# Consecutive Fragmentations in Mass Spectrometry

By Jože Marsel, Miran Medved, Bogdan Kralj, and Vili Kramer
*(Institute Jožef Stefan, University of Ljubljana, Yugoslavia)*

John H. Beynon*
*(University College of Swansea, Swansea* SA2 8PP)

and Teodor Ast
*(Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Yugoslavia)*

*Summary* Consecutive ion fragmentation processes can be studied in the separate field-free regions of a mass spectrometer; the case of both fragmentation steps occurring in a single region can also be studied.

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The advent of double-focussing mass spectrometers, in which the electric and magnetic sector fields can be controlled independently of the accelerating voltage, enables fragmentations of metastable ions to be studied in either of the field-free regions in front of the sectors.[1]

By suitably adjusting the sector fields, it is then possible to study the fragmentation of a parent ion, $M_1^{+\cdot}$ in the first field-free region and that of its daughter ion, $M_2^{+\cdot}$ in the second field-free region. In this way, consecutive fragmentation processes can be identified with certainty. In most work done to date, single step fragmentations, $M_1^{+\cdot} \rightarrow M_2^{+\cdot}$, $M_2^{+\cdot} \rightarrow M_3^{+\cdot}$, *etc.*, have been studied by selecting the ions $M_1^{+\cdot}$, $M_2^{+\cdot}$, $M_3^{+\cdot}$ formed in the ion chamber and examining the metastable peaks arising from each of them in turn. The ions selected in this way are the products of relatively fast reactions, will usually have different internal energy distributions, and may even have different structures from those formed as daughters of decompositions of metastable ions. Fragmentation maps based on single step fragmentations of metastable ions are thus unreliable in this respect.

We report here some initial results obtained on a commercial double-focussing mass spectrometer of Mattauch Herzog geometry, the Consolidated Electrodynamics Corporation type 21-110C, modified for recording of ion kinetic energy spectra.[2] The sample used was 1,2-dihydroxybenzene which shows *inter alia* strong peaks in its mass spectrum corresponding to the molecular ion of mass 110 and fragment ions of masses 92, 82, and 64. Metastable peaks corresponding to transitions $110^+ \rightarrow 92^+$, $110^+ \rightarrow 82^+$, $92^+ \rightarrow 64^+$, and $82^+ \rightarrow 64^+$ can be seen. When consecutive fragmentations are observed, however, it is clear that the process $110^+ \rightarrow 92^+ \rightarrow 64^+$ is dominant and that the process $110^+ \rightarrow 82^+ \rightarrow 64^+$ occurs hardly at all in spite of a strong primary signal for the expulsion of neutral CO in the process $110^+ \rightarrow 82^+$.

Valuable information can obviously be obtained from such results concerning energy partitioning in the various fragmentation reactions, especially when such observations are coupled with appearance potential data.

Additional modifications have recently been made to the instrument[3] in which an extra electric sector has been fitted behind the original collector slit so that there are then three instead of two useful field-free regions in which the fragmentations of metastable ions can be observed.

The consecutive fragmentation processes can then be studied in any two of these three regions, namely 1 and 2, 1 and 3, or 2 and 3, giving further information concerning the relative rate constants for the individual steps.

Consider the settings required on the various sectors in a typical experiment. Assuming that to transmit stable ions of mass:charge ratio $M_1:I$ the first electric sector voltage has to be set to $E_1$, the magnet to a field $B_1$ and the second electric sector voltage to $E_2$, then if the consecutive reactions occur in regions 1 and 2, the settings required to transmit the $M_3^+$ ions through the final slit are: $M_2E_1/M_1$, $M_3B_1/M_1$, and $M_3E_2/M_1$, respectively. (If there is no accurate magnetic field meter available and the magnet is initially set to transmit stable ions $M_1^+$ it must be adjusted to transmit ions of apparent mass $M_3^2/M_1$. The ratios of these masses is the square of the ratio of the respective magnetic fields). If the reactions occur in regions 1 and 3, respectively, the settings must be changed to $M_2E_1/M_1$, $M_2B_1/M_1$, and $M_3E_2/M_1$ and if the reactions occur in regions 2 and 3, the required settings are $E_1$, $M_2B_1/M_1$ and $M_3E_2/M_1$. The relative signal strengths measured at the final detector in these 3 cases, for the arrival of ions of mass: charge ratio 64:1 formed from molecular ions of 1,2-dihydroxybenzene, were, respectively, in the ratios 13:52:1. Necessary corrections to these results are discussed below.

The various sectors can also be adjusted to observe the case when both steps in the overall fragmentation occur in the first, in the second or in the third field-free region. When this is done, relative signal strengths of 7:1:8 are obtained. These results do not distinguish each separate step of the fragmentation, however, and if $110^+ \rightarrow 64^+$ occurs in a single step also, the $64^+$ ions from this reaction will be included in the measured signal. To obtain a preliminary comparison of these results with the relative signals obtained when various single step fragmentation processes occur in the respective field-free region, measurements were made on the reactions listed in the Table where the peak height ratios are also listed.

TABLE

| Reaction | Compound | Ratio for regions 1, 2, and 3 |
|---|---|---|
| $110^+ \rightarrow 92^+$ | 1,2-dihydroxybenzene | 38:1:1·4 |
| $110^+ \rightarrow 82^+$ | 1,2-dihydroxybenzene | 16:1:3·0 |
| $78^+ \rightarrow 52^+$ | benzene | 36:1:2·1 |
| $103^+ \rightarrow 76^+$ | benzonitrile | 36:1:2·3 |

Even without correction of the results in the Table it already seems clear that most fragmentation takes place in the first field-free region for these compounds. Correction factors must be applied to all the above results to take into account the relative lengths of the three field-free regions and the relative collection efficiencies at the final collector of ions formed in the various regions. Additions to the instrumentation to enable such corrections to be made are now being undertaken, and corrected and more extensive results will be reported in a later paper. It can be seen, however, from the uncorrected results that the fall-off in metastable peak intensity as a function of time is less steep in the case of loss of CO from the molecular ion of 1,2-dihydroxybenzene corresponding to both a smaller activation energy and a lower frequency factor for this fragmentation reaction. A plot of $k$ versus $\epsilon$ must be less curved in the case of this reaction than the curve for the loss of $H_2O$ in the region corresponding to metastable ions.

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[2] J. Marsel, V. Kramer, B. Kralj, and V. Vrščaj, 2nd European Conf. on Analyt. Chem. (Euroanalysis), Budapest, August 1975 (Contribution no. I-51).

[3] Unpublished results.