

Further Interference Peaks in Mass Analysed Ion Kinetic Energy Spectra

Bernd Schaldach and Hans-Friedrich Grützmacher

Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse, D-4800 Bielefeld 1, West Germany

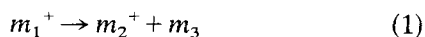
It is shown that interference peaks in mass analysed ion kinetic energy spectra can also occur from ions decomposing in the accelerating region of the ion source.

INTRODUCTION

Recently, Beynon and co-workers reported¹ on interference peaks in mass analysed ion kinetic energy (MIKE) spectra. We have been confronted with this problem too,² and arrived principally at the same explanations concerning the origins of certain interference peaks in MIKE spectra.³ However, in addition to the cases mentioned by Ast *et al.*,¹ there are often a lot of sharp peaks observed in MIKE spectra which do not fit the equations given by these authors and which arise from decompositions of metastable ions in the acceleration field. These interference peaks are easily distinguished from normal signals in a MIKE spectrum by their much smaller peak width (see Fig. 2). Decompositions occurring within the accelerating region of the ion source have also been considered by Lacey and Macdonald.⁴ Their generalized treatment of ion fragmentations within the various regions of a mass spectrometer of conventional geometry is not directly related to MIKES, however.

RESULTS AND DISCUSSION

Considering the fragmentation



ions m_1^+ continuously decompose along their flight path through the mass spectrometer. The local point of decomposition is determined by the rate constants of reaction (1) and by instrumental parameters. Those ions m_2^+ which are formed within the accelerating region of the ion source will obtain a *continuum* of kinetic energies, given by Eqn (2)

$$1/2 m_2 v_f^2 = z V_0 \left\{ \frac{m_2}{m_1} f + (1-f) \right\} \quad (2)$$

where v_f = velocity of daughter ions, V_0 = accelerating voltage and f = fraction of V_0 . Ions m_2^+ formed at the fraction f of V_0 will pass the magnetic sector with an apparent mass m_f given by Eqn (3)⁵

$$m_f = \frac{m_2^2}{m_1} \left[f + \frac{m_1}{m_2} (1-f) \right] \quad (3)$$

Similarly, the electric sector voltage E_f at which these ions pass the electric sector is given by Eqn (4) derived from Eqn (2)

$$E_f = E_0 \frac{m_2}{m_1} \left[f + \frac{m_1}{m_2} (1-f) \right] \quad (4)$$

From Eqns (3 and 4) the range of apparent masses m_f and the range of the electric sector voltages can be evaluated for reaction (1) occurring in the accelerating region of the ion source. Setting $f=0$ is equivalent to regarding ions m_2^+ generated in the ion source before acceleration, i.e. $m_f = m_2$ and $E_f = E_0$. The other extreme, $f=1$, is equivalent to observing ions m_2^+ formed in the first field free region, i.e.

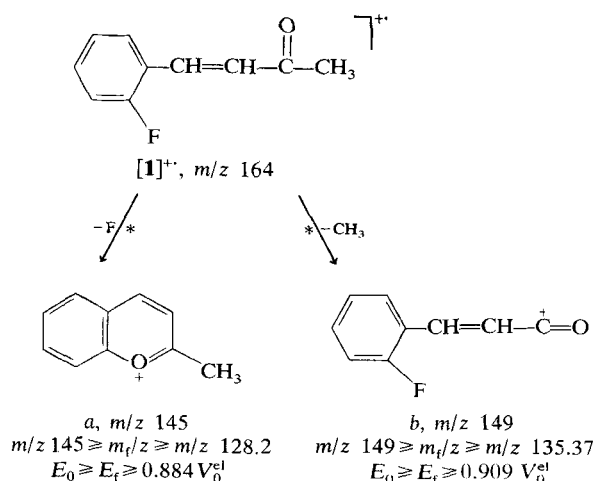
$$m_f = \frac{m_2^2}{m_1} \quad \text{and} \quad E_f = \frac{m_2}{m_1} \times E_0$$

Thus, by preselecting m_f values in between these extremes the fraction f of V_0 [Eqn (2)] at which the observed m_2^+ is formed is predetermined and can be calculated explicitly from Eqn (5)

$$f = \frac{\frac{m_f}{m_2} - 1}{\frac{m_2}{m_1} - 1} \quad (5)$$

Having determined f the corresponding E_f can be calculated [Eqn (4)] and the interference peak can be recorded. This is most easily done on a mass spectrometer with 'reversed geometry' by setting the magnet current to the appropriate m_f/z value and scanning E over a small region around E_f . In this way any slow fragmentation reaction can be followed step by step from the ionization chamber to the 1st field free region (FFR).⁶

