References and Notes

(1) H. Grade, N. Winograd, and R. G. Cooks, *J. Am. Chem. Soc.*, **99**, 7725 (1977).

(2) (a) A. Benninghoven and W. K. Sichtermann, *Org. Mass Spectrom.*, **12**, 595 (1977); (b) A. Benninghoven and W. K. Sichtermann, *Anal. Chem.*, **50**, 1180 (1978).

(3) H. Grade and R. G. Cooks, *J. Am. Chem. Soc.*, **100**, 5615 (1978).

(4) Instrument parameters and sample preparation have been described (see ref 3 and H. Grade, M.S. Thesis, Purdue University, 1977). The organic compound was physically mixed with the metal salt(s) and the mixture burnished onto Pt foil. Samples (~1 cm^2) were bombarded with a 5-keV argon ion beam of 5 × 10^{-9} A at ~45° from the target normal. The vacuum chamber pressure remained between 5 × 10^{-9} and 2 × 10^{-8} Torr during the experiment.

(5) Our earlier studies[1,3] showed exclusive metal attachment whereas similar experiments[2] showed only protonation. Recent results by DeCorpo, et al. (R. J. Colton, J. S. Murday, J. R. Wyatt, and J. J. DeCorpo, paper presented at the 26th Annual Conference on Mass Spectrometry and Allied Topics, ASMS, St. Louis, Mo., 1978) show both protonation and metal attachment.

(6) Masses above $(C + M)^+$ suggest that the observed ions may arise, at least in part, from dissociation of the bis(tetradentate) species $(C + 2M)^+$

(7) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5237 (1962).

(8) Factors such as ligand field stabilization energies, oxidation states, and sputter yields must be considered in attempting to explain ion intensities of the different chelated metals. We believe that the chelates form just above the surface by the reaction $C^+ + M \rightarrow (C + M)^+$. This mechanism seems to be consistent with our earlier results[3] and with dynamic calculations of SIMS sputtering.[9]

(9) N. Winograd, B. J. Garrison, and D. E. Harrison, Jr., *Phys. Rev. B*, submitted for publication.

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Ionization of Quaternary Nitrogen Compounds by Secondary Ion Mass Spectrometry

Sir:

Previously used primarily for analysis of metals, the technique of secondary ion mass spectrometry (SIMS) has recently emerged as an ionization method for studying organic compounds.[1] Earlier work from this laboratory reported the cationization of organic molecules by metals and the resulting fragmentation observed from the parent organometallic ion.[2] Reported here are studies of the direct ionization of quaternary ammonium salts which requires no cationizing metal. Previous work has shown that ammonium salts may be analyzed by field desorption.[3] This report on the direct ionization of quaternary ammonium salts via SIMS further extends the phenomenological similarities between the two techniques. These include the use of alkali metal attachment in both FD and SIMS.[4]

The SIMS spectrum[5] of $N(CH_3)_4Cl$ on Pt shows emission of the intact quaternary ammonium ion (*m/e* 74) as the most intense ion above *m/z* 30. Fragment ions were observed corresponding to loss of one and two molecules of methane to yield *m/z* 58 and 42 with relative abundances of 80 and 90%, respectively. Hence, the SIMS spectrum contains information on both the molecular weight and the structure of the quaternary ammonium salt. The salts *N*-methylpyridinium iodide, *N*-methyl-2,2′-bipyridinium iodide, and *N*-methylphenanthrolinium iodide all gave spectra in which the intact organic cations were the most abundant high mass ions.

