Organic and Biological Chemistry

The Variation of Metastable Ion Abundance Ratios with Internal Energy in the Mass Spectrometer

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Abstract: The ratio of metastable abundances for two competing reactions at any given internal energy has been shown to be a function of the internal energy of the ions generating the metastables. Therefore ions with the same structure but different internal energies can give rise to significantly different metastable abundance ratios. It follows that ions decomposing in the first field-free region can also give rise to metastable abundance ratios significantly different from those decomposing in the second field-free region. This conclusion is supported by experimental data. Theoretically, the width of the energy band giving rise to metastables varies with the frequency factor of the reaction, from about 0.2 eV for reactions with high frequency factors ($\sim 10^{13}$) to about 4 eV for reactions with low frequency factors ($\sim 10^8$), but the latter situation appears unlikely to be realized in practice.

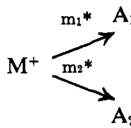
The use of "metastable characteristics"[1,2] as a tool for structural assignment of ions giving rise to common metastables has been applied to various ions in the mass spectrometer. The conclusion drawn from these studies was that "the ratio of abundances of different metastable ions from the same precursor ion can be used to characterize the structure of that ion *independent of its energy*."[2a] Ions with significantly different ratios of metastable abundances were therefore thought to have different structures.[2b,2c]

We now report evidence (both theoretical and experimental) to show that the ratio of metastable abundances of ions of a given structure is in general *dependent* on the internal energy of the ions giving rise to the metastables; small differences in metastable abundance ratios therefore do not necessarily imply ions of different structures. In the following discussion, we attempt to give guidelines to the variation in metastable ion abundance ratio which might occur due to the decomposition of ions of a given structure merely because the ions possess different internal energy distributions (*e.g.*, because they are generated from different precursors under a given set of experimental conditions). There are two possible approaches to the problem. One is to look at the variation in metastable ion abundance ratio which might be observed from ions of the same structure but varied energy distributions, using a specific instrument and a specific set of operating parameters. The other is to examine the variation which might be observed as the energy distribution giving rise to metastable transitions from a given ion is slightly changed by sampling metastable ions at different electron voltages, or in different field-free regions, or at different accelerating voltages. We have adopted the latter approach and from the variations observed infer that variations are possible under the former conditions. Our experiments do not prove that in prior work, where different ion structures have been inferred on the basis of small differences in the abundance ratios of competing metastable transitions, the conclusions are wrong. They merely emphasize that small differences in ratios are also conceivable from ions of the same structure, and that such results should therefore be interpreted with caution.

Discussion

Recent applications of the principles of the quasi-equilibrium theory[3] to the calculation of the mass spectra of various aromatic compounds[4,5] suggested that the approach might be useful in investigating the fragmentation of ions in the field-free regions of the mass spectrometer.

For an ion M^+ undergoing the reactions



the fractional abundance of the metastable ion for the first process, derived from ions with internal energy between E and $E + \delta E$, is given by $[m_1^*]_E$

$$[m_1^*]_E = f(E)\frac{k_1}{k_1 + k_2} \times \{\exp(-(k_1 + k_2)t_1) - \exp(-(k_1 + k_2)t_2)\}\delta E \quad (1)$$

where $f(E)$ is the fraction of ions having internal energy E to $E + \delta E$, δE is a small increase in E, k_1 and k_2 are the rate constants of the reactions at an energy E, and t_1 and t_2 are the times required to enter and leave the field-free region, respectively.

The total metastable ion intensity for the first reaction, designated $[m_1^*]$, is then given by eq 2, where E_1° is the activation energy for the reaction $M^+ \rightarrow A_1^+$, and E_{max} is the maximum internal energy of the ions.

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(1) T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 5021 (1966).

(2) (a) F. W. McLafferty and W. T. Pike, *ibid.*, **89**, 5951 (1967); (b) F. W. McLafferty and W. T. Pike, *ibid.*, **89**, 5953 (1967); (c) W. T. Pike and F. W. McLafferty, *ibid.*, **89**, 5954 (1967).

(3) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U.S.*, **38**, 667 (1952).

(4) I. Howe and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 7137 (1969).

(5) (a) A. N. H. Yeo and D. H. Williams, *ibid.*, **92**, 3984 (1970); (b) A. N. H. Yeo and D. H. Williams, *Org. Mass Spectrom.*, in press.

