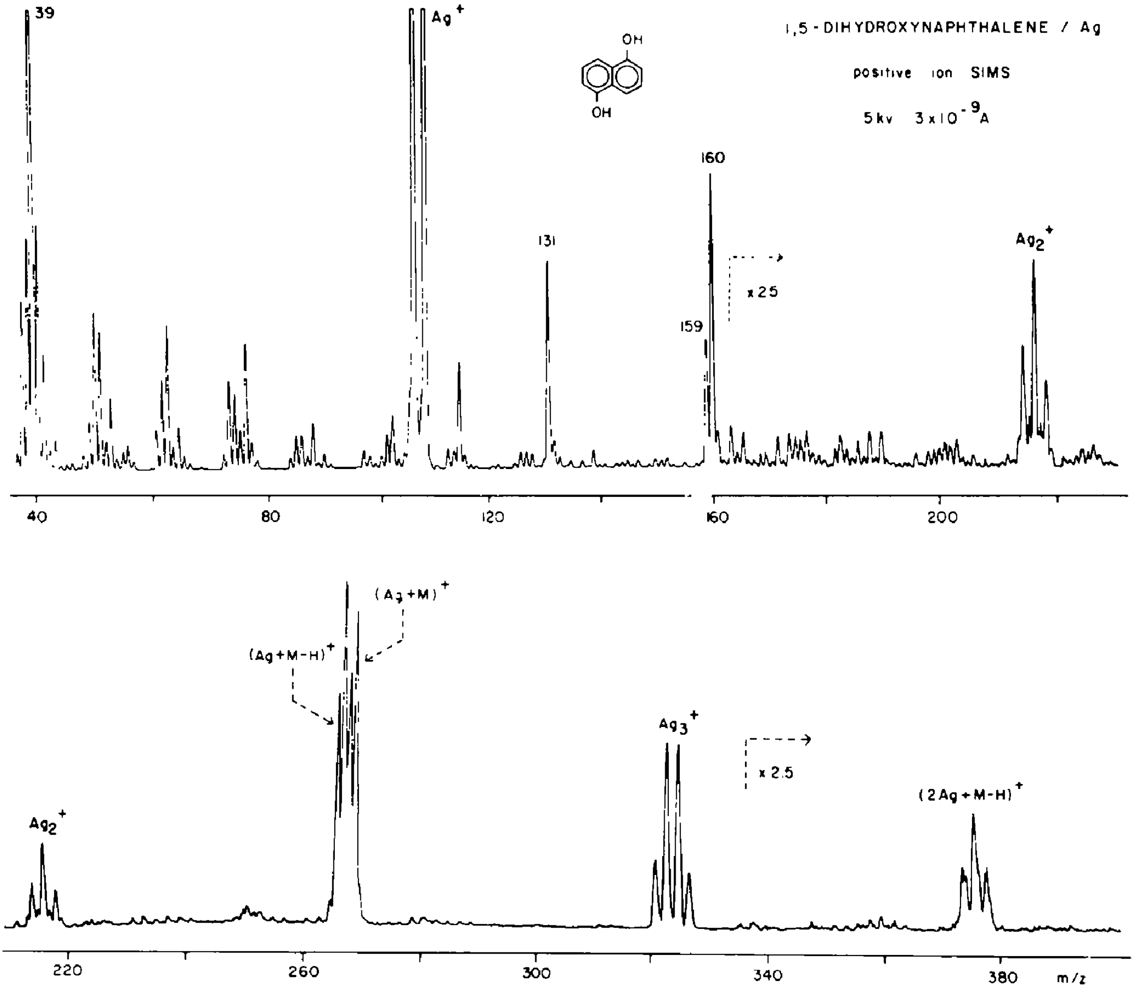


Fig. 3. Positive ion SIMS spectrum of 1,5-dihydroxynaphthalene. Note the formation of cluster ions between the substrate (Ag) and the sample (M).

peaks can be rationalized and the loss of CO to give 131^+ from 159^+ is a useful guide to molecular structure.