The procedure outlined above is illustrated by the reactions shown in Scheme 1. The ranges of m_f and E_f values are also given in Scheme 1. Three regions of m_f values can be distinguished in this case: (i) $149 \geq m_f \geq 145$, only ions *b* are expected to be transmitted, (ii) $145 \geq m_f \geq 135$, both ions *a* and ions *b* can be transmitted, (iii) $134 \geq m_f \geq 128$, only ions *a* will be observed. The results of the respective MIKE scans obtained with a Varian MAT 311A mass spectrometer are shown in Fig. 1 and the detailed values are given in Table 1. Thus, by tuning in the magnet to the value



m_f/z 147 a sharp interference peak is expected at $E_f = 0.9865 E_0$. The experiment gives an intense signal at $E_f = 0.9866 E_0$ (Table 1) in excellent agreement with expectation. According to Eqn (6) (see below) this signal corresponds to ions b which have been formed after the acceleration of ions $[1]^+$ to $f = 0.1468$ (see Table 1). With the magnet at the value $m_f/z = 145$, the peak for ions b is shifted to $E_f = 0.9731 E_0$ (calc. $E_f = 0.9731 E_0$) (see Fig. 1(a) and Table 1) and the point of formation has shifted to $f = 0.2935$. In progressing to lower m_f/z values there are now two intense sharp peaks observed [Fig. 1(b-g)] at exactly the positions calculated for ions b and a from Eqns (4 and 5) (Table 1). In the case of m_f/z 136 and m_f/z 135 [Fig. 1(f and g)] a dramatic increase in intensity of the peak belonging to ions b is observed. This is due to approaching the value $f = 1$. The ions b are now sampled from the 1st FFR and the ion current is integrated over a relatively large range of lifetimes. In previous cases the sampling area and the span of lifetimes were much shorter and were related to the

Table 1. Calculated and experimental values for E_f/E_0 for the formation of ions a and b (Scheme 1) in the accelerating region of the ion source

m_f/z	Ions b			Ions a		
	E_f/E_0 (calc.)	E_f/E_0 (obs.)	f	E_f/E_0 (calc.)	E_f/E_0 (obs.)	f
147	0.9865	0.9866	0.1468	—	—	—
146	0.9798	0.9798	0.2201	—	—	—
145	0.9731	0.9731	0.2935	1.0000	1.0000	0
144	0.9663	0.9664	0.3668	0.9930	0.9935	0.0595
143	0.9596	0.9596	0.4402	0.9861	0.9858	0.1191
142	0.9529	0.9530	0.5136	0.9792	0.9792	0.1786
141	0.9462	0.9466	0.5869	0.9723	0.9724	0.2381
140	0.9395	0.9396	0.6603	0.9654	0.9654	0.2976
139	0.9328	0.9328	0.7337	0.9585	0.9585	0.3572
138	0.9261	0.9261	0.8070	0.9516	0.9516	0.4167
137	0.9723	0.9724	0.8804	0.9447	0.9448	0.4762
136	0.9127	0.9128	0.9538	0.9378	0.9379	0.5358
135	—	—	—	0.9309	0.9291	0.5953
134	—	—	—	0.9240	0.9239	0.6548
133	—	—	—	0.9171	0.9168	0.7143
132	—	—	—	0.9102	0.9099	0.7739
131	—	—	—	0.9033	0.9032	0.8334
130	—	—	—	0.8965	0.8965	0.8929
129	—	—	—	0.8896	0.8894	0.9525

resolving power of the magnetic sector. Thus, by opening the intermediate slit located between the magnetic and the electric sector it is possible to increase the abundances of ions formed in the accelerating region. By further lowering m_f/z , peaks due to ions b are no longer observed [Fig. 1(h-l), Table 1]. However, the peaks related to ions a are still observed until m_f/z 128 is reached. Again a dramatic increase in intensity indicates the formation of ions a in the 1st FFR [Fig. 1(l)].

If it is necessary to determine the origin of an unknown interference peak appearing in a MIKE spectrum the difficulty arises that there are only two equations [Eqns (4 and 5)] but three unknowns (m_1 , m_2 , f). From the combination of Eqns (4 and 5) it is possible to determine m_2 [Eqn (6)].

$$m_2 = m_f \times \frac{E_0}{E_f} \quad (6)$$

The parent ions belonging to m_2 can be identified by applying the refocusing technique. If there is more than one parent m_1 observed, the various m_1 can be checked with the aid of Eqn (5). Negative values or values larger than 1 are not possible for f and the corresponding m_1 is discarded. If there remains ambiguity one has to follow the peak by successively lowering both m_f/z and E_f until a steep increase in the