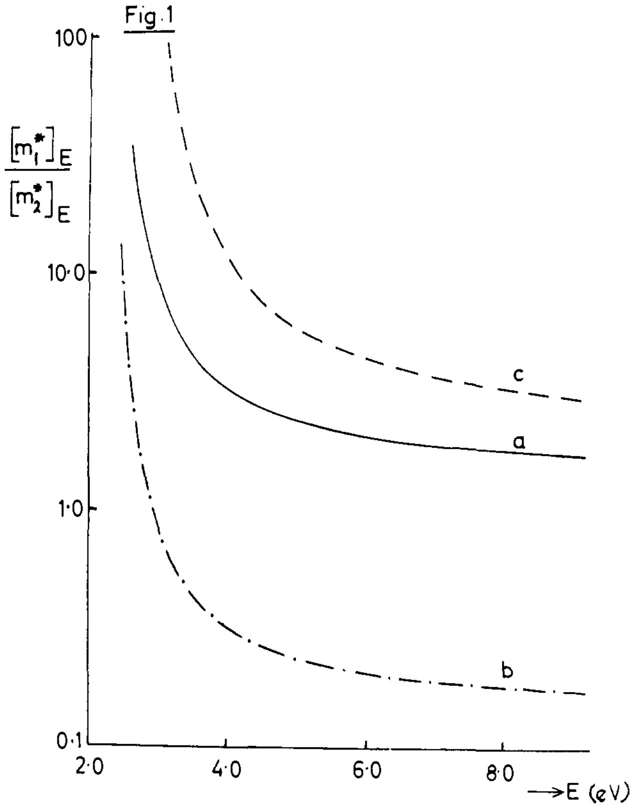


Figure 1. The variation of metastable ratio $[m_1^*]_E/[m_2^*]_E$ as a function of internal energy E of the ions generating the metastables: (a) the parameters used for calculation are given in Table I; (b) the same parameters as in a except with $\nu_2 = 10\nu_1$; (c) the same parameters as in a except with $E_1° = 2.0$, $E_2° = 2.4$ eV.

Similar equations hold for the second metastable ion intensity.

$$[m_1^*] = \int_{E_1^\circ}^{E_{max}} f(E)\frac{k_1}{k_1 + k_2}\{\exp(-(k_1 + k_2)t_1) - \exp(-(k_1 + k_2)t_2)\}dE \quad (2)$$

The rate constant k_i for a given reaction is given by eq 3 where ν_i is the frequency factor for the reaction, s is

$$k_i = \nu_i\left(\frac{E - E_i^\circ}{E}\right)^{(s-1)x} \quad (3)$$

the number of oscillators in M^+, and x is a factor ($^1/_5$ at the threshold, rising linearly with energy to $^1/_2$ at 10 eV in excess of the activation energy) used to correct for the approximations invoked in the derivation of the original equation. It is emphasized that eq 3 is strictly empirical, but the k *vs.* E curves that result seem entirely realistic since they give in many cases calculated metastable abundances[5a] and kinetic shifts which are in reasonable accord with experiment. Equation 3 therefore seems sufficiently precise for the semiquantitative discussion which follows.

For a compound for which the parameters given in Table I are applicable, the $[m_1^*]_E/[m_2^*]_E$ ratio is calculated as a function of the internal energy E (Figure 1, curve a).

When $\nu_1 = \nu_2$, then $k_1/k_2 = ((E - E_1°)/(E - E_2°))^{(s-1)x}$ and it is apparent that $[m_1^*]_E/[m_2^*]_E$ is independent of the value of the frequency factors. The shape of the $[m_1^*]_E/[m_2^*]_E$ *vs.* E curve is not surprising because $k_1 \gg k_2$ near the threshold (low E), but at higher energies, the log k *vs.* E curves converge and k_2 approaches the value of k_1 (Figure 2). Variation of the parameters $E°$ and ν would give other similar curves (*e.g.*, Figure 1, curve b, for $\nu_2 = 10\nu_1$ and $E_1° = 2.0$ eV, $E_2° = 2.2$ eV; and Figure 1, curve c, $\nu_1 = \nu_2$ and $E_1° = 2.0$ eV, $E_2° = 2.4$ eV). It is noteworthy that if $E_1° = E_2°$, the curve becomes a straight line with $[m_1^*]_E/[m_2^*]_E = \nu_1/\nu_2$ for all the values of the internal energy (this conclusion is correct only to the extent that the approximate equation for k_i is valid).