Figure 4 shows the negative ion SIMS spectra of *o*-, *m*-, and *p*-hydroxybenzoic acid. All of which show considerable contributions at low mass from background ions. As in the spectrum of *o*-mercaptobenzoic acid, the $(M-H)^-$ ion at m/z 137 and the $(M-H-CO_2)^-$ ion at m/z 93 are virtually the only ions in the spectrum of the *ortho* compound (excluding background ions). The *meta* and *para* isomers show much less CO_2 loss from $(M-H)^-$. The same relative trend in the extent of decarboxylation is observed for the various positional isomers of the mercapto and aminobenzoic acids (Table 1). This offers the possibility of using SIMS for isomer distinction.

In the positive SIMS spectra of organic salts, large increases in primary ion flux (10^{-9}–10^{-5} A/cm^2) resulted in increased fragmentation of the organic cation.[14] This observation was paralleled in negative SIMS spectra of the substituted benzoic acids, where the extent of decarboxylation could be increased by a factor of two by increasing the primary ion current density. Therefore, primary ion current densities were maintained at constant levels (3×10^{-7} A/cm^2; 5 KeV) throughout the different experiments to insure reproducible spectra.

The positive ion SIMS spectra can also be used to distinguish positional isomers of carboxylic acids as summarized in Table 2. These spectra, as in the example of 1,5-dihydroxynaphthalene, are considerably more complex than their negative ion analogs. In addition, the fragments associated with the $(Ag_2+M-H)^+$ion are often different from those associated with the $(Ag+M)^+$ ions. Of particular note is the lack of dehydration of the silver dimer adducts, whereas this is an important fragmentation for both the $(M+H)^+$ and the $(Ag+M)^+$ ions. Other cases of differing reactivity for different organometallic cluster ions have recently been observed.[20]

MIKE spectra of $(M+H)^+$ ions of substituted benzoic acids (Table 3) show loss of H_2O presumably to generate the respective acylium ions which undergo subsequent loss of CO to yield ions at $(M+H-46)^+$. This process parallels those occurring for $(Ag+M)^+$ ions in SIMS. In MIKES as in SIMS, the *ortho* isomer is easily dis-

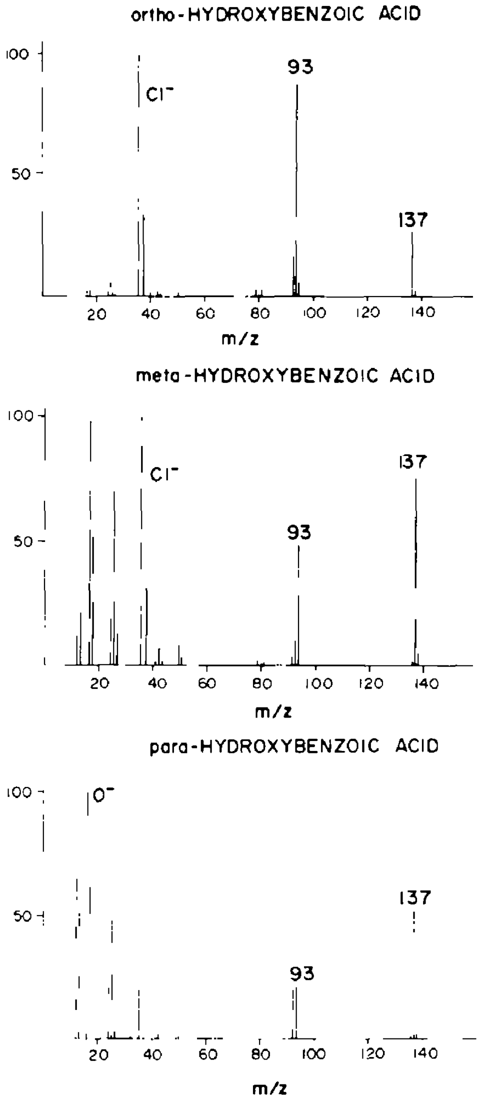


Fig. 4. Isomer distinction by negative ion SIMS. The three hydroxybenzoic acids give characteristic abundances for decarboxylation.

Table 1. Negative ion SIMS[1]

	RELATIVE ION INTENSITY[2]		
COMPOUND	$(M-H-CO_2H)^-$	$(M-H-CO_2)^-$	$(M-H)^-$
benzoic acid	0	100	100
o-aminobenzoic acid	0	100	30
m-aminobenzoic acid	10	20	100
p-aminobenzoic acid	10	20	100
o-hydroxybenzoic acid	20	100	30
m-hydroxybenzoic acid	20	60	100
p-hydroxybenzoic acid	40	40	100
o-mercaptobenzoic acid	30	100	70
p-mercaptobenzoic acid	60	70	100

[1] Primary ion beam is Ar^+, 5kV, 3×10^{-9} A, 3×10^{-7} A/cm^2.

