ferrihemoproteins merits detailed examination of parameters which affect the cyanide resonance position in model iron(III) porphyrin complexes. Thus, carbon-13 enriched cyanide ion may ultimately provide a probe for ferrihemoprotein structure, much as carbon monoxide serves as a powerful probe for ferrohemoproteins.[13]

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Cationization of Organic Molecules in Secondary Ion Mass Spectrometry

Sir:

We show that organic molecules can be ionized from the solid by cationization in secondary ion mass spectrometry (SIMS) and that such ionization shows significant similarities to other recently developed methods of ionizing organic compounds in the solid state. Observed in the SIMS spectra are organometallic ions which are formally due to (i) addition of cations (Ag^+, Pt^+) to the intact organic molecule (M), (ii) fragmentation of the cationized species by loss of simple neutral molecules, and (iii) processes yielding more complex surface-derived entities containing several metal atoms. These novel observations may have importance in the theory of secondary ion emission as well as in the analysis of thermally sensitive organic compounds.

Figure 1 shows the high mass region of the spectrum of *p*-aminobenzoic acid supported on silver.[1] The argentated molecule ($(M + Ag)^+$, m/e 244 and 246) is clearly present in good yield. Other ions of interest are m/e 226 and 228 (loss of water from the argentated molecule), and m/e 199 and 201 (loss of CO_2H). The silver dimer ions (Ag_2^+) are present in high intensity, and they are accompanied by several other sets of ions which appear from the isotopic patterns to include two silver atoms.[3] At lower masses, this spectrum shows m/e 150 and 152 $(Ag + 43)^+$, intensity 35 s^{-1} (count rate corresponding to that given in Figure 1); 145 and 147 $(Ag + 38)^+$, 25 s^{-1}; 137 $(M)^+$, 80 s^{-1}; 120 $(M - OH)^+$, 1×10^3 s^{-1}; 92 $(M - CO_2H)^+$, 700 s^{-1}; 77 $(C_6H_5^+)$, 300 s^{-1}; and 65 $(M - CO_2H - HCN)^+$, 1.6×10^3 s^{-1}. The base peak in the spectrum at 4×10^4 s^{-1} is K^+ (m/e 39), followed by Ag^+ (m/e 107 and 109) at 5×10^3 s^{-1}. Other intense organic fragments and other inorganic species appear below m/e 65.

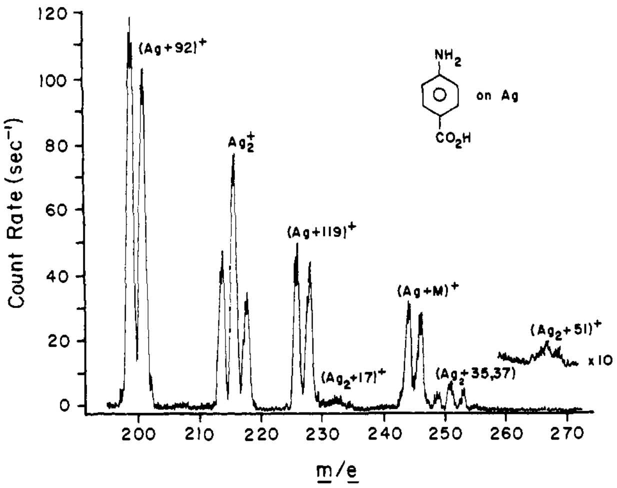

Figure 1. Secondary ion mass spectrum (SIMS) of *p*-aminobenzoic acid on silver. The primary ion current was 3×10^{-9} A cm^{-2} and the scan time ~20 min.

The most important feature of these results, metal cationization of complex organic molecules, has not been observed previously in SIMS, although alkali metal addition does occur in some other ionization techniques.[4-8] Only protonation was observed in SIMS studies on organic compounds carried out elsewhere under similar conditions.[9] Our results were unchanged when the primary ion energy, primary ion flux, the solvent from which the organic compound was evaporated (ethanol and water were tried), and the chemical state of the metal (oxidized and reduced) are altered. Some variations in relative ion intensities and sensitivities were, however, observed.

