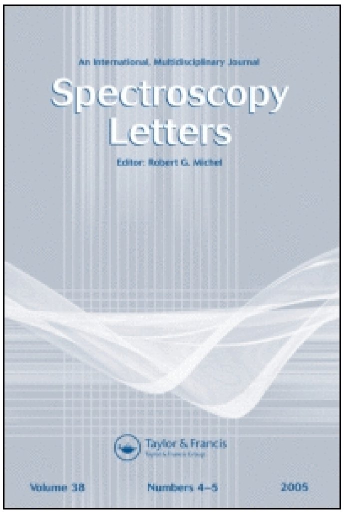

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Bombardment-Induced Polymerization of Nitrobenzyl Alcohol in Fast Atom Bombardment Mass Spectrometry

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BOMBARDMENT-INDUCED POLYMERIZATION OF NITROBENZYL ALCOHOL IN FAST ATOM BOMBARDMENT MASS SPECTROMETRY

Keywords: FAB-MS, beam-induced polymerization, nitrobenzyl alcohol

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ABSTRACT

Bombardment-induced polymerization of meta-nitrobenzyl alcohol, widely used as a liquid solvent matrix in fast-atom bombardment mass spectrometry, produces an insoluble product presumably through any of several polymerization condensation reactions that involve expulsion of water. The product is insoluble in common organic solvents and in mNBA itself, and forms a brownish film on the surface of the liquid nitrobenzyl alcohol. Processes of oxidation and reduction of the alcohol may contribute to the formation of polymerized products.

INTRODUCTION

In the past decade, fast-atom bombardment (FAB) mass spectrometry has become a widespread ionization method used for measurement of mass spectra of non-volatile molecules. At the core of the method is preparation of a solution of the sample in a vacuum-compatible liquid solvent, and subsequent sputtering of that sample solution by an energetic particle beam of atoms or ions. Many details of the sputtering, desorption and ionization processes are uncharacterized. Further, although the number of liquid solvents examined for use in FAB is large, the fundamental properties of these solvents are not generally known. Several recent reviews include a compilation of the most commonly used solvents in FAB mass spectrometry[1-3].

The sputtering of a sample solution rather than the sample itself generates a general spectral background in FAB. In general, the ions due to the sample are intermixed with dominant ions from the solvent, both of which are superimposed on a background level of signal at every mass that extends throughout the mass range. This extraordinary phenomenon has elicited little interest from the practitioners of FAB; background subtraction yields the appropriate mass spectrum of the sample, although there is generally a reduction in the accuracy of the absolute and relative ion intensities for the sample mass spectrum, especially below m/z 500.

There are several intriguing characteristics of the background spectrum generated by particle bombardment in fast-atom bombardment mass spectrometry. First among these is the presence of ion signals at each and every mass unit, extending even to masses many times that of the solvent molecule itself. This background signal, although lower in absolute intensity at higher masses, seems to form instantly upon initiation of particle bombardment. In the mid-mass range of 100-500 daltons, there is an odd-even intensity distribution of background ions, with the odd-integer mass ion present with an intensity approximately twice that of adjacent even-mass ions. Finally, the composition of the background signal seems to remain constant with time. No particular ion signals are significantly depleted, nor do ions corresponding to background grow in intensity with continued irradiation.

There have been several reports in the literature that study the products formed upon particle bombardment of glycerol, the first and most widely used of the FAB liquid solvents. Exact mass measurements have been used to delineate the empirical formulas of many of the ions in the background[4]. Gas chromatography coupled with mass spectrometry has been used to study some of the neutral compounds formed upon particle bombardment of glycerol[5,6].

Although glycerol is probably still the most widely used liquid solvent for fast-atom bombardment mass spectrometry, meta-nitrobenzyl alcohol (NBA) has seen increasing use in the analysis of small organic salts and organometallic compounds by FAB. As with glycerol, particle bombardment does yield discrete products, manifest in this case by the change in the color of the solution and the formation of the dark brown film overlayer. Characterization of this film was the purpose of this research.