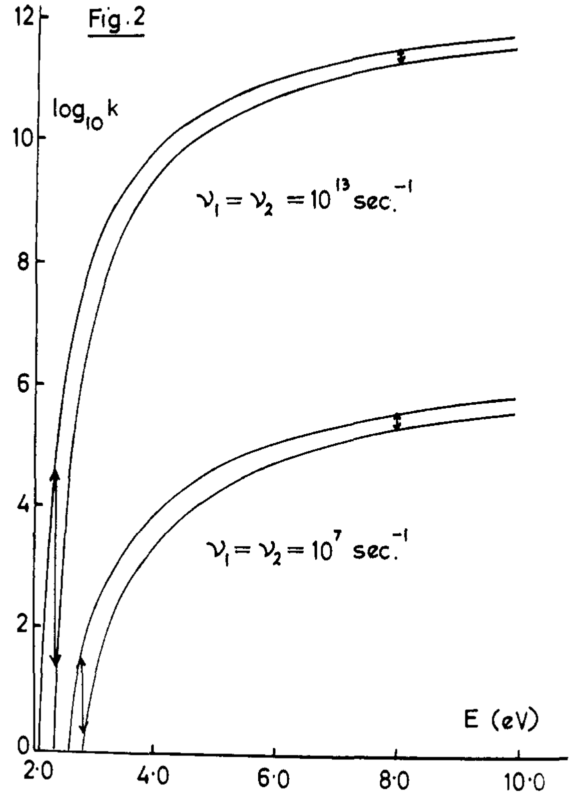


Figure 2. The variation of the rate of reactions (k_1 and k_2, sec^{-1}) as a function of E; parameters for calculation, with the exception of the frequency factors, are given in Table I.

Table I. Parameters Used in the Calculations of Metastable Ratios

Parameter	Value
N^a	20
M^b	2
IP^c	10 eV
t_1^d	9.8 μsec
t_2^d	14.5 μsec
$E_1°\,^e$	2.0 eV
$E_2°\,^e$	2.2 eV
ν_1^f	1 × 10^{13} sec^{-1}
ν_2^f	1 × 10^{13} sec^{-1}

[a] N, number of atoms in the molecule. [b] M, number of decomposition pathways of the molecular ion. [c] IP, ionization potential of compound. [d] t_1 and t_2, time estimated for a molecular ion of m/e 120 to reach and leave the second field-free region of the AEI MS9 mass spectrometer. [e] $E_1°$ and $E_2°$, activation energies of the first and second reactions. [f] ν_1 and ν_2, frequency factors of the first and second reactions.

From Figure 1, three qualitative generalizations can be made. First, $[m_1^*]_E/[m_2^*]_E$ tends to ν_1/ν_2 at high values of E; yet it must not be assumed that in practice metastable ion abundance ratios could under certain circumstances reflect the relative values of the frequency factors rather than the relative activation energies, for reasons which are outlined subsequently. Second, at low values of E, a slight increase in the difference in activation energies ($E_1^\circ - E_2^\circ$) results in a large increase in the $[m_1^*]_E/[m_2^*]_E$ ratio (*cf.* Figures 1a and 1c). This is why, in general, competing reactions which both give rise to metastable transitions usually have very similar appearance potentials.[6] Third, for two competing reactions which involve single bond cleavages with large frequency factors (where the metastables are formed from ions with energy just above the threshold, *vide infra*), the ratio of the metastable abundances will often be very large.

The values of $[m_1^*]_E/[m_2^*]$[7] for the hypothetical compound having the parameters given in Table I are plotted for different values of the frequency factors (Figure 3). For reactions with large frequency factors (*e.g.*, $\nu_1 = 10^{12}$ sec^{-1}), the metastables come from ions with energies just above the threshold, and the half-width of the energy band giving rise to the metastables is narrow (~0.2 eV). When the value of the frequency factors is decreased, the energy band giving rise to metastables is shifted toward higher energies so that ions that give rise to metastables have on the average much more internal energy than in the previous case (*i.e.*, an increase in the kinetic shift[8]). The half-width of the energy band is also progressively broadened with decrease in frequency factor, so that for $\nu_1 = \nu_2 = 10^7$ sec^{-1}, the half-width of the energy band is about 4.5 eV. Similar curves for $[m_2^*]_E/[m_2^*]$ are obtained.

From a consideration of Figures 1 (curve a) and 3, it would be expected that for reactions with high frequency factors, the ratios of metastable abundances $[m_1^*]/[m_2^*]$ would be relatively large given only slightly different activation energies for reaction; the reaction with the lower activation energy will have the more abundant metastable peak.

In the hypothetical case of two competing reactions both having low frequency factors (*e.g.*, ~10^8 sec^{-1}), it might be argued from a theoretical standpoint that energies some 4–6 eV in excess of threshold would be weighted in metastable decompositions (Figure 3) and that the observed metastable ratio $[m_1^*]/[m_2^*]$ could approximately reflect the relative frequency factors (*e.g.*, $E_1 < E_2$, $\nu_1 < \nu_2$, and $[m_2^*] > [m_1^*]$; see curve b in Figure 1). However, the weighting of energies 4–6 eV in excess of threshold for metastable transitions seems very unlikely to be ever realized in practice. Even if frequency factors as low as 10^7 or 10^8 sec^{-1} are appropriate for describing some reactions of a large molecule, it appears highly probable that some competing reaction having a considerably higher frequency factor (*e.g.*, 10^{11} sec^{-1}) will "come in" at an activation energy sufficiently close to the activation energy of the lower frequency factor process to at least compete, if not totally take over, at energies corresponding to most of the metastable range for the low ν process. It might be added however that there are prior examples of calculations which indicate that in two competing reactions it is possible for the reaction with higher activation energy and frequency factor to give the more abundant metastable transition (*e.g.*, the loss of CH_3, in competition with the loss of H_2, from the propane molecular ion).[9]