When *p*-aminobenzoic acid was supported on platinum, analogous results were obtained. In particular, ions centered on m/e 259 $(Pt + 64)^+$, 287 ± 1 $(Pt + 92)^+$, 314 ± 2 $(Pt + 119)^+$, and 332 ± 2 $(Pt + M)^+$ were detected. The latter three ions, $(M + Pt)^+$, $(M + Pt - H_2O)^+$, and $(M + Pt - CO_2H)^+$, correspond to peaks observed in the spectrum taken on silver. Platinum has a very poor sputter yield and resolution had to be sacrificed to gain the sensitivity required to observe the platinated species. Other platinated ions appeared centered on m/e 212 $(Pt + 17)^+$, 222 $(Pt + 27)^+$, 233 $(Pt + 38)^+$, 246 ± 1 $(Pt + 51)^+$, and 271 ± 1 $(Pt + 76)^+$. A series of $(Pt_2 + \text{organic})^+$ ions which corresponded to the Pt_1 series was also observed.

Phenylalanine on silver exhibited results similar to those obtained for *p*-aminobenzoic acid. Its SIMS spectrum included the ions Ag_3^+, Ag_2^+, $(Ag_2 + 35)^+$, $(Ag + M - 46)^+$, and $(Ag + M - 73)^+$. The parent argentated molecule was not detected, perhaps because the benzylic hydrogens promote a rearrangement in which the species can readily eliminate H_2CO_2 ($CO + H_2O$) to give the abundant $(Ag + M - 46)^+$ ion. Benninghoven and coworkers[9] observed $(M + H - 46)^+$, as the major ion for phenylalanine supported on silver; in our experiments Ag is incorporated instead of H in this ion.

A further significant observation closely links these experiments to other ionization methods. When a solution of *p*-aminobenzoic acid and lithium chloride (mole ratio 2:1) in ethanol is evaporated onto silver and bombarded, a spectrum results in which the cationized species shown in Table I are seen. Note that the addition of lithium as well as some argentation occurs. This lithiation is analogous to the alkali metal addition seen in field desorption,[5] plasma desorption,[6] and electrohydrodynamic ionization.[7] The analogy even extends

Table I. Cationized Species in the SIMS Spectrum of *p*-Aminobenzoic Acid and LiCl on Ag[a]

m/e	Rel intensity, %	Ion
137	12	M^+
143, *144*	12	$(M + Li)^+$
149, *150*, 151	35	$(M - 1 + 2Li)^+$
155, *156*, 157, 158	5	$(M - 2 + 3Li)^+$
199, 201	2	$(Ag + 92)^+$
213, *214*, 216, 218	1	Ag_2^+ and $(Ag + Li + 91/92)^+$
226, 228	0, 8	$(Ag + 119)^+$
244, 246	1	$(Ag + M)^+$

[a] Intensities are expressed relative to *m/e* 120. Lithiation of lower mass fragments did not occur to an appreciable extent. The italicized ion is the most abundant in each cluster.

to the substitution of successive hydrogen atoms by lithium.

Our results are most simply interpreted in terms of an ionization mechanism in which the major primary ion is (M + cation)$^+$. The organometallic ions falling below the cationized molecule in mass are believed to have the cationized molecule as their precursor. Evidence for this view was obtained by preparing the protonated molecule by chemical ionization (CI) and observing its fragmentation pattern.[10] The fragmentation pattern observed for $(M + Ag)^+$ in SIMS is similar to that of $(M + H)^+$ in CI.[11]

It now seems possible that, through cationization, SIMS may find a role in the analysis of labile materials such as compounds of biological origin. The cationization observed here will undoubtedly prove important in extending our understanding of the SIMS mechanism. More important still, these results indicate that there may be common features to all of the ionization methods in which a neutral molecule in the solid state is directly converted into a gas phase ion. Further exploration of this possibility would seem to be of value.[12]

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References and Notes

(1) SIMS spectra were obtained using instrumentation previously described[2] under conditions of low primary ion flux (Ar$^+$, 5 keV, 4×10^{-10} to 5×10^{-9} A/cm^2). The organic compound ($\simeq$0.1 mg) was evaporated onto the metal support most generally from ethanol, and experiments were done at 1×10^{-8} Torr or less. The base pressure was $<10^{-9}$ Torr. The absolute ion yield for *m/e* 199 (cf. Figure 1) was 3×10^{-5}, and the sensitivity was estimated by a standard method to be $<10^{-11}$ g (cf. A. Benninghoven, *Surf. Sci.*, **35**, 427 (1973)).