EXPERIMENTAL

Positive ion FAB mass spectra were recorded on a VG-70SEQ hybrid mass spectrometer of EBQQ geometry. The primary beam consisted of 35 keV Cs^+ ions emitted from a thermionic source. The standard VG FAB probe was used. The source block of the instrument was heated to 40 °C. GC/MS spectra were recorded under standard electron ionization conditions on a VG70S double focusing mass spectrometer. Preparative FAB was carried out on a large sample platform with argon atom bombardment and a saddle-field primary particle source. Nitrobenzyl alcohol was used as obtained from the Aldrich Chemical Company.

RESULTS AND DISCUSSION

The background mass spectrum of NBA alone is shown in Figure 1. The base peak in the mass spectrum at m/z 154 corresponds to $(M+H)^+$ for NBA. Predominant ions at higher masses are m/z 460 $(3M+H)^+$, m/z 307 $(2M+H)^+$ and m/z 289 $(2M+H-OH)^+$. Fragment ions at m/z 137 $(M+H-OH)^+$ and m/z 136 $(M+H-H_2O)^+$, m/z 123 $(C_6H_5NO_2^+)$, m/z 107 $(C_6H_5CH_2O^+)$, m/z 89 $(C_6H_3N^+)$ and m/z 77 $(C_6H_5^+)$ are readily identified and rationalized. Ions at m/z 219 and m/z 341 are variable in relative intensity, but are almost always observed in the mass

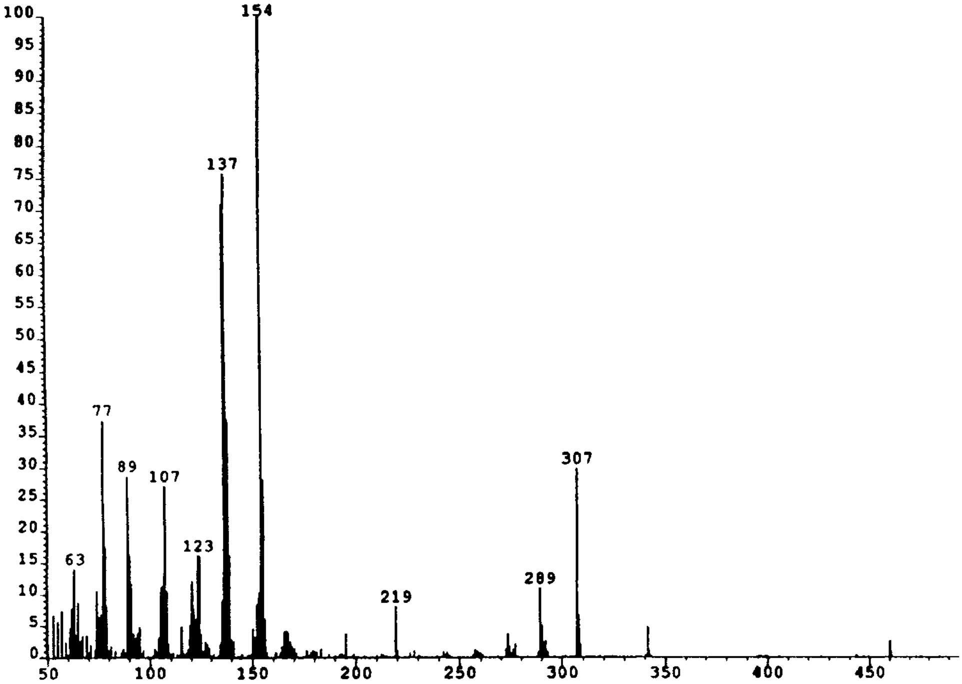

FIG. 1. Positive ion FAB mass spectrum of nitrobenzyl alcohol.

spectrum of the NBA solvent. The ion at m/z 341 is the addition of nitrobenzene ($C_6H_5NO_2$) to the ion at m/z 219. The composition of this latter ion is a matter of some debate; it may arise from one of the anti-oxidant components of commercial NBA (vide infra).

It can be seen that there are numerous background ions present at the 1-5% relative intensity level that extend to masses well above that of the solvent molecule itself. None of these ions are present without NBA on the FAB probe. The background level is present without significant change for the duration of the analysis. When NBA is used as the liquid solvent in FAB analysis, extended particle bombardment of the sample solution produces a thin film on the surface of the liquid droplet. Formation of this film is accompanied by color change of the solvent from the pale yellow color of the NBA liquid to a brown liquid with an overlayer of the brown film, which is formed in visible amounts after 1--15 minutes of particle bombardment. In shorter analyses, no explicit change in the sample solution was observed, but the formation of the film was reproducibly observed with longer irradiation times with both cesium ion and xenon atom bombardment.

