

Ion Formation from Organic Solids (IFOS III)

Mass Spectrometry of Involatile Material

Proceedings of the Third International Conference
Münster, Fed. Rep. of Germany, September 16–18, 1985

Editor: A. Benninghoven

With 171 Figures

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Ion Bombardment MS: A Sensitive Probe of Chemical Reactions Occurring at the Surface of Organic Solids

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Organic chemical reactions occurring in the solid state or at a gas-solid interface are of interest in a number of fields including solid state polymerization and other chemical syntheses, the long-term stability of drugs, the degradation of plastics, catalysis, and a range of analytical chemical procedures. We have recently investigated the use of energetic heavy ion bombardment mass spectrometry as a new technique for monitoring microscale chemical reactions in films of nonvolatile organic solids with thicknesses ranging from submonolayers to $\sim 10^3$ molecular layers. The investigations were performed using a ^{252}Cf fission fragment induced ionization time-of-flight mass spectrometer [1] (bombardment with ~ 100 Mev fission fragments) and a pulsed ion bombardment time-of-flight mass spectrometer [2] (bombardment with ~ 30 keV ions), both constructed at the Rockefeller University.

The technique involves the following steps: (1) A thin film of the organic compound of interest is deposited on a metallic substrate. (2) The film is then analyzed (essentially nondestructively) by ion bombardment mass spectrometry. (3) The same film is then exposed to the reagent(s) of interest, which causes reaction to occur. (4) The chemically modified film is then reanalyzed mass spectrometrically. Differences in the mass spectra prior to and after reaction of the film gives detailed information regarding the extent of reaction and the identity of the reaction products.

To establish the generality and to investigate some applications of the procedure, the surface reactions of several organic solids were investigated with three major reagent classes:

1. LIGHT REACTIVE GASES

Unsaturated fatty acid salts when exposed to ozone undergo cleavage at the double bond(s) to yield aldehyde and carboxylic acid products [3]. Thus, for example, Fig. 1 shows the high mass portion of the mass spectrum of the sodium salt of vaccenic acid [$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_9\text{COONa}$] prior to and after exposure of the thin film to ozone. Prior to exposure, the spectrum is dominated by the $(\text{M}+\text{Na})^+$ ion at m/z 327 as shown in Fig. 1(a). After exposure of the sample to a 1% O_3 in O_2 mixture for a time of 2 sec. the spectrum shown in Fig. 1(b) is obtained. The $(\text{M}+\text{Na})^+$ peak has disappeared, indicating complete reaction of the starting material, and is replaced by three new peaks corresponding to reaction products of the ozone with the fatty acid salt. The product peaks which occur at m/z 245 ($\text{OHC}(\text{CH}_2)_9\text{COONa}.\text{Na}^+$), m/z 261 ($\text{HOOC}(\text{CH}_2)_9\text{COONa}.\text{Na}^+$), and m/z 283 (the $(\text{M}+2\text{Na}-\text{H})^+$ ion corresponding to the m/z 261 ion) unambiguously define the position of the double bond. The mass spectra subsequent to ozone exposure of a series of monounsaturated positional isomers of vaccenic acid as well as of a set of polyunsaturated fatty acid salts (containing as many as four double bonds) similarly yield the position(s) of all the double bonds present. The present surface reaction probe thus appears to constitute a rapid, sensitive and unambiguous technique for determining double bond position(s) in nonvolatile olefinic compounds.

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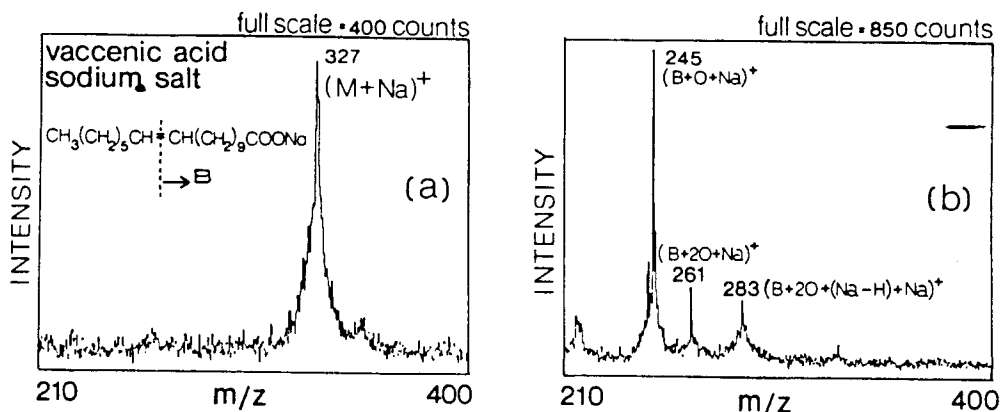