[2] Largest peak is assigned an intensity of 100.

Table 2. Positive ion SIMS

RELATIVE ION INTENSITY[1]

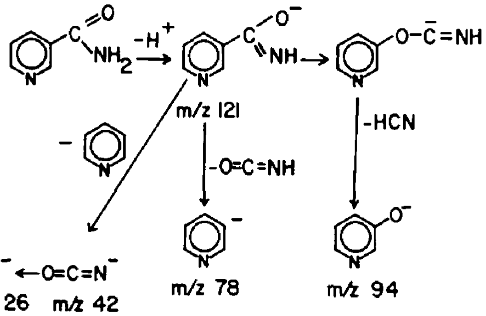
COMPOUND	$(Ag+M-CO_2-XH_n)^+$ [2]	$(Ag+M-CO_2H)^+$	$(Ag+M-H_2O)^+$	$(Ag+M)^+$	$(Ag_2+M-CO_2H)^+$	$(Ag_2+M-H)^+$
benzoic acid	0	20	0	30	50	30
o-aminobenzoic acid	40	170	50	230	80	50
m-aminobenzoic acid	0	150	0	110	160	60
p-aminobenzoic acid	0	60	30	100	30	20
o-hydroxybenzoic acid	0	0	40	40	20	30
m-hydroxybenzoic acid	0	20	0	30	50	40
p-hydroxybenzoic acid	0	30	20	140	30	20
o-mercaptobenzoic acid	120	100	190	80	0	170
p-mercaptobenzoic acid	0	10	30	190	0	10

[1] The $(M+H-H_2O)^+$ ion is assigned an intensity of 100. Intensities are the sum of Ag isotopic contributions.

[2] n = 2 for X = S, O ; n = 3 for X = N.

tinguished from either the *meta* or *para* isomer by showing no loss of CO_2 from $(M+H)^+$, a fragmentation pathway common to both the *meta* and the *para* isomer. This isomer is also distinguished by the fact that loss of 19 amu (H_2O and H·) from $(M+H)^+$ occurs (Table 3). It is possible that the strong intramolecular H-bonding in the *ortho* isomer stabilizes the molecular ion so that decarboxylation is not possible. Hence the *ortho* interaction channels fragmentation mainly via water and (H_2O + H·) losses.

The preceding results show that for aromatic acidic compounds negative SIMS is a useful method of ionization. Its application to natural products, biological compounds, and to mixtures in general is therefore worth consideration. Nicotinamide gives a simple negative SIMS spectrum (Fig. 5). The $(M-H)^-$ ion is the dominant high mass ion while its fragment ions are readily rationalized (Scheme 3). A simple mixture, buffered aspirin, gives the SIMS spectrum shown in Fig. 6. Apparent in this spectrum is the $(M-H)^-$ ion of salicyclic acid, m/z 137, its decarboxylation ion, m/z 93, and the acetate anion, m/z 59. It is not yet known if isomers can be distinguished in such complex mixtures.



Scheme 3.

The present results, taken in conjunction with published data on positive SIMS, show that analogous processes occur in both modes of ionization. Evident in these spectra are (1) the direct ejection of anions from the solid to the gas phase, (2) the attachment of electrons to molecules, and (3) the attachment of anions to molecules. This last process, anionization, has so far been demonstrated only for inorganic molecules such as $AgCl_2^-$ (Fig. 3). The absence of ready anionization of

Table 3. Positive ion MIKES

RELATIVE ION INTENSITY[1]

COMPOUND	$(M+H-H_2O-CO)^+$	$(M+H-CO_2)^+$	$(M+H-H_2O-H\cdot)^+$	$(M+H-H_2O)^+$
benzoic acid	1.3	0.5	0	1.3
o-aminobenzoic acid	1.1	0	1.6	6.4
m-aminobenzoic acid	0.5	0.5	0	0.7
p-aminobenzoic acid	0.4	0.4	0	1.2
o-hydroxybenzoic acid	1.0	0	2.0	7.8
m-hydroxybenzoic acid	0.8	1.1	0	3.3
p-hydroxybenzoic acid	0.4	0.4	0	1.2
o-mercaptobenzoic acid	1.2	0	2.5	11.0
p-mercaptobenzoic acid	0.4	0.3	0	0.6

[1] The $(M+H)^+$ ion is assigned an intensity of 1000.