Prior to analysis of the film, the NBA solvent used was examined with GC/MS. Our source of NBA stated a label purity of 98%. GC/MS analysis on separate occasions with different instruments confirmed the presence of several additional components in the NBA. A small amount of m-nitrobenzaldehyde was shown to be present as determined by a match between the measured electron ionization mass spectrum from the GC/MS analysis to the spectrum stored in the NBS spectral library. Also present was a small amount of 2,6-ditertbutyl-4-methylphenol, commonly known as BHT anti-oxidant. Presumably, the BHT is added to the NBA to prevent oxidation to the nitrobenzaldehyde.

We performed the same GC/MS analysis on NBA that had been irradiated on the FAB probe for approximately 45 minutes. The GC/MS showed no additional chromatographic peaks; the total ion current trace shows only a peak for the solvent NBA and approximately the same proportion of nitrobenzaldehyde as previously, despite the fact that a visible amount of film had been formed and was included with the sample. Products of irradiation that are volatile will evaporate during the extended bombardment. However, products that are of the same volatility as NBA and nitrobenzaldehyde should be held within the solvent and should be apparent in the GC/MS analysis. Since no such products are apparent, we conclude that the brown film is a higher mass material of low volatility that does not pass through the gas chromatograph.

This lack of initial success forced the development of procedures to optimize the production of what we colloquially term "FAB flakes". The VG70SEQ instrument used for FAB mass spectral acquisition could not be occupied with FAB ionization in a preparative mode. However, a much higher loading of NBA could be accommodated in the imaging SIMS instrument[7], which uses a 10 kV beam of argon ions to form the solid film from NBA. About 25 uL of NBA is placed on the FAB probe. The NBA solution turns brown after only 3 minutes of irradiation at the high particle flux from the saddle-field particle source; the film is visible after 15-20 minutes of continuous bombardment. We determined that 45 minutes of bombardment was optimum for the balance between production of the FAB flakes and the ease with which remaining liquid NBA and the film could be removed from the probe. The film and liquid NBA are removed from the probe by washing the remaining NBA solvent from the probe with methanol. Attempts were made to filter the film from the washing, but these were not successful. The film is retained irretrievably on filter paper and Nylon 66 membranes. Centrifugation was only marginally successful. Best results were obtained simply by drying the film under vacuum, or over an extended period of time in a drying oven held at 125oC.

The solubility of the film was assessed. It was found to be insoluble in all common solvents, including water, glycerol, chloroform, dimethylsulfoxide, acetic acid, nitric acid, hydrochloric acid, ammonium hydroxide, acetonitrile, hexane, benzene, and methylene chloride. As mentioned, the film is not soluble in NBA itself. Due to the insolubility of the film, an NMR spectrum could not be recorded.

The sample of FAB flakes was prepared in KBr pellet for measurement of the IR spectrum. A strong absorbance at 1400 cm^{-1} suggests an aromatic dimer of a nitroso compound. Other strong peaks observed at 3427, 3132 and 1626 cm^{-1} suggest the presence of a quaternary ammonium salt or a primary amine salt. The IR spectrum is not conclusive in terms of a suggested structure.

The information from the mass spectrum of the FAB flakes is similarly uninformative. The FAB mass spectra do not change perceptibly with increased irradiation time. The total ion current decreases with time as NBA is lost by a combination of evaporative and sputtering processes, and most ions follow the