Fig. 1 High mass portion of the ^{252}Cf mass spectrum of vaccenic acid sodium salt (a) prior to and (b) after exposure of the sample film to a 1% O_3 in O_2 mixture for 2 sec.

Studies of the reaction kinetics for the ozonolysis reaction showed marked differences in the reaction rate for cis- and trans-stereoisomers of fatty acid salts. The trans-isomers had considerably lower rate constants for reaction with ozone than did the corresponding cis-isomers. We hypothesize that the different rate constants arise largely from differences in the molecular packing of the stereoisomers in the solid.

Large differences were also observed in the yields of the cluster ion species, $(n\text{M}+\text{Na})^+$ where $n=2-30$, for the cis- and trans-stereoisomers of monounsaturated fatty acids salts. The trans-isomers exhibit a much higher propensity for cluster formation than do the cis-isomers. We hypothesize that the differences in the cluster yields also arise from differences in the molecular packing of the stereoisomers in the solid.

Deductions concerning the mode of formation of the cluster ions $[(n\text{M}+\text{Na})^+]$ where $n=2-30$ could also be made by comparing cluster yields prior to and after partial ozonolysis of the fatty acid salts. The data is consistent with direct cluster emission from the surface, as opposed to formation of the clusters above the surface by statistical recombination of independent molecules ejected by a single primary ion.

Exposure of a variety of other organic compounds to O_3 , NO , and NO_2 further demonstrated that the production of new materials could be sensitively followed and their masses readily identified.

2. PHOTONS

The positive ion spectrum of an unirradiated sample film of the dye crystal violet exhibits a dominant cation peak at m/z 372 and several less intense fragment ion peaks (e.g. at m/z 356 and 340) arising from successive loss of methane. Brief irradiation of the sample with visible wavelength photons in an atmosphere of O_2 with H_2O present gives rise to intense product peaks at m/z 358, 344 and 330 arising from a series of photodemethylation reactions. Irradiation of Rhodamine B under the same conditions as those for crystal violet gave analogous de-ethylation photoproducts. Irradiation of a substituted stilbene (diethyl-stilbestrol) with 254 nm photons in air yielded a major photoproduct with a molecular weight 2μ below that of the starting material.

3. COMPLEX VAPORS

To demonstrate the feasibility of carrying out and detecting on a surface film products of a complex reaction, we carried out and monitored mass spectrometrically the coupling and cleavage steps of the Edman sequencing reaction on the terminal residue of the peptide leucine-enkephalin.

The general properties of the mass spectrometric surface reaction probe are summarized as follows: Sensitivity is high; our experience is that 10^{-9} to 10^{-15} moles of material can be measured in solid phase particle bombardment mass spectrometry. Low yields (1-2%) of selected product can be detected reliably. The method has a high surface specificity. The analysis is essentially non-destructive. The mass spectrometric analyses are rapid (typically a few minutes). The present system does not allow for the measurement of volatile compounds and volatile reaction products.

We conclude that the technique has wide potential utility for the study of surface reactions of solids with a multitude of potential practical applications.

Acknowledgment

This work was supported in part by the Division of Research Resources, National Institutes of Health.

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2. B.T. Chait, and F.H. Field: *Proceedings of 32nd Annual Conf. Mass Spectrom. and Allied Topics*, May 1984, San Antonio, p. 237.
3. P.S. Bailey: "Ozonation in Organic Chemistry, Vol. 1," Academic Press New York, 1978.

Ion-Neu

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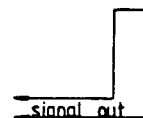
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