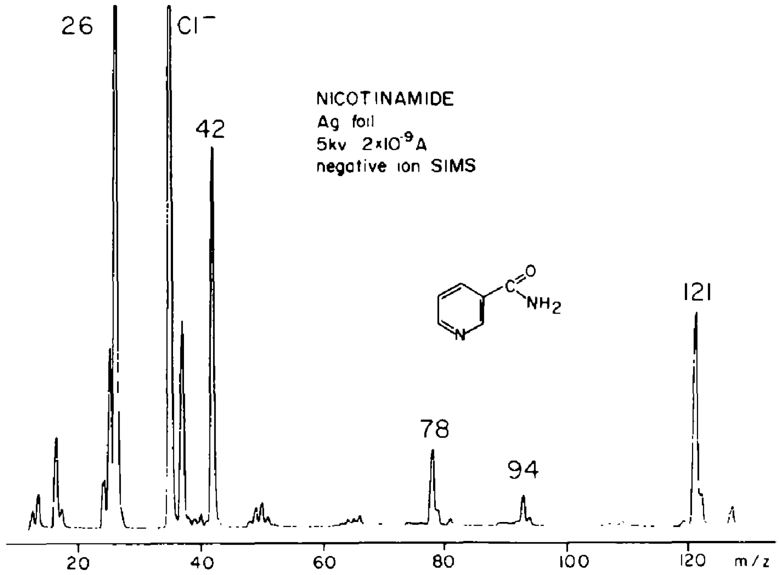


Fig. 5. Negative ion SIMS spectrum of nicotinamide, M = 122. The chloride is an impurity.

organic molecules, in spite of the intense signals for Cl^- and CN^- in some of the above spectra, is in marked contrast to the cationization of organic molecules by metal ions. This feature is also largely responsible for the negative ion SIMS spectra being simpler than the positive ion SIMS spectra.

In an attempt to obtain examples of molecular anionization, the spectra of 9-borabicyclo[3.3.1]nonane, was obtained. Adducts with the halides and cyanide are not observed in detectable quantities. However, the borohydride $(M+H)^-$, is the largest high mass peak in the negative SIMS spectrum (Fig. 7). This compound also shows cationization to give $(Ag+M)^+$ and fragmentation from the cationized molecule by loss of BH_3 and HCB in the positive SIMS spectrum. The borenium ion $(M-H)^+$ is also formed (Fig. 7).

CONCLUSIONS

SIMS provides negative ion mass spectra of both free carboxylic acids, phenols, and their corresponding salts. Intensities are comparable to, and in many cases exceed, the intensities of ions found in the positive SIMS spectrum, therefore, detection limits are expected to be correspondingly low. The spectra are relatively easy to interpret and they provide structural information. Negative SIMS is therefore expected to play a complementary

