

FAST ATOM BOMBARDMENT MASS SPECTROMETRY OF ISOMERIC
PYRAZOLINIUM SALTS UNDER MATRIXLESS CONDITIONS

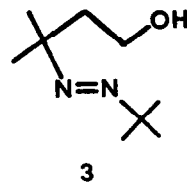
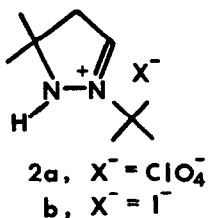
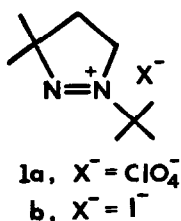
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Abstract: Fast atom bombardment mass spectrometry of solid matrixless samples of pyrazolinium salts give spectra with molecular ions that are suitable for structural analysis and differentiation between isomeric structures.

Fast atom bombardment (FAB) mass spectrometry using liquid matrices is rapidly becoming an important technique for the structural analysis of organic and organometallic compounds with higher molecular weights (>300 daltons).¹⁻⁴ The report that FAB mass spectra of alkali metal halide salts can be obtained from solid samples without the use of a matrix liquid^{5,6} suggested to us that it might be possible to generate mass spectra of low molecular weight organic cations by a "matrixless" procedure and thereby avoid such matrix-caused complications as background interference and reaction with the cation. To test this hypothesis, the labile isomeric pyrazolinium salts 1 and 2 were subjected to FAB under matrixless conditions. We report here observations showing that this technique can be useful in determining cation molecular weights, structural characterization, and differentiation of one isomer from the other.

1-Pyrazolinium perchlorate 1a was obtained from the treatment of the azoalcohol 3⁷ with perchloric acid in chloroform.⁸ Reaction of 3 with



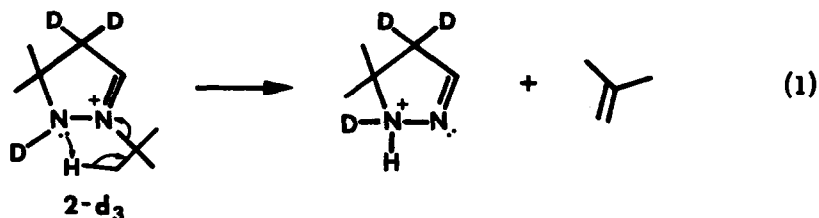
trimethylsilyl chloride/sodium iodide in acetonitrile⁹ gave the iodide 1b.⁸ Treatment of 1a and 1b with sodium carbonate in ethanol effected isomerization to 2a and 2b, respectively.⁸

The pyrazolinium salt sample to be examined was dissolved in a small amount of acetone, and this solution was applied to a clean FAB target. Most of the acetone was allowed to evaporate in the air. Final traces of solvent were pumped away as the FAB probe was inserted through the vacuum lock into the mass spectrometer.

Mass spectral observations were made with a VG Analytical 7070-E instrument operating at +5 kV accelerating potential, with resolving power at approximately 1000, and scanning over a 10-300 dalton mass range at 20 s/decade. A neutral 6-7 keV argon beam produced by an Ion Tech saddle field gun operated at 1-1.5 mA was used to bombard the sample. Repetitive scan spectra were recorded by a VG DS2050 data system, mass calibrated with the cluster ion spectrum of H₂SO₄. The samples of 1 and 2 used for FAB were never above ambient temperature (ca. 35 °C).

Representative FAB mass spectra of the cations 1a and 2a perchlorate salts are shown in Figures 1 and 2, respectively. These are the direct results of the experiments and they have not been subjected to background subtraction or any other spectral enhancement technique. Repeated experiments show that both cation mass spectra can be generated readily and reproducibly. In addition, the iodide salts 1b and 2b also give the same spectra as 1a and 2a, within the range of normal relative variation to be expected from repetitive scanning. As can be seen in Figures 1 and 2, the "molecular ion" peaks at m/z 155 are easily observable for both cations 1 and 2.

One of the significant features of the FAB spectra of 1 and 2 is the observation that both cations show the first major fragmentation ion at m/z 99 arising from neutral loss corresponding to C₄H₈. The spectrum of ring-deuterated cation 2-d₃ also shows loss of a neutral species with an equivalent mass of C₄H₈. This indicates that the t-butyl group is the source of the neutral since any ring fragmentation process would have shown loss of one or more deuterium atoms. The simplest explanation for these fragmentations is the transfer of a t-butyl group hydrogen to a ring nitrogen accompanied by the loss of isobutylene as formulated in eq 1 for 2-d₃.