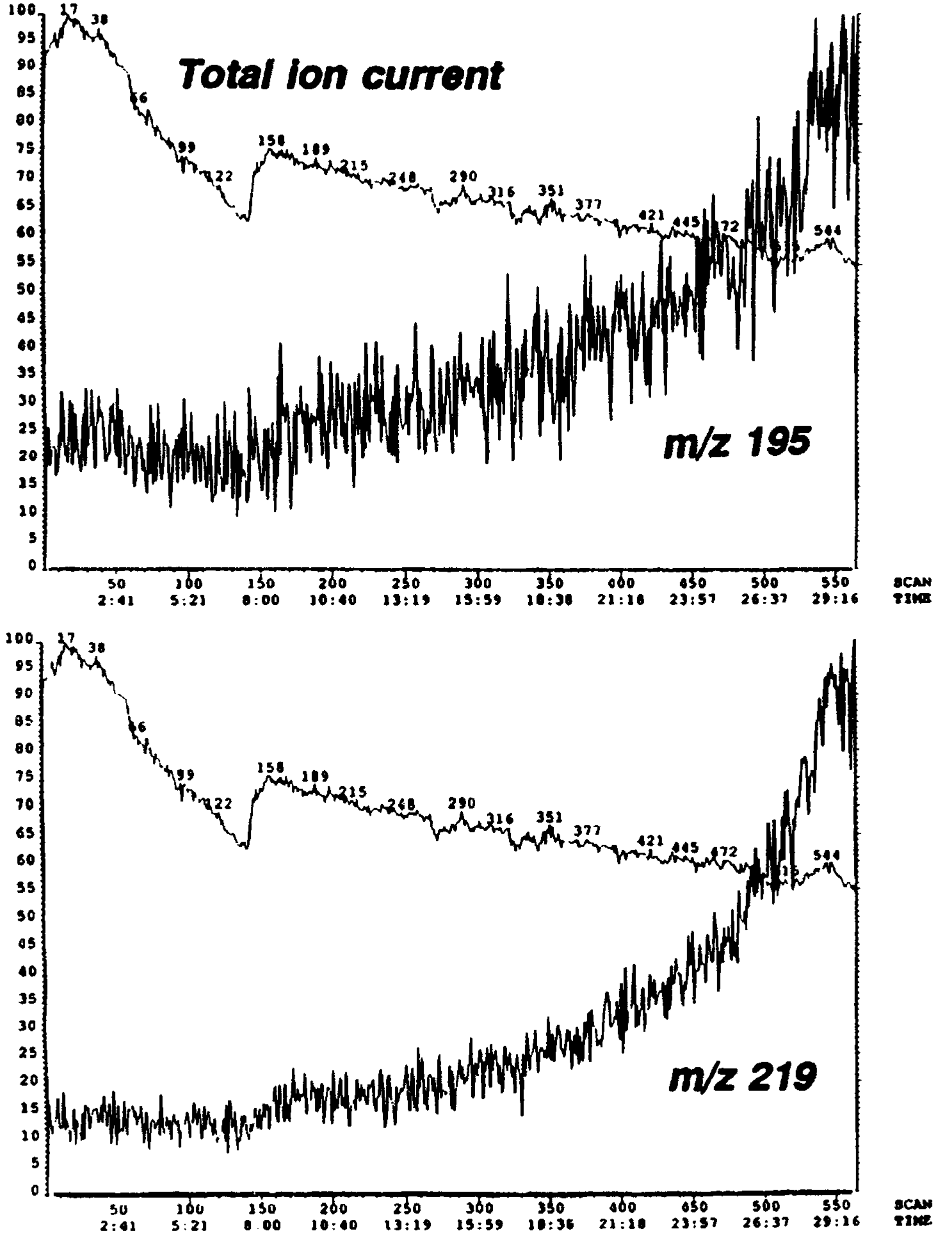

FIG. 2. Intensity changes for ions at m/z 195 and 219 with prolonged sputtering.