The spectrum of ethyltrimethylammonium iodide (Figure 1) was obtained in order to investigate the ionization mechanism. The base peak at *m/z* 88 corresponds to the intact quaternary ammonium ion. The virtual absence of exchange of methyl and ethyl groups indicates that emission of the cation occurs directly from the solid phase. This result excludes both emission from a plasma and ion formation via a gas-phase reaction of tertiary amine with alkyl iodide. Either of these alternatives would have resulted in formation of far larger amounts of $N(CH_3)_4^+$ and $N(CH_3)_2(C_2H_5)_2^+$ than were observed. A ratio of $N(CH_3)_2(C_2H_5)_2^+$ to $N(CH_3)_3(C_2H_5)^+$ to $N(CH_3)_4^+$ of 10:3:3 was expected for complete randomization. The observed ratio of 1:100:2 is only consistent with emission directly from the solid phase as the major ionization mechanism.[7]

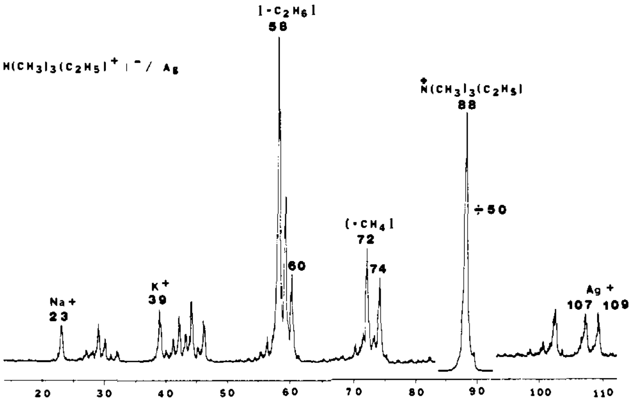

Figure 1. SIMS spectrum of ethyl trimethylammonium iodide showing emission of the intact cation and its characteristic fragmentation pattern.

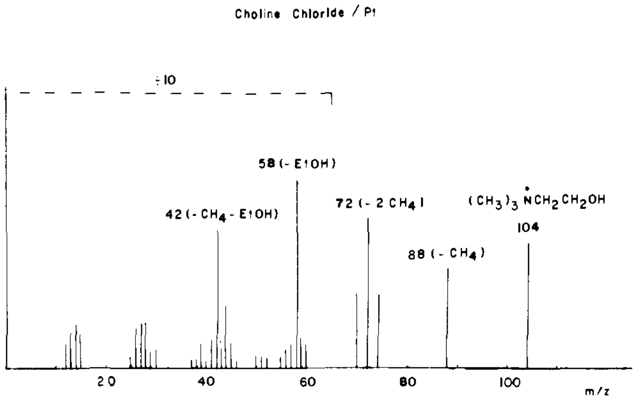

Figure 2. SIMS spectrum of choline chloride.

To further test this mechanism a mixture of *N*-methylpyridinium iodide and its d_3 analogue (methyl deuterated) was examined. Both the d_0 and d_3 analogues of the intact cations were observed. Cations with one or two deuteriums would be expected should intermolecular hydrogen exchange occur, but such species did not appear in the SIMS spectrum. Apparently no significant intramolecular hydrogen exchange occurs, either, since only $CH_3\cdot$ and $CD_3\cdot$ losses were observed. These results support the direct cation emission mechanism.

Fragmentation patterns observed in the SIMS spectra parallel those determined for even-electron ions in the gas phase. In particular, Levsen and co-workers have studied the collision-induced dissociation of quaternary ammonium salts.[8] They observe elimination of alkane molecules and alkyl radicals from these species. These are exactly the processes seen in SIMS spectra, e.g., the methane losses from the tetramethylammonium ion discussed above. Similarly, *N*-methylbipyridinium iodide gives abundant fragments 92^+ and 78^+ corresponding to cleavage between the rings with and without hydrogen transfer, respectively.

