Energetic Metastable Ion Decompositions

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RECENTLY, a number of decompositions of metastable ions have been reported which do not give rise to peaks of the usual Gaussian shape.[1-5] Instead, the peaks are considerably broader than normal and have a flat or concave top. This peak shape is the result of the release of internal energy of the parent ion as kinetic energy of the fragments.[2] Our studies of this type of decomposition on two different mass spectrometers indicate that instrumental parameters must be considered in interpreting such peaks. Also, flat-topped "metastable" peaks are much more common than previously suspected, and a number of new examples are reported.

The transition $139^+ \to 109^+ + 30$, $m^* = 85\cdot5$, occurring in *p*-nitrophenol[2] and *p*-nitrophenetole, was studied using two mass spectrometers; a 90° sector, single-focussing, Hitachi RMU-6A and a Mattauch–Herzog, double-focussing CEC 21-110B. Figure 1 shows this flat-topped peak in *p*-nitrophenol obtained from the two instruments operating at an accelerating potential of 2500 v. The values of the energy released, as calculated from the apparent widths of the peaks[2] (Table 1) differ seriously. The average value for p-nitrophenol from the Hitachi data is in excellent agreement with that of Beynon[2] whose results were supported by measurements of the retarding voltage necessary to stop the ions. Both the Hitachi and the instrument used by Beynon,[2] the A.E.I. MS-9 mass spectrometer, have a very narrow slit defining the ion beam entering the drift

region in which the observed metastable decompositions take place. However, in the CEC 21-110B instrument this slit is the relatively wide β-stop between the electrostatic and magnetic sectors. It may be that ions formed from decompositions in the electrostatic sector can enter the drift region at a much greater divergence angle, and thus produce a much broader image at the collector. The trend to increasing "metastable" peak width with decreasing accelerating voltage supports this, and further experiments are in progress to check this theory.

The existence of broad metastable peaks with concave tops has been attributed to decompositions in which the kinetic energy released is sharply peaked about a particular value.[5] Such peaks have been observed in the decomposition of doubly-charged species[4] where the energy released is of the order of 2·5 ev. The flat-topped peaks have been attributed to transitions involving a larger range of energy, but an additional explanation is also possible. Figure 2 illustrates a peak from a metastable decomposition observed in methanol using the 21-110 double-focussing instrument. The measured kinetic energy in this case is approximately 1 ev. A concave top with two prominent "wings" can be developed by lowering the accelerating potential to approximately 1700 v, although this decrease should not affect the kinetic energy distribution. This suggests that the change in peak shape is due to discrimination effects. Consider transitions in which the daughter

TABLE 1

Transition $139^+ \to 109^+ + 30$

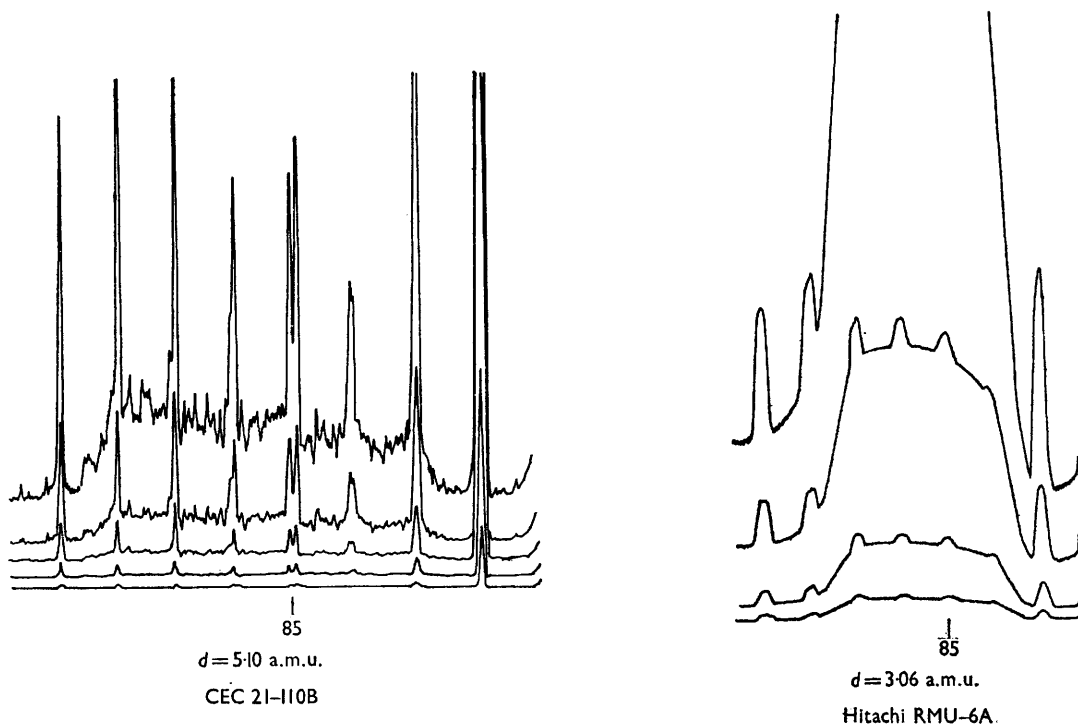| *p*-Nitrophenetole | | | | *p*-Nitrophenol | | | |
| 21-110B | | RMU-6A | | 21-110B | | RMU-6A | |
V_a	T^a	V_a	T^b	V_a	T^a	V_a	T^a
7170	1·55 ± 0·17	3000	0·77	7160	1·65 ± 0·20	3000	0·72 ± 0·01
4420	1·89 ± 0·06	2500	0·72	3580	1·76 ± 0·25	2500	0·72 ± 0·01
3515	2·19 ± 0·12	1980	0·69	2440	1·90 ± 0·12	1980	0·75 ± 0·02
2800	2·15 ± 0·09	1470	0·64			1470	0·64 ± 0·02
		970	0·80			970	0·73 ± 0·03
		720	0·80			720	0·77 ± 0·07
Average	1·95		0·74		1·77^c		0·72^c

