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FIELD DESORPTION MASS SPECTROMETRY
QUATERNARY AMMONIUM SALTS

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The new technique of field desorption (FD) mass spectrometry[1] holds great promise for analysis of compounds not conveniently evaporated by direct-probe techniques. In field desorption, a sample deposited on the surface of a prepared wire is ionized apparently by tunneling of an electron under the influence of a high electric field gradient from the molecule to the metal. Coulombic repulsion of the positive ion and the carbon microneedles is considered to drive the ion into the gas phase.

Previous reports from the laboratory originating this technique, the Institute for Physical Chemistry of the University of Bonn, have indicated its utility in obtaining useful information about the gram-formula weights of alkali metal salts of typical organic acids such as acetic acid[2] and of more thermally unstable acids such as the nucleotides.[3] We wish to report that the technique of field desorption is also useful for obtaining gram-formula weights of at least the cation, and sometimes of both anion and cation, of quaternary ammonium salts.

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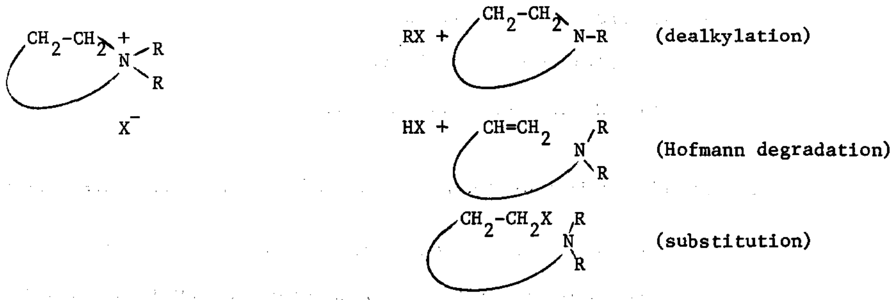
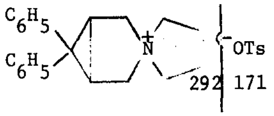
The FD spectra were obtained with a FD/FI source custom-built at the University of Bonn for operation on a CH5-DF mass spectrometer. The compounds were adsorbed from a methanol solution onto a 10μm tungsten wire emitter prepared by the high-temperature technique[2,4] and supplied by Professor Beckey and Dr. Schulten. The spectra were calibrated against the high-temperature FI spectrum of perfluorotributylamine.[2] The EI spectra were obtained using a Varian CH5-DF mass spectrometer. These samples were introduced *via* a direct probe and ionized with 70-V electrons.

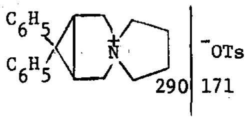
Quanternary salts must undergo thermal rearrangement and/or decomposition prior to volatilization and ionization by EI, FI, and CI techniques. The following routes have been reported.[5,6,7]



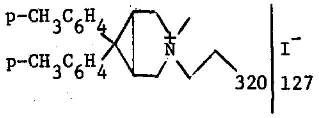
The EI spectra of I through V exemplify this behavior. Compound I, III, choline chloride (IV)[8], and acetylcholine bromide (V)[8] undergo the dealkylation process. Compound II



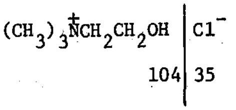
I



II

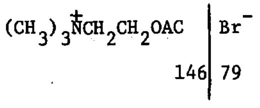


III



$$\left.(CH_3)_3\overset{+}{N}CH_2CH_2OH\ \right|\ Cl^-$$

IV



$$\left.(CH_3)_3\overset{+}{N}CH_2CH_2OAC\ \right|\ Br^-$$

V

exhibits a base peak at m/e 206 whose elemental composition was determined to be $C_{16}H_{14}$ by high resolution mass spectrometry (calcd. for $C_{16}H_{14}$: 206.1096: found: 206.1087). In contrast, the base peak in the FD spectra of I through V, and of other quanternary ammonium salts which we have run, is the quanternary ammonium ion.

