Metastable-ion Characteristics: Characterization of Isomeric Molecules

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RECENT communications[1] from this laboratory have demonstrated the use of metastable-ion characteristics in distinguishing between isomeric structures for fragment ions of the same elemental composition in mass spectra. We now report that it is possible to identify isomeric molecules by the relative abundance of their major metastable ions; there are often striking differences between the metastable spectra ("metastable maps"[2,3]) of compounds whose mass spectra are similar. Additionally, the measurement of metastable-ion characteristics adds a new dimension to mass spectrometric analysis when used in conjunction with the normal ion-abundance information. For example, in a complex mixture of saturated hydrocarbons it would be impossible to determine the amounts of the five hexane isomers from a conventional mass spectrum because of the overlap of their cracking patterns; however, the metastable spectra of these compounds show five unique metastable transitions involving $C_6H_{14}^{\cdot+}$ as the precursor ion which would make possible quantitative determination of these isomers.†

The metastable ions measured were those formed in the field-free region between the ion source and the electrostatic analyzer of a CEC 21-110B double-focussing mass spectrometer.[2,3] This technique has several advantages when compared to the conventional observation of metastable ions: it is possible to identify unequivocally the transition giving rise to the metastable ion; sensitivity for detection of metastables has increased *ca.* 50 times; and the possibility of a normally focused ion interfering with a metastable ion is removed. The present results were obtained by tuning to the mass of a normally-focused daughter ion and scanning the accelerating voltage while keeping the fields on the electric and magnetic sectors (and thus the mass scale) constant.[3]

The Table gives the abundances of the major metastable ions relative to the abundances of the normal $C_6H_{14}^{\cdot+}$ ions in the mass spectra of the five isomeric hexanes. There is a wide variation between isomers in the abundance of the metastable ion formed in a given transition; for each isomer except n-hexane there is a metastable transition for which that isomer yields the largest peak. For example, 2,3-dimethylbutane gives a distinctively abundant metastable ion for the transition $86^{\cdot+} \rightarrow 71^{+}$, and 2,2-dimethylbutane can be readily identified from the unusually high abundance of the metastable ion from the $71^{+} \rightarrow 43^{+}$ transition. Note also that some of the compounds give no detectable peak for particular

TABLE

Prominent metastable transitions in the mass spectra of isomeric hydrocarbons

	Abundance[a]				
Transition	n-Hexane	2-Methyl-pentane	3-Methyl-pentane	2,3-Dimethyl-butane	2,2-Dimethyl-butane
$86^{\cdot+} \rightarrow 71^{+}$	0·5	2·8	0·3	26·0	4·0
$86^{\cdot+} \rightarrow 70^{\cdot+}$	0·5	4·0	0·2	2·3	
$86^{\cdot+} \rightarrow 57^{+}$	3·1	22·0			
$86^{\cdot+} \rightarrow 56^{\cdot+}$	11·0	12·0	29·0	0·2	13·0
$85^{+} \rightarrow 57^{+}$			1·7[b]	1·3[b]	25·0[b]
$86^{\cdot+} \rightarrow 42^{\cdot+}$	0·5	0·1	0·2	14·0	
$85^{+} \rightarrow 43^{+}$	0·3[b]	0·8[b]	1·0[b]	1·4[b]	17·0[b]
$71^{+} \rightarrow 43^{+}$	3·8	45·0	17·0	43·0	3200·0
$70^{\cdot+} \rightarrow 42^{\cdot+}$	0·1	0·8	0·5	0·8	36·0
$43^{+} \rightarrow 41^{+}$	2·0[c]	1·3[c]	1·6[c]	1·4[c]	0·8[c]
	n-Octane	2,2,4-Trimethyl-pentane			
$114^{\cdot+} \rightarrow 99^{+}$	0·2	2·2			
$114^{\cdot+} \rightarrow 98^{\cdot+}$	0·1	14·0			
$114^{\cdot+} \rightarrow 85^{+}$	52·0	20·0			
$114^{\cdot+} \rightarrow 84^{\cdot+}$	19·0	6·5			
$114^{\cdot+} \rightarrow 71^{+}$	2·5				
$114^{\cdot+} \rightarrow 70^{\cdot+}$	5·3	1·0			
$113^{+} \rightarrow 71^{+}$		4·3[b]			
$113^{+} \rightarrow 57^{+}$	0·8[b]	14·0[b]			
$114^{\cdot+} \rightarrow 56^{\cdot+}$	2·2	46·0			
	Hex-1-ene	Hex-2-ene			
$84^{\cdot+} \rightarrow 69^{+}$	4·9	1·5			
$84^{\cdot+} \rightarrow 68^{\cdot+}$	0·1				
$84^{\cdot+} \rightarrow 56^{\cdot+}$	16·0	2·0			
$83^{+} \rightarrow 55^{+}$	1·3	1·9			

[a] Relative to the molecular ion as 100 units, except for the $43^{+} \rightarrow 41^{+}$ transition.
[b] Confirmed by the simultaneous addition of n-decane and comparison with its known transition (*c* ., ref. 3).
[c] Abundance relative to the C_3H_7 ion as 100 units.