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(11) The methane CI mass spectrum of *p*-aminobenzoic acid shows, in order of abundance, *m/e* 138 $(M + H)^+$, 120 $(M + H - H_2O)^+$, and 94. Collision-induced dissociation of *m/e* 138 showed loss of 1, 18, 45, and 46 amu. The corresponding pattern in SIMS for the argentated ion (*m/e* 244), is the loss of Ag, Ag + 17, and Ag + 45. An analogous pattern in which the silver is retained is represented by the losses of 18 and 45 from *m/e* 244.

(12) Since submission of this manuscript, we have observed, under strictly static SIMS conditions, the argentation of hexamethylbenzene and *o*-phenylenediamine. We have also observed the metalation of several involatile polycyclic heteroaromatics.

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Ring-Strain-Promoted 1,2-Carbanionic Rearrangements

Sir:

Unequivocal examples of concerted all-carbon 1,2-anionic rearrangements involving migration of sp^3-hybridized carbon are unknown.[1] There appear to be two primary reasons for this: (1) orbital symmetry considerations[2] predict sterically unlikely suprafacial-inversion or antarafacial-retention pathways, and (2) as Zimmerman[2a,3] and Phelan, Jaffé, and Orchin[4] have pointed out, the energetics of the reaction are unfavorable (relative to the analogous carbocationic and free radical processes) owing to the necessity of accommodating four electrons in one bonding and two antibonding molecular orbitals at the transition state.

It occurred to us that the energetic disadvantage inherent in the migration of saturated carbon to an anionic center could be overcome at least in part by designing a system in which relief of ring strain provides the driving force for rearrangement while at the same time the starting and final carbanions maintain equal degrees of resonance stabilization or better.

An ideal preliminary substrate for such a study appeared to be diketone **1a** (Scheme I) which is readily available in gram quantities via irradiation of the duroquinone-2,3-dimethylbutadiene Diels-Alder adduct.[5] The present communication reports on the base-catalyzed rearrangement of **1a** and on labeling studies which establish the overall 1,2 nature of the process.

Refluxing a 40% aqueous dioxane solution of cyclobutanone **1a** (0.03 M) in the presence of 0.04 M potassium hydroxide for 24 h afforded the known [5,6] diketone **2a** in essentially quantiative yield. Two label-specific general mechanistic possibilities present themselves for this reaction: path 1, a 1,2-shift process of an as yet unspecified nature yielding **2a,** and path 2, a double homoenolate anion rearrangement[7] affording **2a′**. Since for **1a** products **2a** and **2a′** are identical, no conclusion can be drawn concerning the relative importance of paths 1 and 2.

We therefore turned our attention to the synthesis of a substrate in which X $\neq$ Y selecting the case X = C_2H_5; Y = CH_3. Cyclobutanone **1b** with the required labeling pattern was available in modest quantities from irradiation of the Diels-Alder adduct between 2,3-dimethylbutadiene and 2,5-dimethyl-3,6-diethyl-*p*-benzoquinone.[8] That the photoproduct was actually **1b** and not its "opposite" was established by NMR which clearly showed the acidic methine hydrogen as a quartet (J = 7.5 Hz) at δ 2.50.

Treatment of **1b** with potassium hydroxide in aqueous dioxane as before afforded exclusively diketone **2b.** This was established unambiguously by NMR shift reagent studies which showed a clean and successively downfield-shifted one-proton triplet (J = 7 Hz) upon addition of increasing concentrations of EuFOD.[9]

The labeling study thus indicates the exclusive occurrence of a 1,2-shift process (path 1). At present, three mechanistic possibilities for this process come to mind.