

Consecutive Metastable Transitions in a Double-focussing Mass Spectrometer

By K. R. JENNINGS

(Dept. of Chemistry, The University, Sheffield, 10)

If an ion m_1^+ dissociates to give an ion m_2^+ in the field-free region between the electrostatic analyser and magnetic analyser of a double-focussing mass spectrometer, a metastable peak is observed at $m/e = m_2^2/m_1$. It is usual to infer that the neutral fragment ($m_1 - m_2$) is lost as a single entity, and this is usually almost certainly correct since the fragments lost are frequently stable molecules such as C_2H_2 , C_2H_4 , H_2O etc., or well known radicals such as CH_3 or C_2H_5 . At low m/e -values, however, one can often observe a number of weaker metastable peaks which correspond to the loss of a relatively large neutral fragment which may or may not be lost as a single entity. For example, in the mass spectrum of toluene, metastable peaks are observed at $m/e = 46.4$ and 23.45 which correspond to the loss of C_2H_2 by $C_7H_7^+$ and $C_5H_5^+$ ions respectively. A much weaker peak can be observed at $m/e = 16.8$, which corresponds to the loss of C_4H_4 by $C_7H_7^+$ to give $C_3H_3^+$. In this case, it seems probable that this peak results from the consecutive loss of two C_2H_2 molecules, *i.e.*, $C_7H_7^+ \rightarrow C_5H_5^+ \rightarrow C_3H_3^+$ in the region between the two analysers.

In a double-focussing mass spectrometer, ions which decompose in the field-free region between the source and the electrostatic analyser are normally lost. However, m_2^+ ions formed from m_1^+ ions in this region are transmitted by the electrostatic analyser if the accelerating voltage V

is increased to m_1V/m_2 , the voltage across the electrostatic analyser remaining unchanged and so maintaining a constant m/e scale.¹ Under these conditions, normal ions are not transmitted and m_2^+ ions may therefore be studied in the absence of intense peaks due to normal ions. Using this technique, the three metastable transitions mentioned above were detected quite readily in the mass spectrum of toluene.

It has proved possible to combine these two techniques to demonstrate the occurrence of consecutive metastable transitions in the two field-free regions of an A.E.I. MS9 double-focussing mass spectrometer. The metastable peak at $m/e = 23.45$ corresponding to the decomposition $C_5H_5^+ \rightarrow C_3H_3^+ + C_2H_2$ in the mass spectrum of toluene was tuned in, using an accelerating potential of 4kv. The accelerating voltage was then increased to $4kv \times 91/65$ when a weak signal was again detected. Under these conditions, $C_5H_5^+$ ions formed in the decomposition $C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2$ in the first field-free region are transmitted by the electrostatic analyser and a fraction of these undergo the decomposition $C_5H_5^+ \rightarrow C_3H_3^+ + C_2H_2$ in the second field-free region; the resulting $C_3H_3^+$ ions are collected at $m/e = 39^2/65 = 23.45$. The same decompositions have been detected in the mass spectrum of *p*-xylene. Other consecutive metastable transitions detected by this technique include the sequence $C_6H_5F^+ \rightarrow C_4H_3F^+ \rightarrow C_4H_2^+$

in the mass spectrum of fluorobenzene and the sequence $C_3H_7^+ \rightarrow C_3H_5^+ \rightarrow C_3H_3^+$ in the mass spectrum of n-butane.

Although these observations cannot rule out the occurrence of decomposition reactions in which a relatively large neutral fragment is lost in a single step, it seems probable that if the neutral fragment is not a well-known stable molecule or radical, the product ion will be formed by the loss of two or more neutral fragments in consecutive decomposition reactions. For example, in the mass spectrum of benzene, metastable transitions can be detected corresponding to the formation of practically all fragment ions from $C_6H_8^+$ in the field-free region between the source and electrostatic analyser.

Most of these are almost certainly to be ascribed to ions formed by stepwise decomposition of $C_6H_6^+$ ions.

Metastable transitions arise from the decomposition of ions possessing relatively small amounts of internal energy such that the rate constant lies in the range 10^6 — 10^9 sec.⁻¹ The observations reported above indicate that sufficient energy may nevertheless be carried over to the product ion which can in turn undergo decomposition at a similar rate. The weakness of the signals precludes any quantitative study of the effect of varying such parameters as electron energy or source of the ion undergoing the initial decomposition.

(Received, April 1st, 1966; Com. 210.)

¹ K. R. Jennings, *J. Chem. Phys.*, 1965, **43**, 4176.