The total FD spectrum I, at 20mA emitter current, is: <u>m/e</u> 292 (100%); 293 (72%). That of compound II at 20 mA is: <u>m/e</u> 172 (2%); 290 (100%); 291 (23%); 292 (3%); 751 (6%).

That of compound III at 16 mA is: m/e 29 (3%); 43 (9%); 304 (6%); 305 (3%); 320 (100%); 321 (40%); 322 (4%); 767 (19%). **That of compound IV at 20 mA is: m/e 31 (2%); 45 (2%); 89 (12%); 104 (100%); 105 (7%); 118 (8%). That of compound V at 20 mA is m/e 131 (5%); 146 (100%); 147 (8%); 148 (2%); 371 (44%); 372 (10%); 373 (50%); 374 (7%).

In some cases, fragment ions were observed. For example, the ions corresponding to the loss of a methyl group from the quaternary ammonium ion were observed in the spectra of III, IV, and V; choline chloride (IV) shows the typical $(CH_2)_nOH^+$ series; and III shows typical alkyl ions. The ion at m/e 118 of IV is consistently present in the FD spectra. The origin of this ion is not clear. An impurity is unlikely because both EI and nmr spectra of IV are consonant with a pure compound.

The peaks of mass equivalent to two cations and one anion arise from an unknown mechanism or mechanisms. A peak corresponding to two cations and one anion is observed in the FD spectrum of sodium acetate,[2] and a peak corresponding to the mass of guanine plus sodium is found in the spectrum of guanine adsorbed from NaOH solution.[2] In the present cases, an actual cluster of two cations and one anion, or of a cation and a neutral formed by the thermal substitution process, may be responsible for the peak. The nature of the bonding is not clear.

In summary, quanternary ammonium salts yield FD spectra whose base peak corresponds to the quanternary ammonium ion and which contain other diagnostic peaks as well. These spectra may therefore be of considerably more analytical utility than conventional EI spectra of such compounds.

Acknowledgement. We are indebted to Professor H.-D. Beckey for arranging the construction of an FD/FI source for us, and for preprints; to Dr. H.-R. Schulten for installation of the source and for practical advice; and to Dr. Nariman Mehta of the Burroughs Wellcome Company for samples[9] of I, II, and III.

**At low emitter temperatures, high-mass ions probably corresponding to an ion cluster of two cations and one anion were observed. Those clusters above m/e 700 are beyond present calibration limits on our instrument and are determined only to ± 1 amu.

REFERENCES

(1) H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 500 (1969); and succeeding papers from Professor Beckey's laboratory. For a synopsis, see *Chem. Eng. News*, **50** (48), 18 (Nov. 27, 1972); *ibid.*, **51** (22), 14 (May 28, 1973).

(2) H. R. Schulten and H. D. Beckey, *Org. Mass Spectrom.*, **6**, 885 (1972).

(3) H. R. Schulten and H. D. Beckey, *ibid.*, in press; private communication.

(4) H. D. Beckey, A. Heindrichs, E. Hilt, M. D. Migahed, H. R. Schulten and H. U. Winkler, *Messtechnik*, **79**, 196 (1971).

(5) M. Hesse, W. Vetter and H. Schmid, *Helv. Chim. Acta*, **48**, 674 (1965).

(6) H. Budzikiewicz, C. Djerassi and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, 1967, pp. 330-333.

(7) H. J. Veith and M. Hesse, *Helv. Chim. Acta*, **52**, 2004 (1969).

(8) G. A. R. Johnston, A. C. K. Triffett and J. A. Wunderlich, *Anal. Chem.*, **40**, 1837 (1968).

(9) R. Baltzly, N. B. Mehta, P. B. Russell, R. E. Brooks, E. M. Grivsky and A. M. Steinberg, *J. Org. Chem.*, **27**, 213 (1962).