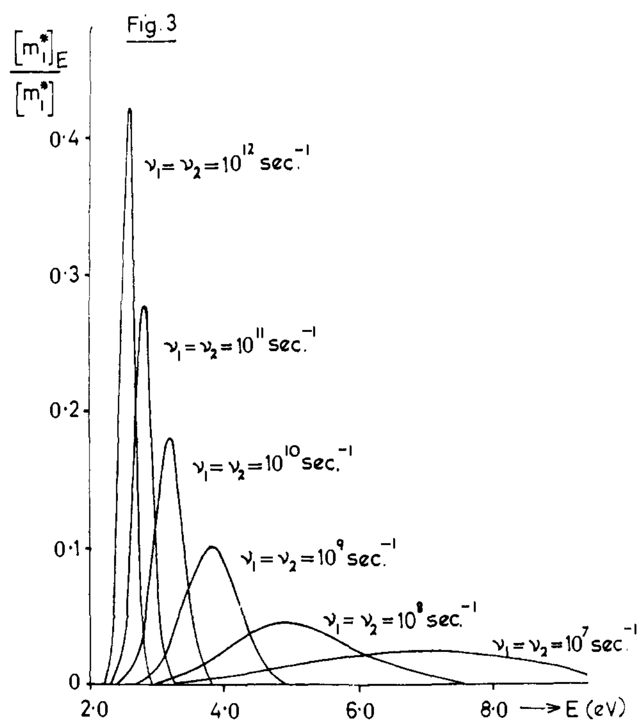


Figure 3. The variation of $[m_1^*]_E/[m_1^*]$ as a function of internal energy for different values of ν_1 (ν_2).

For reactions with high frequency factors, the metastables come from ions with low internal energy; the relevant section of the $[m_1^*]_E/[m_2^*]_E$ *vs.* E curve varies very rapidly with E so that a slight change in internal energy of the ions giving rise to metastables will result in a significant change in $[m_1^*]_E/[m_2^*]_E$ value and hence in the $[m_1^*]/[m_2^*]$ value. This contention is supported by experimental data for *n*-butyl *n*-amyl ketone in Table II.

Table II. The Variation of Metastable Ratio (First Field-Free Region) for the Loss of *n*-Butyl and *n*-Amyl Radicals from *n*-Butyl *n*-Amyl Ketone

Accelerating voltage, kV	Electron beam energy, eV	$[m^*]_{M^+-C_4H_9}/[m^*]_{M^+-C_5H_{11}}$
4	70	17.8
4	20	20.9
4	18	22.4
4	14	26.4
2	70	33.7

In the second field-free region, the loss of an *n*-amyl radical is of such low intensity that it could not be detected on our instrument in contrast to the loss of an *n*-butyl radical which gives rise to a peak at m/e 62.8.

(6) H. M. Rosenstock and M. Krauss in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 1.

(7) The ratio $[m_1^*]_E/[m_1^*]$ is the abundance of the metastable peak arising from ions with internal energies in the range E to $E + \delta E$ expressed as a fraction of the total abundance of metastables arising from ions undergoing the first reaction with internal energies over the whole energy range from E_1° to E_{max}.

(8) W. A. Chupka, *J. Chem. Phys.*, **30**, 191 (1959).

(9) M. L. Vestal, *ibid.*, **43**, 1356 (1965).

Thus, for the ions of longest lifetimes (lowest energies), the loss of an amyl radical is effectively unable to compete.

A convenient way of studying metastables derived from ions of slightly different energies is to compare the ratio of metastable intensities of competing reactions in the first and second field-free regions. Ions decomposing in the first field-free region have shorter lifetimes and hence higher internal energies than those decomposing in the second field-free region. From Figure 1, it would be expected that the $[m_1^*]/[m_2^*]$ ratio for metastables in the second field-free region would be greater than the same ratio in the first field-free region (providing $E_1° < E_2°$), *i.e.*, decrease in internal energy increases $[m_1^*]$ relative to $[m_2^*]$. This is indeed the case as seen in the calculated values obtained by reducing the values of t_1 and t_2 from 9.8 and 14.5 μsec (for the second field-free region) to 2.5 and 4.0 μsec (for the first field-free region) (Table III).[10]

Table III. Calculated Variation of Metastable Ratio with Ion Lifetime (and Internal Energy) of Decomposing Ions

