

Negative Ion Production by Secondary Electrons in a Mass Spectrometer Ion Source

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Summary Experiments on negative ion production by the electron capture process in an ion cyclotron resonance (ICR) mass spectrometer indicate that secondary electrons are responsible for the ionization observed at a primary electron beam energy of 70 eV.

interesting effects which help to resolve the paradox of Bowie's negative ion mass spectra. The following products

It is usually assumed in studies of negative ion mass spectra that the ion pair formation process predominates at high electron energies, since electron capture is a resonance process with a maximum cross section at very low energies.¹ However, recently published negative ion mass spectra by Bowie *et al.*² seem to contradict this assumption, in that they show a relatively intense parent negative ion contribution at an electron beam energy of 70 eV. The substances investigated by Bowie *et al.* were chosen for their potential for forming stable parent negative ions: anthraquinone and nitrobenzene derivatives were typical compounds. From a theoretical point of view, it would be logical to expect that the parent negative ions in these compounds were formed by an electron capture process. Thus it appears that in Bowie's experiments, electron capture and not ion pair formation is predominant at 70 eV electron beam energy.

During the course of experiments on negative ion production in an ICR mass spectrometer, I have noted some

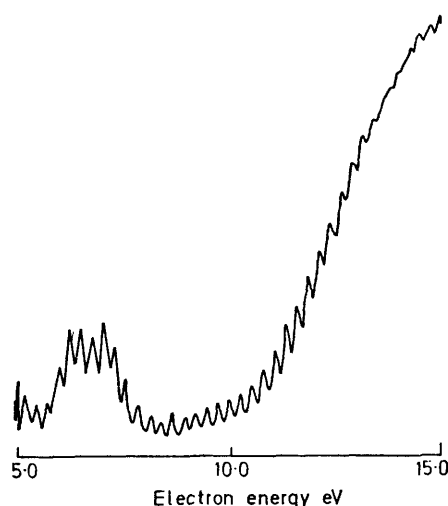


FIGURE. Spectrum of PhNO_2^- ion cyclotron resonance intensity with electron beam energy.

of electron capture processes, Cl^- from CCl_4 ,³ NO_2^- from

EtNO_2 and PhNO_2^- from PhNO_2^4 (a compound similar to those investigated by Bowie) all gave an ICR signal intensity which increased with electron beam energy to a maximum in the region above 30 eV. Significantly, if the intensities of these ions are monitored in the region of 5–15 eV on the electron beam, the onset of positive ion production can be distinguished in what is effectively an electron impact spectrum similar to those obtained by Schulz⁵ and Ridge and Beauchamp⁶ for N_2 . Figure 1 shows the spectrum of PhNO_2^- ICR intensity with electron beam energy: emission current was 1.0×10^{-6} A and PhNO_2 pressure was about 5×10^{-7} Torr. There is a noise pattern superimposed on the trace due to difficulties in tuning the very sharp-topped PhNO_2^- peak. An excitation peak is evident at about 7.0 eV and the onset of positive ionization is shown in the region of 10.0 eV. This experiment indicates that above the positive ionization threshold the supply of low energy electrons in the ICR cell is increasing substantially due to the contribution of secondary electrons from the

positive ionization process. As the electron beam energy increases above the positive ionization threshold, one would expect that the supply of secondary electrons would be augmented by emission from the ICR cell electrodes bombarded by the primary electron beam and, indeed, such secondary electrons may be the major ionization agent at 70 eV.

It is likely that the same phenomenon occurred in the ion source used by Bowie *et al.* on their Hitachi RMU6 mass spectrometer, giving rise to the predominance of the electron capture process at 70 eV. Both the geometry and focusing conditions of the ion source should be critical to the production of negative ions by this method, as the likelihood of electron capture should increase with the residence time of low energy electrons in the source. The ICR is favoured in this respect, as the electrons may be trapped in the cell for times of the order of ms.

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