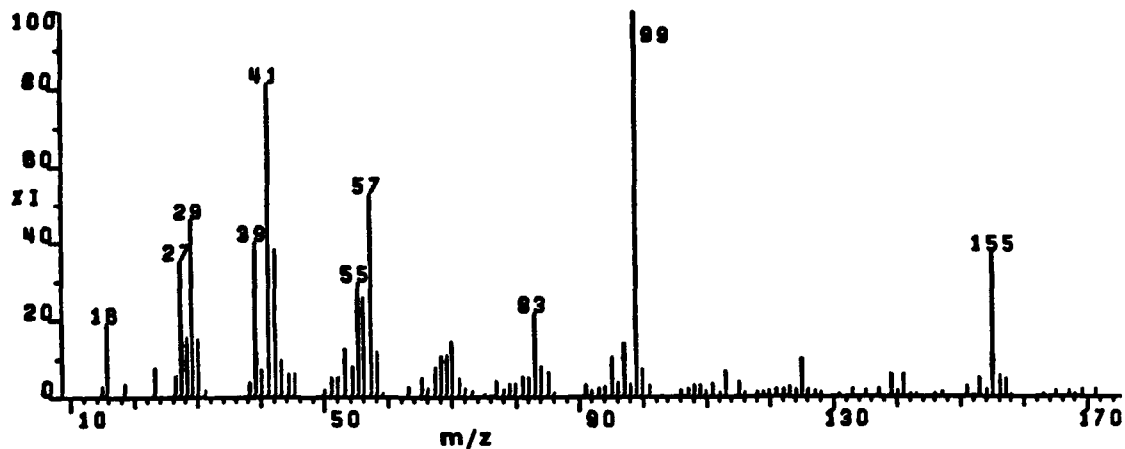


Figure 1: Matrixless FAB mass spectrum of 1-pyrazolinium perchlorate salt 1a. The spectrum is normalized to the intensity of m/z 99.

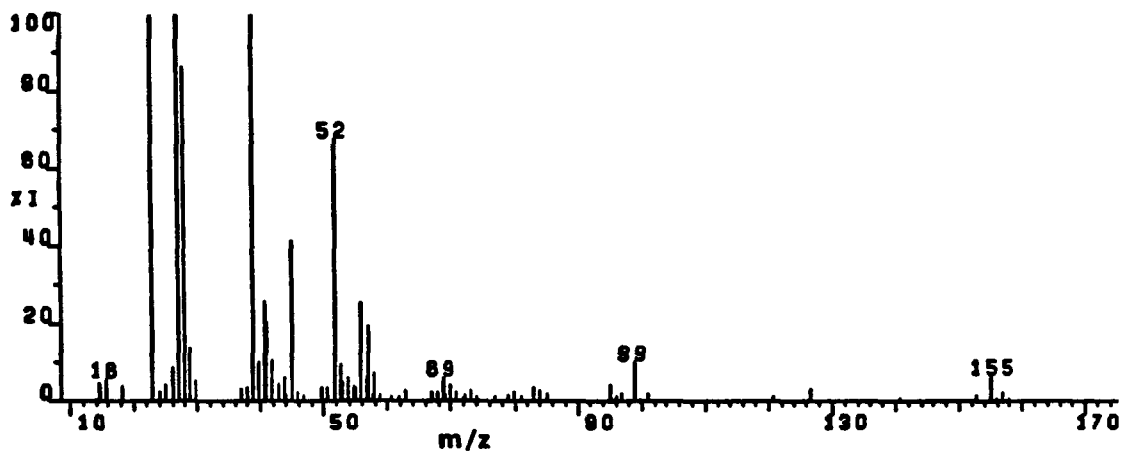


Figure 2: Matrixless FAB mass spectrum of 2-pyrazolinium perchlorate salt 2a. The spectrum is normalized to the intensity of m/z 27. (The off scale peaks at m/z 23, 39, and 41 (multiplet) are $^{23}\text{Na}^+$, $^{39}\text{K}^+$, and $^{41}\text{K}^+$, respectively.)

There are a number of features of the spectra in Figures 1 and 2 that illustrate the different behavior of salts 1 and 2 to FAB. For instance, the two spectra show substantial differences in the percentages of total ion current appearing in the molecular ion (m/z 155) and first fragment ion (m/z 99) peaks. The fact that both peaks are significantly more intense for cation 1 than for cation 2 is indicative that 1 is much more stable towards the desorption and mass analysis process. Other fragmentation differences occur beyond the initial C_4H_8 loss from the molecular ion. Cation 1 shows a major m/z 57 fragment peak likely to be a C_4H_9^+ ion in contrast to a significantly less intense m/z 57 peak with cation 2. Similarly, the m/z 55 peak is noticeably more intense for 1 than for 2. The situation is reversed at m/z 52 with this peak being considerably more intense for 2 than for 1. At this time the identity and elemental composition of these ions are uncertain.

The overall significance of this FAB mass spectrometry study is threefold. Solid matrixless samples of 1 and 2 salts give interference-free spectra with molecular ions that provide molecular weights of the parent cations. Substantial differences between the two spectra allow for clearcut differentiation between the quite thermally and chemically labile isomeric cations. Comparison of unlabeled and deuterium labeled cation spectra indicates that valuable structural information can be obtained from analysis of the fragmentation processes.

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References and Notes

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8. All new compounds had correct elemental analyses and spectral properties in complete agreement with the assigned structures. In addition, 1a and 2a have been prepared by independent synthesis. 1a mp 201-203 °C; 1b mp 173-174 °C; 2a mp 179-180 °C; 2b mp 187-188 °C. Further details will be published elsewhere.
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