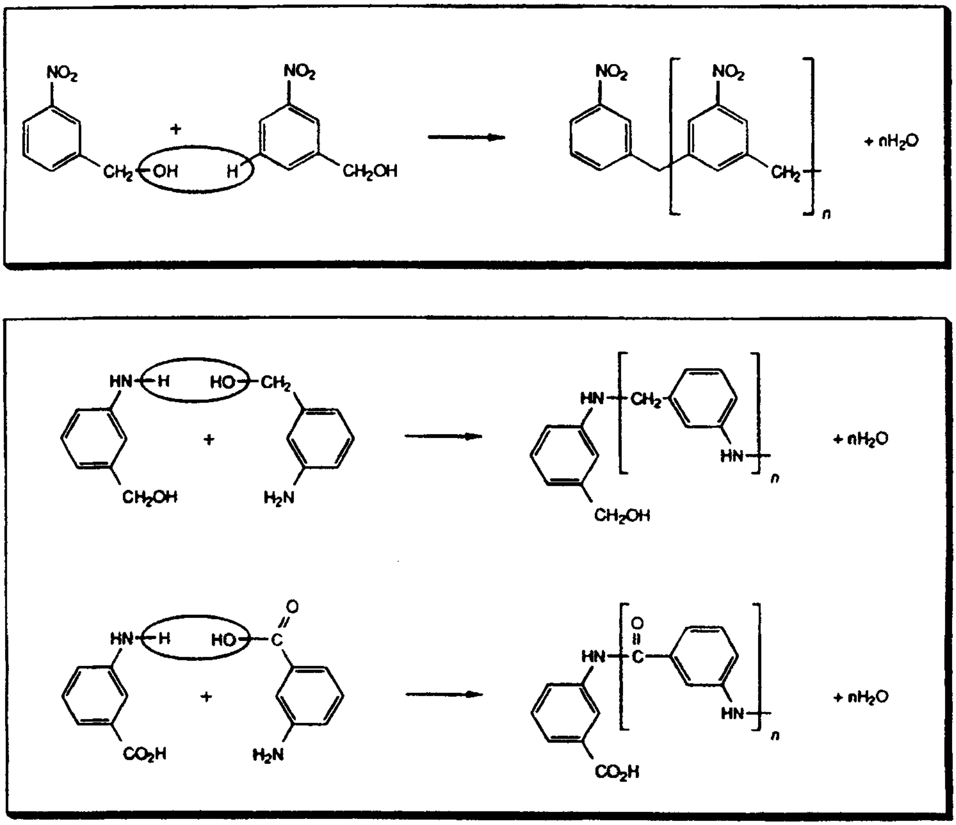

FIG. 3. Schemes for polymerization condensation reactions of nitrobenzyl alcohol.

total ion current trace faithfully. Three ions at m/z 195, m/z 219, and m/z 341 do generally increase in relative intensity with time of sputtering. Figure 2 highlights this behavior for m/z 195 and m/z 219. The ion at m/z 341 follows a similar profile. However, none of these ions can be rationalized in terms of the structure of the polymeric compound formed upon particle bombardment.

With the limited spectral information available, definitive conclusions as to the nature of the material formed are difficult to form. Solubility data and IR data are consistent with the formation of a polymeric material. Figure 3 (top window) suggests two reactions based on condensation reactions that can lead to polymeric forms of nitrobenzyl alcohol. We must also consider that NBA can be oxidized or reduced by the particle bombardment, and these products may participate in polymerization reactions. The product of oxidation of mNBA will be meta-nitrobenzoic acid, which can react in a condensation polymerization reaction shown in Figure 3 (bottom window). Reduction of mNBA produces meta-amino benzylalcohol, which can also participate in a condensation reaction.

CONCLUSIONS

Many aspects of the background ions generated in fast-atom bombardment mass spectrometry are yet unexplained. In this investigation, we have concluded that the film produced upon prolonged bombardment of meta-nitrobenzyl alcohol solvent is probably a polymeric material formed in a condensation reaction. An implicit assumption in fast-atom bombardment is that the background signals can clearly be differentiated from those of the dissolved sample itself, and that the solvent does not react with the sample or with itself under the conditions of the analysis. For mNBA, this is not the case. More definitive conclusions as to the structure of the polymerized material await spectroscopic results from NMR or with other ionization methods in mass spectrometry. An additional avenue of investigation is the extent of occurrence of such polymerization reactions in the presence of anti-oxidants (such as additional BHT) or oxidants.

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References

1. De Pauw, E. Mass Spectrom. Rev. **1986**, 5, 191.
2. Gower, J. D. Biomed. Mass Spectrom. **1985**, 12, 191.
3. Cook, K. D.; Todd, P. J.; Friar, D. H. Biomed. Environ. Mass Spectrom. **1989**, 18, 492.
4. Martin, S. A.; Costello, C. E.; Biemann, K. Anal. Chem. **1982**, 54, 2362.
5. Field, F. A. J. Phys. Chem. **1982**, 86, 5115.
6. Keough, T.; Ezra, F. S.; Russell, A. F.; Pryne, J. D. Org. Mass Spectrom. **1987**, 22, 241.
7. Duffin, K. L.; Flurer, R. A.; Busch, K. L.; Sexton, L. A.; Dorsett, J. W. Rev. Scient. Instrum. **1989**, 60, 1071.

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