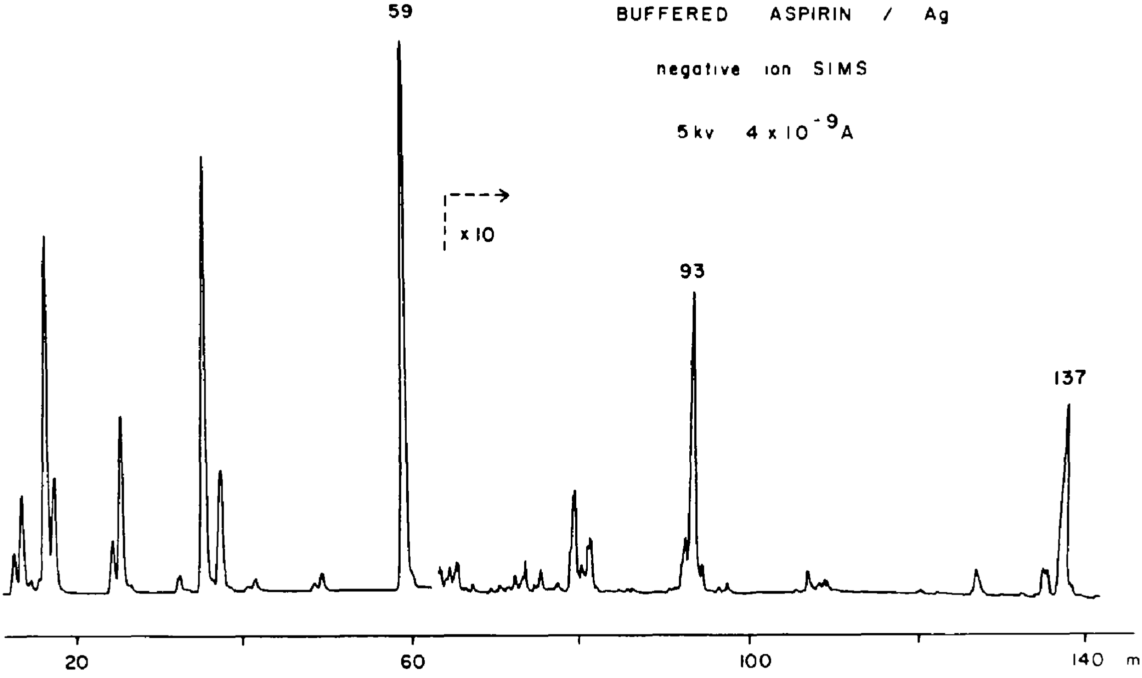


Fig. 6. Negative ion SIMS spectrum of buffered aspirin.

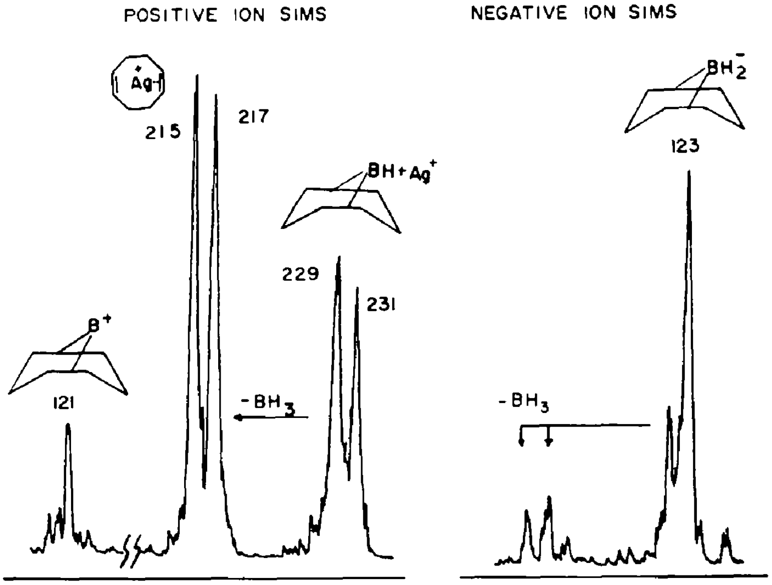


Fig. 7. Comparison of positive and negative ion SIMS spectra of 9-borabicyclo[3.3.1]nonane, 9-BBN.

role in molecular analyses to its positive ion counterpart. The combination of both modes yields a wealth of molecular structural information.

As in the case of other forms of negative ionization, negative SIMS may not apply to all classes of compounds (for example, steroids have failed to yield negative SIMS spectra). It is, therefore, a selective as well as a sensitive method of analysis, applicable as shown above to the direct analyses of some simple mixtures. This, in combination with its sensitivity, structural specificity, and surface sensitivity, might make it useful in the study of active surfaces, such as catalysts.

The mechanisms of dissociation in negative SIMS appear to be simple, predictable gas phase processes. Ions are formed by three processes, (1) direct sputtering of pre-existing anions, (2) electron attachment, and (3) anionization. All three processes find parallels in positive ion SIMS.

Acknowledgements—This work was supported by the National Science Foundation CHE-78-08728 and MRL Program DMR-77-23798. L.K.L. thanks National Science Council of the Republic of China for a fellowship. S.E.U. acknowledges receipt of a David Ross Fellowship.

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