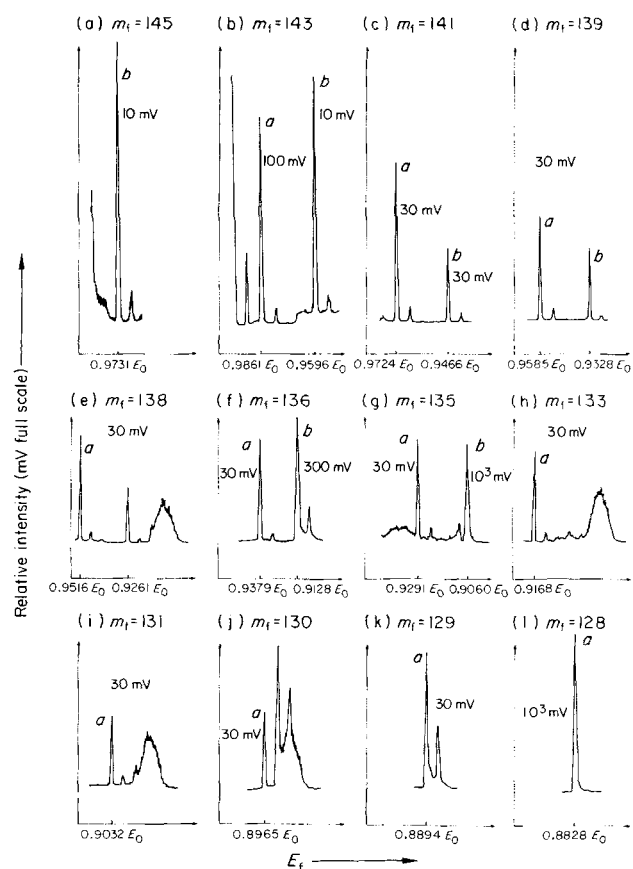


Figure 1. Interference peaks due to the formation of ions a and b^7 (Scheme 1) within the accelerating region of the ion source.

intensity of the daughter ion indicates that one has arrived at the special situation $f=1$. In this case the unknown value of m_1 can be calculated from m_f or E_f according to Eqns (3 or 4), respectively. The significance that interference peaks originating from decompositions within the accelerating region may have in MIKE spectra is illustrated in Fig. 2.

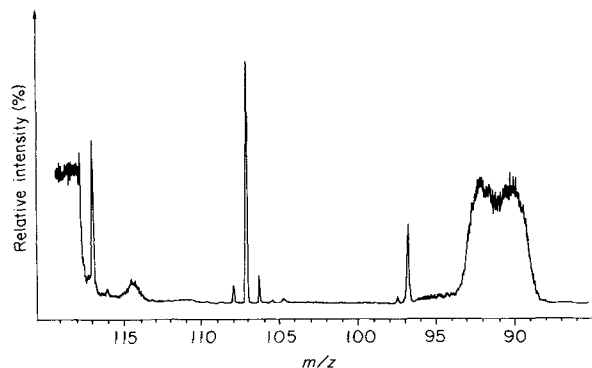


Figure 2. MIKE spectrum of ions m/z 118 obtained from *p*-nitrobenzalacetone.

The broad signal centred at m/z 91 is composed of two unresolved typical MIKE peaks. They indicate the loss of 26 u and 28 u in the 2nd FFR from ions m/z 118 obtained from *p*-nitrobenzalacetone. In contrast, the sharp peaks at the apparent masses $m_{app} = 96.7, 106.3, 107.1$ and 107.9 all indicate reactions occurring in front of the magnetic analyser and which are not connected with fragmentations of ions m/z 118. Application of Eqn (6) gives the various m_2^+ ions in a straightforward way. The refocusing technique gives two parent ions m_1 for each daughter ion, $m_2 = 130$ and $m_2 = 144$, respectively (Table 2). Thus, the peak with the apparent mass 107.1 (Fig. 2) originates from two reactions occurring at different positions in the accelerating region (see Table 2). The ions $m_2 = 144$ also possess two parent ions. The f value for $m_1 = 174$, however, is larger than 1. To observe an intense interference peak due to this reaction, the m_f value had to be raised to $m_f = 144^2/174 = 119.17$. With $m_f = 118$, however, probably only a small part of the tail of the momentum distribution due to kinetic

Table 2. Origins of interference peaks occurring in the MIKE spectrum of ions m/z 118 obtained from *p*-nitrobenzalacetone

E_f/E_0	m_{app}	m_2	m_1	f
0.9077	107.11	130.00	176	0.3532
			160	0.4923
0.8193	96.68	144.02	174	1.0472
			190	0.7458

energy release is recorded. Therefore, the predominant component of the peak with the apparent mass 96.7 (Fig. 2) belongs to the reaction of $m_1 = 190$ being accelerated to $0.7458 V_0$.

Besides being a nuisance in MIKE experiments the interference peaks described in this paper may give useful information about the time dependence of unimolecular reactions of ions in the gas phase. By varying f and correspondingly the sampling region for metastable ions decomposing in the accelerating field of the ion source the lifetime of the metastable parent ions is also varied. Although the span of the lifetimes of reacting ions which can be investigated by this technique corresponds only to about a factor of 10 (which, however, can be enhanced by measurements at different accelerating voltages) this is of interest for certain reactions.

EXPERIMENTAL

The following conditions were used: electron energy 70 eV, emission current 2 mA, accelerating voltage 3 kV, $V_0 = 510.63$ V, ion source pressure $10^{-6} - 2 \times 10^{-6}$ Torr, ion source temperature 150°C , direct insertion of the sample.

Acknowledgement

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