A feature of these spectra is the occurrence of low abundance peaks corresponding to ions in which a hydrogen atom of the quaternary has been substituted by a halogen. This is evident from the spectrum of tetramethylammonium iodide which showed an abundant ion corresponding to iodine substitution for a hydrogen atom in the intact cation. A related

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phenomenon was observed with trimethylphenylammonium iodide, the SIMS spectrum of which showed the intact cation *m/z* 136 (52% relative abundance) and fragments due to loss of $CH_3\cdot$ (121^+, 22%), CH_4 (120^+, 30), $2CH_4$ (104^+, 10), C_6H_6 (58^+, 100) and $CH_4 + C_6H_6$ (42^+, 70). However, when this salt was mixed with approximately equimolar amounts of KF, KCl, KBr, and KI, the major ions observed were the series $C_6H_5F^{+\cdot}$, $C_6H_5Cl^{+\cdot}$, $C_6H_5Br^{+\cdot}$, and $C_6H_5I^{+\cdot}$. The fragment ion $C_6H_5^+$ was also present. Reversal of the quaternization reaction accounts for $C_6H_5X^{+\cdot}$ formation, although its observation as a charged species was unexpected given that trimethylamine has the lower ionization energy. Tetraphenylarsonium chloride mixed with the potassium salts of the halides showed exactly analogous results.

To further test the potential of this methodology, several compounds of biological significance were examined. Choline chloride was selected for comparison with the results of desorption from a field desorption emitter in a chemical ionization source.[9] The spectrum (Figure 2) shows the intact cation together with fragment ions due to the expected elimination of an alkane or substituted alkane molecule, in this case CH_4 and CH_3CH_2OH. The field emitter procedure gave similar results,[9] although an ion at *m/z* 90 due to dealkylation and protonation of choline was seen in this latter experiment.

The possibility of observing organic dications in SIMS was of interest, although the absence of these ions in gas-phase chelation[10] must be noted. The diquaternary *N,N'*-dimethyl-4,4'-bipyridyl dichloride did not yield an observable dication in SIMS but showed an ion at *m/z* 171 which corresponds to methyl cation loss from the dication.

Traditionally, involatile and unstable compounds have been derivatized for mass spectrometry by forming volatile and often less polar compounds. To study gas-phase ions from such involatile compounds, it may be advantageous to employ SIMS and start with fully ionized species in the solid phase.

Acknowledgment. This work was supported by the National Science Foundation CHE 77-01295 and NSF-MRL DMR 76-00889A1.

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(3) (a) F. W. Röllgen, H. J. Heinen, and U. Giessmann, *Naturwissenschaften*, **64**, 222 (1977); (b) H. J. Heinen, U. Giessmann, and F. W. Röllgen, *Org. Mass Spectrom.*, **12**, 710 (1977).
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(5) Instrument parameters and sample preparation processes for SIMS have been described.[6] In all cases the organic was physically mixed with the metal salt and burnished onto Pt foil. A 5-keV Ar^+ primary ion beam of 1-5 × 10^{-9} A was used to bombard the sample. The mass-analyzed primary ion beam is deflected 3° to eliminate neutrals before entering the ultra-high-vacuum bell jar and striking the sample at ~45° to the target normal. Secondary ions pass through an energy prefilter and are mass analyzed in a quadrupole mass analyzer.
(6) H. Grade and R. G. Cooks, *J. Am. Chem. Soc.*, **100**, 5615 (1978).
(7) Ions 14 mass units above and below the intact cation were observed for the tetramethylammonium salts as well. An origin other than simple dealkylation-realkylation must be entertained for these species.
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Reactions in Dry Media. Cleavage of Carbon-Carbon Single Bonds by Ozonation

Sir:

Ozonation of compounds adsorbed on silica gel has recently become a method of general applicability for the hydroxylation of tertiary C-H bonds in saturated compounds.[1-4]

We have recently observed that ozone cleaves not only C-H bonds but also $C-CH_3$ bonds. Thus dry ozonation of *trans*-1,4-dimethylcyclohexane gave in addition to *trans*-1,4-dimethylcyclohexanol small amounts of 2,5-dimethylcyclohexanones and 4-methylcyclohexanone.[5] Similar cleavage of $C-CH_3$ bonds was observed in ozonation of 3,7-dimethyloctyl acetate by Beckwith et al.[3a]

