Use of Metal Dendrites for Aromatisation in Field Ionisation Mass Spectrometry

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Summary Samples held in the mass spectrometer source during a field ionisation experiment aromatise on the new nickel and cobalt emitters.

USE of metal dendrites for field desorption mass spectrometry as an alternative to high-temperature carbon microneedles grown on thin wires[1] has met with success in several applications. We now report a new aspect of the utility of these dendrites in field ionisation experiments which has evident implications for structural determination by mass spectrometry.

The standard application of nickel[2] and cobalt[3] dendrites to field ionisation analysis of the compounds we have examined in preliminary studies, *viz.*, cyclohexa-1,3- and 1,4-diene, tetralin, and cyclohexanone, produces only a single ion at the expected molecular mass. However, when the sample remains in the source for moderate periods of time instead of being continuously pumped, new peaks corresponding to expected catalytic products from the metal surface appear. In no case do these peaks appear in less than 20 min contact time in a closed source, and never in a pumped system. Thus the utility of nickel and cobalt emitters for determining molecular weights in the usual fashion is not compromised.

After being in a closed source for 30 min, however, the compounds above show new peaks. The cyclohexadienes, for example, in addition to the molecular ion at *m/e* 80, have new ions at *m/e* 78, 82, and 84, which become more intense with time. That at *m/e* 78 is more intense than the others, for example amounting to 15% of the base peak (*m/e* 80) in cyclohexa-1,4-diene after 60 min contact. Small peaks ($<2\%$) also appear at *m/e* 158 and 160. We interpret these results to indicate the disproportionation of cyclohexadiene to benzene on the one hand and cyclohexene and cyclohexane on the other, probably through formation of radicals and hydrogen atoms, since evidence of dimeric products is present.

Tetralin undergoes a similar reaction. Although it behaves as expected in field ionisation when continuously pumped through the source, tetralin trapped in the source for more than 30 min begins to produce ions 4 atomic mass units lower in mass, corresponding to the mass of naphthalene. Ions at *m/e* 130 corresponding to dihydronaphthalene are formed too. No dimeric product was observed in this case; we have not yet determined if this absence is due to a change in mechanism or the low volatility of the product.

In the case of cyclohexanone, the usual behaviour, formation of only the molecular ion, was observed under standard conditions. After trapping the compound in the source for more than 30 min, ions from two to four mass units lower were again observed, the last corresponding in mass to phenol.

No reaction of n-heptane was observed even after 1 h.

These results have been observed in both an A.E.I. MS-702 instrument modified for field ionisation–field desorption studies[4] and in a DuPont 21-492B instrument. The formation of the disproprotionation and dehydrogenation products depends upon the presence of the metal emitter. If a sample is trapped in the source with the emitter removed, and an electron impact spectrum recorded after 1 h, no spectral changes are seen.

Whilst catalytic reactions on specially prepared surfaces have been studied with mass spectrometers,[5] we think it of compelling interest that these new emitters, prepared in a few seconds for use in commercial mass spectrometers for organic analysis, give results of considerable analytical value in a few minutes. We propose that the aromatisation process, in particular, is capable of giving information distinguishing between rings and double bonds in an empirical formula deduced by the usual interpretation rules, and are now evaluating the behaviour of other compounds to determine the generality of our first results.

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