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† G. G. Wanless and G. A. Glock jun., (*Analyt. Chem.*, 1967, **39**, 2) have reported that metastable ions formed by field ionization mass spectrometry may be used similarly in the analysis of mixtures. However, in field-ion mass spectra the low abundance of normal fragment ions and the low precision possible with present instrumentation make quantitative determination of even simple mixtures extremely difficult to do by conventional techniques.

metastable transitions; this in itself is sufficient to distinguish between several of the isomers. In general the most intense metastable ions correspond qualitatively to the abundant normal fragment ions in the mass spectrum.

Similarly there is a wide variation in metastable ion abundances in the spectra of pairs of isomeric octanes and hexanes (Table). For example, the abundances of the $84^{\cdot +} \rightarrow 56^{\cdot +}$ transition of the hexenes differ by a larger factor than that for any of the normal fragment ions in their mass spectra. The similarities in metastable fragmentation pathways of the corresponding hexane and octane isomers suggest that metastable maps can be used for structure determination.

In contrast, 11 metastable transitions studied for the isomeric *o*- and *p*-xylenes showed very similar abundances, suggesting that the molecular ions may rearrange to a common structure before decomposition.[4]

The normal mass spectra of n- and iso-propyl bromide are quite similar, exhibiting $[C_3H_7^+]/[C_3H_7{}^{79}Br^{\cdot +}]$ of 415 and 580%, respectively, but the corresponding metastable transitions differ strikingly in the opposite direction, exhibiting abundances of 26 and 1·6% respectively.‡

There is considerable evidence that $C_3H_7^+$ ions from n-C_3H_7Y compounds are isomerized.[4,5] The metastable ion characteristics[1] of these ions support this; abundances for the $C_3H_7^+ \rightarrow C_3H_5^+$ transition relative to $[C_3H_7^+]$ are 2·0 and 1·9, respectively, for 1- and 2-bromopropane.§ However, the data shows small but significant differences in metastable abundances of the $C_3H_7^+$ ions from the hexanes (see Table); these appear to correlate qualitatively with the abundance of the $71^+ \rightarrow 43^+$ transitions. A possible explanation is that the $C_3H_7^+$ ions from the propyl bromides and n-hexane have predominantly the iso-structure, while for other hexane isomers a substantial proportion (for 2,2-dimethylbutane, the major portion) of the $C_3H_7^+$ ions have the protonated cyclopropane structure.[4]

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‡ The transition $C_3H_7{}^{79}Br^{\cdot +} \rightarrow C_3H_7^+$ is incompletely resolved from the transition $C_3H_7{}^{81}Br^{\cdot +} \rightarrow C_3H_7^+$. The abundances of the metastable peak at *m/e* 15·2 corresponding to $C_3H_7{}^{79}Br^{\cdot +} \rightarrow C_3H_7^+$ measured on a Hitachi RMU-6D single-focusing mass spectrometer are 0·33 and 0·08%, respectively. The appearance potential of the normal and metastable propyl ions is closely similar, and their abundance remains constant to just above the appearance potential of the $C_3H_7^+$ ion.

§ The only other observed $C_3H_7^+$ decomposition, $C_3H_7^+ \rightarrow C_2H_3^+$, which is known to be collision induced, (*cf.*, H. M. Rosenstock and C. E. Melton, *J. Chem. Phys.*, 1957, **26**, 314) proved to be too weak to give reliable measurements.

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[3] T. W. Shannon, T. E. Mead, C. G. Warner, and F. W. McLafferty, *Analyt. Chem.*, 1967, in the press.

[4] H. M. Grubb and S. Meyerson "Mass Spectrometry of Organic Ions", ed. F. W. McLafferty, Academic Press, New York, 1963, ch. 10.

[5] F. H. Field and J. L. Franklin, *J. Chem. Phys.*, 1954, **22**, 1895; D. P. Stevenson, *Trans. Faraday Soc.*, 1953, **49**, 867.