$\nu_1 = \nu_2$, sec^{-1} [a]	$[m_1^*]/[m_2^*]$ 9.8–14.5 μsec[b]	2.5–4.0 μsec[c]
1×10^7	2.0	1.9
1×10^8	2.4	2.4
1×10^9	3.6	2.8
1×10^{10}	6.4	4.5
1×10^{11}	14	8.7
1×10^{12}	43	22
1×10^{13}	210	79

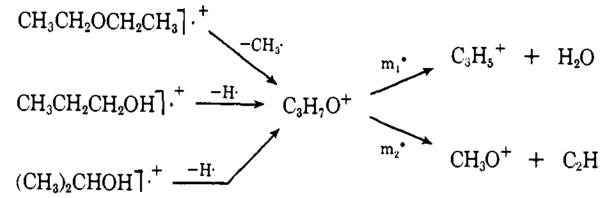
[a] All calculations refer to $E_1° = 2.0$ eV and $E_2° = 2.2$ eV, with $\nu_1 = \nu_2$ and varied as shown in the table. [b] Time estimated for decomposition in the second field-free region. [c] Time estimated for decomposition in the first field-free region.

It is therefore not surprising that metastable ratios measured on different instruments under different conditions (*e.g.*, repeller potential, accelerating voltage, and source alignment) can be significantly different (*vide infra*).

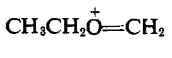
For reactions with low frequency factors, a slight shift in the ion lifetimes sampled may not result in a significant difference in the metastable ratio since the energy band giving rise to metastables is broad (Figure 3), and $[m_1^*]_E/[m_2^*]_E$ changes only slightly with change in E when energies considerably in excess of threshold are weighted (Figure 1). Calculations show that this is indeed the case (*e.g.*, $\nu < 10^9$ in Table III).

If, however, the frequency factors are large, and there is a small shift in the ion lifetimes sampled, then for reactions of slightly different activation energies, it is probable that the metastable ratio will be altered (see Table III).[11] The difference would be the result of different weightings of the $[m_1^*]_E/[m_2^*]_E$ curve (Figure 1) with the relevant section of the energy distribution curve (Figure 3).

To show that the ratio of metastable abundances from the same precursor ion is dependent on its energy, the $[m_1^*]/[m_2^*]$ ratio in the first and in the second field-free regions at various electron voltages and accelerating voltages for the reactions

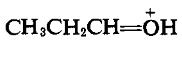


were determined (Table IV). The structures of the ions generated *initially* from diethyl ether, *n*-propyl alcohol, and isopropyl alcohol can be represented by I, II, and III, respectively. In the case of diethyl ether



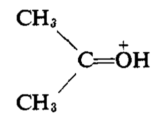
$CH_3CH_2\overset{+}{O}{=}CH_2$

I



$CH_3CH_2CH{=}\overset{+}{O}H$

II



III

and *n*-propyl alcohol, the $[m_1^*]/[m_2^*]$ ratio showed a large dependence on the energy of the precursor ion $C_3H_7O^+$ (Table IV). The difference between the ratios of the metastables formed in the first field-free regions and those formed in the second field-free region is striking (for diethyl ether as precursor, 2.42 and 29.6,

Table IV. The Variation of the Metastable Ratios for the Loss of H_2O and C_2H_4 from $C_3H_7O^+$ Ions Generated from Diethyl Ether, *n*-Propyl Alcohol, and Isopropyl Alcohol[a]

	$[m^*]_{(C_3H_7O^+ - H_2O)}/[m^*]_{(C_3H_7O^+ - C_2H_4)}$ Diethyl ether	*n*-Propyl alcohol	Isopropyl alcohol
$^1m^*$			
4 kV, 70 eV	2.42	1.91	0.34
4 kV, 20 eV	2.94		
4 kV, 16 eV	3.24		0.52
4 kV, 14 eV	3.94	3.26	0.55
3 kV, 70 eV	2.54		
2 kV, 70 eV	2.56		
1 kV, 70 eV	3.23		
$^2m^*$			
8 kV, 70 eV	25.4	16.0	0.67
8 kV, 20 eV	26.4		
8 kV, 18 eV	26.8		
8 kV, 16 eV	27.8		
8 kV, 14 eV	28.1		
6 kV, 70 eV	27.5		
4 kV, 70 eV	29.6	18.0	0.55
2 kV, 70 eV	35.4		

[a] In the table $^1m^*$ and $^2m^*$ refer to ratios observed in the first and second field-free regions, respectively.

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(10) The values of t_1 and t_2 are estimated by consideration of the geometry of the AEI MS9 mass spectrometer; see, for example, J. H Beynon, J. A. Hopkinson, and G. R. Lester, *Int. J. Mass Spectrom. Ion Phys.*, 1, 343 (1968).

