Chemical Ionization–Fast-atom Bombardment Mass Spectrometry: a Novel Ionization Method

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Chemical ionization reactions have been used with the fast-atom bombardment mass spectrometry technique to post-ionize desorbed neutral species by proton transfer, charge exchange, and association reactions in order to enhance molecular parent ions.

A novel, high-pressure (0.1—0.5 Torr) fast-atom bombardment (F.A.B.) ion source has been constructed to study ion–molecule reactions of sputtered ions and neutral species. A number of studies have been performed with this chemical ionization–fast-atom bombardment (C.I.–F.A.B.) ion source giving evidence for significantly enhanced sensitivity and selectivity over the revolutionary F.A.B. technique.

F.A.B. has proven to be a useful desorption technique for the mass spectrometric analysis of a variety of intractable organic and biological compounds.[1] In the particle bombardment process, ions and neutral species are sputtered or desorbed from solid surfaces, molecular overlayers, or more typically from liquid matrices by an energetic beam of fast atoms or energetic ions. The secondary or desorbed ions are then analysed mass spectrometrically. The number of sputtered or desorbed neutral organic molecular species should be considerably larger than the number of secondary molecular ions as in the case of particle-induced emission from single-element solids. Therefore, the selective ionization of the abundant sputtered neutral species by chemical ionization could extend considerably the usefulness of all the particle-induced emission techniques, particularly when the secondary molecular ion yield is low. We demonstrate this unique C.I.–F.A.B. method here by an example.

Post-desorption ionization of sputtered neutral species was accomplished by ion–molecule reactions through the generation of reagent ions with reagent gas and ionizing electrons within a closed F.A.B. ion source (specially designed). The primary particles (Xe^0) were generated externally using a conventional fast-atom source, and the primary beam was admitted into the C.I.–F.A.B. source through a small aperture. The post-desorption ionization of sputtered neutrals was observed to increase the abundance of the protonated molecule, $[M+H]^+$ (m/z 437), of pentaerythritol tetrapentanoate (PETP) by almost three orders of magnitude under some experimental conditions in the C.I.–F.A.B. source.† The ratio of abundances of the $[M+H]^+$ molecular parent species to the only unimolecular dissociation product ion (m/z 371; acyl loss) in the mass-analysed ion kinetic energy spectrum of PETP generally decreased with increasing ionization potential of the charge-exchange reactant gas. The ion abundance ratio was also affected (without ionizing electrons) in direct proportion to the effective collisional-stabilization cross section of the reactant gas. This latter observation demonstrates that excited secondary ions are also collisionally relaxed, resulting in a molecular ion enhancement.

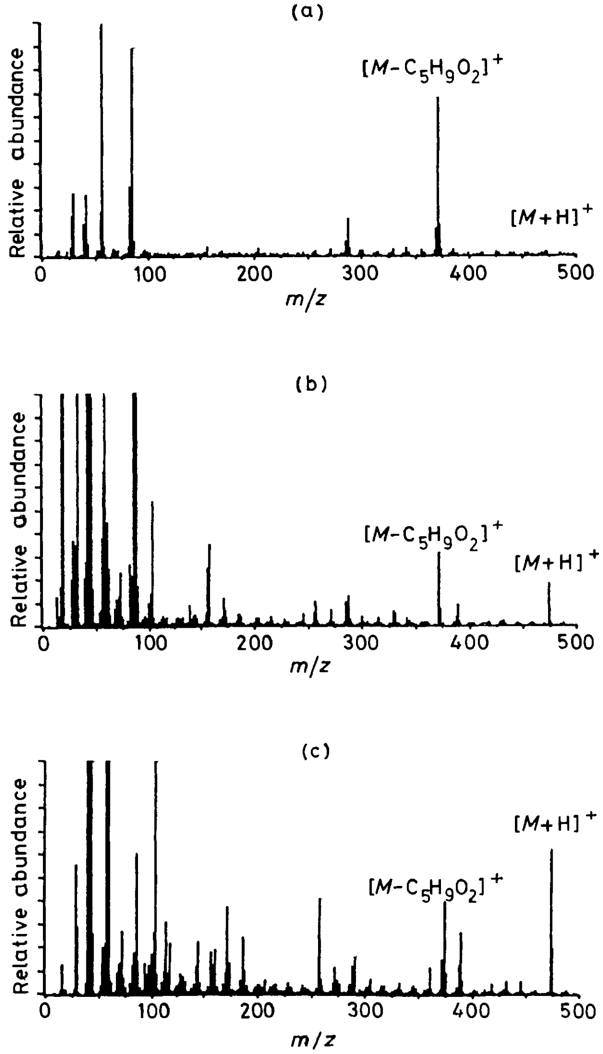

Figure 1. (a) F.A.B. mass spectrum of neat PETP. (b) CO_2 C.I.–F.A.B. mass spectrum of neat PETP. The source pressure was 0.15 Torr. (c) The isobutane C.I.–F.A.B. mass spectrum of neat PETP. The source pressure was 0.15 Torr. (The large ion peaks below m/z 200 are due to reagent ions and impurities.)

The dramatic spectral differences between the F.A.B., carbon dioxide C.I.–F.A.B., and the isobutane C.I.–F.A.B. spectra of PETP are illustrated in Figure 1. The F.A.B. spectrum (Figure 1a) yields a protonated molecular ion (m/z 473) that is <0.5% of the intensity of the base peak. The CO_2 C.I.–F.A.B. spectrum (Figure 1b) shows a fifty-fold enhancement of the protonated molecule relative to the F.A.B. spectrum (Figure 1a) resulting from charge-exchange and collisional stabilization reactions. In the isobutane C.I.–F.A.B. spectrum (Figure 1c) the protonated molecule is over 100 times more abundant that in the F.A.B. spectrum, and it is the most abundant PETP-related ion. This enhancement results from proton transfer reactions with neutral species and

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† The absolute ion abundance of a molecular ion (chlorophyll A) is an order of magnitude less from the C.I.–F.A.B. source compared to the F.A.B. source under identical conditions (no reactant gas and a resolving power of 1000). This attenuation of ion signal is a result of the small ion beam exit aperture required on the C.I.–F.A.B. source to obtain high-pressure chemical ionization conditions.

collisional stabilization of desorbed secondary protonated molecules. We have observed significantly greater enhancements (1000 fold) at higher ion source pressures (0.18 Torr of isobutane). The use of ammonia as a reagent gas results in the formation of an $[M{+}NH_4]^+$ species. This association reaction has permitted the analysis of the composition of a number of different pentaerythritol tetraester isomers in a complex mixture of homologues using tandem mass spectrometry techniques. Likewise, reagent gases could be chosen to enhance selectively the ionization of particular classes of compounds or for *in situ* derivatization of desorbed intractable species.

The use of this new ionization method has led to the enhancement of the molecular parent ion through various ion–molecule interactions. These include charge exchange, proton transfer, association reactions, and collisional stabilization. We have obtained comparable results to those reported here with fatty acids and amines, and with negative ion reagents.

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References

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