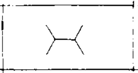
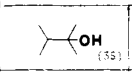
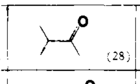
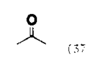
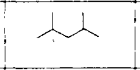
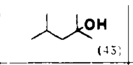
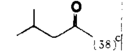
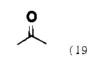
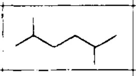
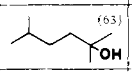
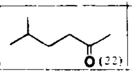
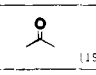
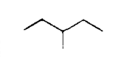
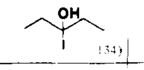
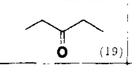
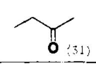
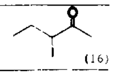
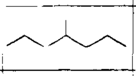
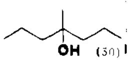
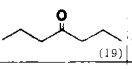
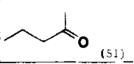
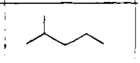
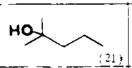
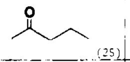
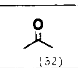
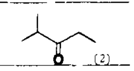
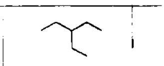
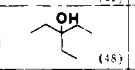
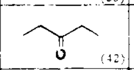
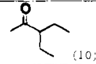
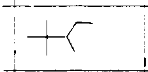
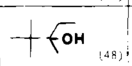
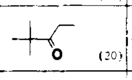
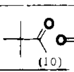
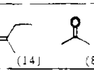
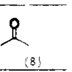
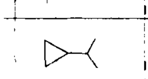
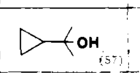
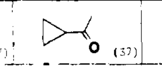
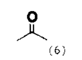
We report here on dry ozonations carried out on a number of aliphatic hydrocarbons (Table I), the results of which show that a substantial cleavage of C-C bonds occurs, caused by a direct insertion of ozone into these bonds.

The reactions were carried out by adsorbing the substrates on silica gel (1%), passing through it a stream of ozone (3% in oxygen) for ~2 h at −45 °C, and then removing the excess of ozone by a stream of argon at the same temperature.[1b,e]

The total yield of the neutral ozonation products was in all cases between 80 and 90%.[6] However, the relative yields of the tertiary alcohols were considerably lower than those obtained on the ozonation of cyclic hydrocarbons, as comparatively large amounts of ketones, originating from the cleavage of alkyl groups, were formed (Table I).

The oxidation of these aliphatic hydrocarbons is a relatively slow process,[7] resulting in constant product ratios throughout the reaction. Thus, 3-methylpentane (Table I, entry 4) was converted after 10 min in 15% yield and after 2 h in 85% yield to the same mixture of an alcohol and ketones. The most significant results emerging from these ozonation data (Table I) are that the ratios of ketones formed by the cleavage of either primary, secondary, or tertiary alkyl groups are in the same order of magnitude and not substantially different. This is best exemplified by a 2:1:1.5 ratio of the ketones formed by the cleavage of methyl, ethyl, and *tert*-butyl groups in 2,2,3-trimethylpentane (Table I, entry 8).

Table I. Product Distribution from Ozonation of Some Hydrocarbons[a] at −45°C

Entry	Starting Material	Product Distribution (molar yield[b], %)				
1		 (35)	 (28)	 (37)		
2		 (43)	 (38)[c]	 (19)		
3		 (63)	 (22)	 (15)		
4		 (34)	 (19)	 (31)	 (16)	
5		 (30)	 (19)	 (51)		
6		 (21)	 (25)	 (52)	 (2)	
7		 (48)	 (42)	 (10)		
8		 (48)	 (20)	 (10)	 (14)	 (8)
9		 (57)	 (37)	 (6)		

[a] The substrates were preadsorbed on silica gel (1% w/w). [b] Based on detected products by VPC analysis. [c] Included small amounts of diisopropyl ketone.

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