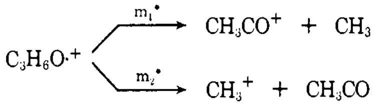
(11) A referee has commented that these arguments seem to imply that reactions with low frequency factors are less susceptible to change in metastable ratio than those with high frequency factors, and one might feel that the reverse would be the case. He points out that a slight shift of ion lifetimes sampled in the former case corresponds to a larger shift in internal energy than in the latter case, and it is more probable to get an energy distribution altered over a large energy range than a narrow one. While this is true, for reactions of high frequency factor only energies very near to threshold are weighted in metastable transitions (Figure 3) and at these energies k_1/k_2 varies very rapidly with energy (Figure 2). Hence $[m_1^*]_E/[m_2^*]_E$ varies very rapidly with energy at energies near threshold (Figure 1) and this more than offsets the effect pointed out by the referee. However, it should be added that if one is investigating the variation of $[m_1^*]/[m_2^*]$ with electron beam energy, a change in beam energy would not normally be expected to significantly change the weighting of a narrow and low band of energies near to threshold. A higher and broader band of energies would be more likely to change significantly, and under these circumstances the $[m_1^*]/[m_2^*]$ ratio would be more susceptible to change if the reactions in question had low frequency factors.

respectively, at 4 kV, 70 eV). Variations in electron beam energy and accelerating voltage also result in significant changes in the metastable ratios. The data clearly show that a change from higher energies to lower energies by (i) reducing the electron beam energy; (ii) looking at ions of longer lifetime (second field-free region metastables); or (iii) reducing the accelerating voltage, results in an increased ratio of $[m_1^*]/[m_2^*]$.[12] This shows that the activation energy for the loss of water from the $C_3H_7O^+$ ion is lower than that for the loss of ethylene. It should be noted that ions from the same precursor can give rise to metastable ratios that vary by a factor of about 15, simply by slight variation of the energies of the ions sampled. It is therefore apparent that the metastable ratios are *dependent* on the energy of the ions, and cannot reliably be used to characterize structures of ions without other considerations, *i.e.*, differences in metastable ratios up to one order of magnitude do not necessarily imply different structures of the precursor ions.[13]

The $C_3H_7O^+$ ion derived from *n*-propyl alcohol by loss of a hydrogen radical represented formally as II gives metastable ratios which are significantly different from those for the $C_3H_7O^+$ ion from diethyl ether under identical instrument conditions (Table IV). Yet the trend in the variation of metastable ratios with lifetime and energy is similar. It seems probable therefore that the $C_3H_7O^+$ ions from both diethyl ether and *n*-propyl alcohol (which give rise to metastables in the first and second field-free regions) have isomerized to a common structure (or mixture of structures) with the $C_3H_7O^+$ ions giving rise to metastable transitions from *n*-propyl alcohol having, on the whole, more internal energy than those from diethyl ether.

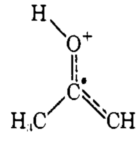
For comparison, the metastable ratios for the two processes for $C_3H_7O^+$ ions generated from isopropyl alcohol are listed (Table IV). The ratios are very different from the two previous cases and it may be concluded that either the structure of the ion is different, or that common ions are still involved in the decompositions but with grossly different energy distributions giving rise to metastable transitions.

To emphasize the point that significant differences in $[m_1^*]/[m_2^*]$ ratios do not necessarily imply different structures, the results of the studies of the structures of $C_3H_6O\cdot^+$ ions from different precursors by McLafferty[2b] and Djerassi[14] are compared. The $[m_1^*]/[m_2^*]$ ratios for acetone, $C_3H_6O\cdot^+$ ions formed *via* a McLafferty rearrangement from 2-alkanones, and $C_3H_6O\cdot^+$ ions formed *via* a double McLafferty rearrangement from 4- and 5-alkanones for the reactions

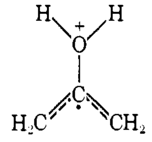


$$C_3H_6O\cdot^+ \begin{cases} \xrightarrow{m_1^*} CH_3CO^+ + CH_3 \\ \xrightarrow{m_2^*} CH_3^+ + CH_3CO \end{cases}$$

are approximately 23, 280, and 110, respectively.[2b] It was therefore concluded that a substantial part of the $C_3H_6O\cdot^+$ ions generated from 2-alkanones *via* a single McLafferty rearrangement was different from those generated from 4- and 5-alkanones *via* a double McLafferty rearrangement. Structures IV and V were assigned to these two classes of ions, respectively.