a Standard deviations calculated for six or more determinations.
b Average of three separate runs.
c Beynon *et al.*[2] report $T = 0\cdot74$ ev for this transition.

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FIGURES 1a *and* 1b

The transition 139⁺ → 109⁺ + 30 *in* p-*nitrophenol.*

ion is released with an excess of kinetic energy in a direction perpendicular to the main ion path. The resultant velocity vector for these ions will differ from the velocity vector of the parent ions so that the daughter ions will enter the magnet sector at some distance from the normal ions. The magnitude of this effect will depend on the position of the decomposition in the flight tube and the magnitude of the excess energy of decomposition relative to the accelerating potential. However, for some decompositions the deviation of the daughter ion from the ion axis may be sufficient to prevent these ions from passing through the β-slit to the collector. This will result in a reduced collection efficiency for the ions which will appear at an apparent mass approximately equal to $m_2{}^2/m_1$. For the peak in Figure 2, recorded at an accelerating potential of 1763 v, the discrimination effects have reduced the peak intensity at the centre by approximately 35%. For transitions in which the energy released is greater than 1ev, "metastable" peaks with concave tops may be expected to appear at accelerating voltages higher than 2 kv. These effects will depend on the geometry of the particular instrument, such as
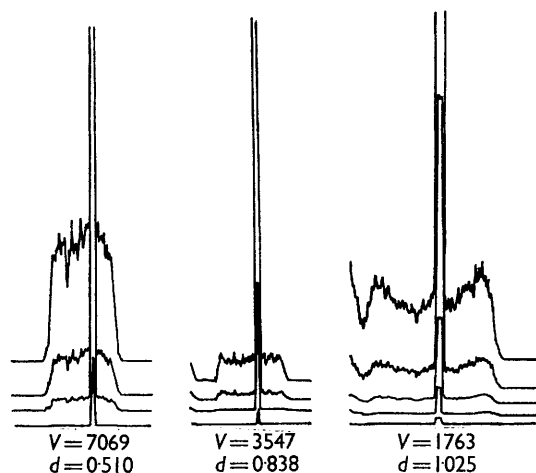

FIGURE 2

Variation of metastable peak shape with accelerating potential. The transition 31⁺ → 29⁺ + 2 *observed in methanol with the* 21-110B *instrument.*

TABLE 2

Compound	Metastable ion	$m_1{}^+$	$m_2{}^+$	Neutral fragment	m^*	T
p-Nitrophenol	$(M - NO)^+$	109	81	CO	60·2	0·14
p-Nitrophenetole	$(M - C_2H_4 - NO)^+$	109	81	CO	60·2	0·18
p-Nitroanisole	M^+	153	123	NO	98·9	0·72
p-Nitroanisole	$(M - NO)^+$	123	95	CO	73·4	0·15
3,6-Dimethyl-s-tetrazine	M^+	110	82	N_2	61·1	0·48
Toluoquinone	M^+	122	94	CO	72·4	0·23
Toluoquinane	$(M - CO)^+$	94	66	CO	46·3	0·19
Methanol	$(M - H)^+$	31	29	H_2	27·1	1·16
Propan-2-ol	$(M - CH_3)^+$	45	29	CH_4	18·7	0·45
Formamide	$(M - 2H)^+$	43	29	N	19·6	0·57
Methyl carbamate	$(M - CH_3O - H)^+$	43	29	N	19·6	0·62

length of the ion flight path and width of the β-stop. The change in shape of the top, however, will not affect the energy determination which is based on the over-all width of the peak. Note that this explanation also suggests that an important fraction of the observed metastable decompositions take place in the electrostatic sector.

We have observed a surprising variety of additional flat-topped transitions; representative examples are listed in Table 2. With the exception of formamide and methyl carbamate, which appear to undergo the surprising loss of atomic nitrogen, the neutral fragments are all small stable molecules. For the aromatic systems the largest energy loss occurs upon ejection of NO. This is most likely due to the high activation energy required to rearrange the nitro- to the nitrite structure prior to the elimination of NO.[6] The succeeding step, elimination of CO, seems to require much less energy. Future publications will deal with the use of such metastable ions in studies of structures and mechanisms.

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[7] Compound kindly provided by Prof. E. W. Thornton, Dept. of Chemistry, Univ. of Pennsylvania.