Thermal Evaporation of Intact Positive Ions of Quaternary Ammonium and Phosphonium Salts

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Summary Evidence is presented for a purely thermal evaporation of intact positive ions of quaternary ammonium and phosphonium salts.

QUATERNARY salts are reported to decompose prior to volatilization and ionization by electron impact[1] or chemical ionization[2] in the gas phase. In order to produce gaseous intact positive ions of onium salts for mass analysis the following surface ionization techniques have been applied: field desorption,[3] fission fragment induced desorption,[4] secondary ion mass spectrometry,[5] and laser desorption.[4,6] The results reported here provide evidence for thermal evaporation of intact positive ions from quaternary ammonium and phosphonium salts.

The samples were deposited on an electrically heated metal ribbon (4 × 1·5 × 0·1 mm) placed in front of a quadrupole mass analyser. A small voltage difference of 20 V was applied between the ribbon and a counter electrode to inject the evaporating ions into the quadrupole. The thermal desorption mass spectra of some quaternary salts X^+Y^-, *viz.* $Me_4N^+Cl^-$, $Me_4N^+I^-$, $Pr_4N^+I^-$, $Bu_4N^+I^-$, $Me_4P^+I^-$, and $EtPh_3P^+I^-$, exhibited only the positive ions X^+ in the evaporation products in each case. No cluster ions or fragment ions could be detected. The positive ion emission was observed for several minutes during the slow heating of the sample. The ratio of intact evaporating positive ions to neutral volatilization products was *ca.* 10^{-5} for $Bu^n_4N^+I^-$. No thermal evaporation of negative ions was observed.

The thermal evaporation of ions other than quaternary ions has so far only been observed with a mixture of NaI and benzo[15]crown-5 which gives a weak $[M + Na]^+$ positive ion signal. In particular no evaporated positive ions were detected with NH_4Cl and NH_4I.

These results lead to the following conclusions. (i) The desorption of positive ions of quaternary salts from heated samples placed inside a chemical ionization source[7] does not provide evidence for a chemical surface ionization process. (ii) The previously reported long-lasting positive ion emission induced by continuous-wave laser irradiation of quaternary ammonium salts[6] is obviously not a specific radiation but a thermal effect. This supports a thermal mechanism of ion formation in i.r.-laser desorption mass spectrometry.

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