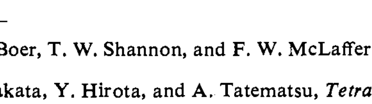
IV



V

However, using the techniques of ion cyclotron resonance and double pulse resonance, combined with deuterium labeling, Djerassi, *et al.*,[14] have shown that the reactions of the ions formed *via* the two different pathways are identical, and conclude that at least a substantial portion of the ions formed *via* the double McLafferty rearrangement must correspond to the ions formed *via* the single McLafferty rearrangement. The suggestion[15] that structure V could be the precursor of structure IV was also shown to be invalid. In fact, the metastable ratio data are perfectly consistent with identity of structure for ions formed *via* a single and double McLafferty rearrangement, in the light of the preceding discussion.

The structure of the $C_4H_4O\cdot^+$ ions generated from 2-pyrone and 4-pyrone *via* loss of CO has been studied by various groups.[16–19] Nakata[16] suggested that the structure of the $M^+ - CO$ ions from 2-pyrones is identical with the molecular ions of corresponding furans. This suggestion was challenged by Pirkle.[17] However, the evidence presented by Pirkle from deuterated 2-pyrones in favor of a non-furan-like structure was based upon invalid assumptions, as pointed out by Brown and Green.[18] In a further study, Pirkle and Dines[19] studied the ratios of metastable transitions for loss of C_2HD (m_1^*) and C_2H_2 (m_2^*) from the $M^+ - CO$ ions generated from *3-d*₁-, *4-d*₁-, *5-d*₁-, and *6-d*₁-2-pyrones. The observed ratios $[m_1^*]/[m_2^*]$ were 1.3, >5, 1.2, and ~0, respectively, conclusively proving that the $M^+ - CO$ ion from 2-pyrone does not in large measure expel acetylene in metastable transitions from an ionized furan structure and further, that the $M^+ - CO$ ion which expels acetylene cannot have passed through an ionized furan structure. However, these studies still leave open the question as to whether the furan molecular ion rearranges to another structure which is the same structure as that attained *via* loss of CO from 2-pyrone, *i.e.*, decomposition from common $C_4H_4O\cdot^+$, nonfuran structures is not precluded. The metastable ratios $[m_1^*]/[m_2^*]$ for the reactions



$$C_4H_4O\cdot^+ \begin{cases} \xrightarrow{m_1^*} C_3H_4\cdot^+ + CO \\ \xrightarrow{m_2^*} C_2H_2O\cdot^+ + C_2H_4 \end{cases}$$

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[12] In general, the average internal energies of the ions giving rise to metastables decrease in the following orders: 70 eV > 20 eV > 18 eV > 16 eV > 14 eV; $^1m^* > {}^2m^*$; 8 kV > 6 kV > 4 kV > 2 kV > 1 kV.

[13] It must be admitted that such a guideline is, at best, crude. Thus the relatively large changes in metastable abundance ratios between the first and second field-free region (Table IV) relate only very indirectly to the changes which might occur due to different energy distributions for a fixed set of operating conditions and a given field-free region. In the latter case, the changes in ratio which are implied might well be considerably smaller.

[14] (a) J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **91**, 2069 (1969); (b) G. Eadon, J. Diekman, and C. Djerassi, *ibid.*, **91**, 3986 (1969).

[15] F. P. Boer, T. W. Shannon, and F. W. McLafferty, *ibid.*, **90**, 7239 (1968).

[16] H. Nakata, Y. Hirota, and A. Tatematsu, *Tetrahedron Lett.*, 123 (1965).

[17] W. H. Pirkle, *J. Amer. Chem. Soc.*, **87**, 3022 (1965).

[18] P. Brown and M. M. Green, *J. Org. Chem.*, **32**, 1681 (1967).

[19] W. H. Pirkle and M. Dines, *J. Amer. Chem. Soc.*, **90**, 2318 (1968).

were found to be 8.4, 3.7, and 2.3 for furan, 2-pyrone, and 4-pyrone, respectively.[2c] From this, it was concluded that a substantial part of the $C_4H_4O\cdot^+$ ions from 2-pyrone and 4-pyrone must not correspond in structure to those ions generated from furan.

By changes in instrumental conditions, which can affect the weighting of the internal energies of the ions giving rise to metastables, the $[m_1^*]/[m_2^*]$ ratio for furan was varied from 3.8 to 9.1 (Table V). This again indicates that the metastable ratio can be dependent on the internal energy of the ions. The ratios for $C_4H_4O\cdot^+$ ions from 2-pyrone and 4-pyrone are both lower than those from furan for any given set of instrumental conditions. From a consideration of the values of the metastable ratios, and the increase in these ratios with decrease in internal energy of the ions generated from furan by direct ionization, it can be concluded that the decomposing $C_4H_4O\cdot^+$ ions from 2-pyrone and 4-pyrone may have the same structure as those *from* furan (but *not* an ionized furan structure), but in terms of the energies weighted in producing metastable transitions, they have a higher mean internal energy than the ions from furan. The $[m_1^*]/[C_4H_4O\cdot^+]$ and $[m_2^*]/[C_4H_4O\cdot^+]$ data of McLafferty (Table VI) are consistent with this conclusion since it has been shown[20] that for the reaction

$$M^+ \xrightarrow{m^*} A^+$$

the $[m]^*/[M^+]$ and $[A^+]/[M^+]$ ratios will normally increase with increase in internal energy of the M^+ ions, *i.e.*, ions with greater internal energy decompose to a greater extent.

Table V. The Variation of the Metastable Ratio for the Loss of CO and C_2H_2 from $C_4H_4O\cdot^+$ Generated from Furan, 2-Pyrone, and 4-Pyrone

	$[m^*]_{(C_4H_4O\cdot^+-CO)}/[m^*]_{(C_4H_4O\cdot^+-C_2H_2)}$		
	Furan	2-Pyrone	4-Pyrone
$^1m^*$			
4 kV, 70 eV	3.80	2.60	2.29
4 kV, 20 eV	3.81		
4 kV, 17 eV	4.06	2.90	2.25
4 kV, 14 eV	8.10		
$^2m^*$			
8 kV, 70 eV	5.27	3.80	2.50
8 kV, 14 eV	9.14	4.30	4.13
4 kV, 70 eV	6.02	3.90	2.78

Thus, the metastable data (Tables V and VI) appear to be consistent either with the conclusions mentioned here, or with those drawn earlier,[2c] and do not appear to settle the problem unambiguously.

Table VI. Metastable Ion/Parent Ion Ratios for CO and C_2H_2 Loss from $C_4H_4O\cdot^+$ Ions Generated from Different Precursors

	Furan	2-Pyrone	4-Pyrone
$[m_1^*]/[C_4H_4O\cdot^+]$[a]	2.0×10^{-3}	1.7×10^{-2}	1.3×10^{-2}
$[m_2^*]/[C_4H_4O\cdot^+]$[a]	2.4×10^{-4}	4.6×10^{-3}	5.7×10^{-3}

[a] $[m_1^*]$ and $[m_2^*]$ are the concentration of the metastables for loss of CO and C_2H_2, respectively, from $C_4H_4O\cdot^+$.[2c]

In a recent paper, Occolowitz[21] has applied a different approach to the question of the validity of metastable characteristics for determination of ionic structures. He concluded that if mettasables come from ions of different states (different structurally or in isolated electronic states), the metastable ratios will in general be different (second model[21]). For metastables coming from a given structure (first model[21]), he showed that the metastable ratios would be independent of the origin of the precursor ion only if the activation energies of the reactions giving rise to metastables are equal (*vide supra*). However, assuming that the rate of formation of the precursor ions is generally much greater than the sum of the rates for their decomposition in metastable transitions, and that the energy distribution is approximately constant over the relatively narrow range of E that is significant, he concluded that the metastable abundance probe will return a nearly constant abundance ratio independent of the origin of the precursor ion.

Our results show that the above assumptions of Occolowitz do not necessarily hold in general so that significantly different metastable ratios do not necessarily imply different structures of the ions. Consideration of variation of the metastable ratio with internal energy by varying the lifetimes of the ions and the electron beam energy should be fully taken into account before ionic structures are assigned.

Conclusion

The present paper outlines the variations in relative metastable ion abundances which are theoretically possible, and illustrates that experimental variations are observed. We emphasize that reactions with frequency factors in the range 10^6–10^9 sec^{-1} are probably only rarely encountered, and that frequency factors in the range 10^{10}–10^{14} sec^{-1} will be more usual. We do not wish to question therefore the useful generalizations that the energy bands generating metastable ions will normally be narrow, and that the lower activation energy process will normally give the more abundant metastable peak. Yet we do wish to emphasize that relatively small changes in the ratio of metastable ion abundances (say, a factor up to five) of two competing processes does not constitute reliable evidence of different structures. Rather, the occurrence of two (or preferably more) identical competing decompositions in the same, or similar, ratios from the two precursors is very good evidence that the two precursors are decomposing from the same structures.

Experimental Section

All mass spectral data were obtained on an AEI MS9 double focussing mass spectrometer. First field-free region metastables ($^1m^*$) were obtained using the metastable refocussing technique.[22] All the compounds studied were commercially available except for 2-pyrone[23] and 4-pyrone which were prepared by the decarboxylation of chelidonic acid.[24]

Calculations were made on a Titan (prototype Atlas 2) computer, University Mathematical Laboratory, Cambridge.

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[23] We thank Dr. M. S. Baird for a generous gift of 2-pyrone.

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