Metastable Ion Intensities and the Comparison of Ionic Structure

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Abstract: The theoretical basis for comparing the structure of reacting ions by measurement of the relative abundance of metastable ions is examined. It is shown that except for those reactions whose rate constants are of the form $k_n(E) = K_n g(E)$ there may be some variation in the metastable abundance ratio for reactions of ions of the same structure derived from different origins. The variation can arise because of different energy distributions of precursor molecular ions and different rates of formation of fragment ions. For reactions arising from separate states (or structures) of an ion, the metastable abundance ratio determined for different origins of the ion will be markedly dependent on the energy distribution of the molecular ions. In these cases, the consideration of more than one metastable abundance ratio can indicate which reactions arise from states which are common to all origins of the reacting ion.

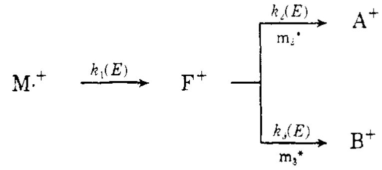
Because of the great difficulty in directly determining the structure of ions in the mass spectrometer, resort has been made to indirect methods for examining ionic reactions. Prominent among these methods are the indirect measurement of ion kinetics by the determination of the relative abundances of normal[1] or metastable ions,[2] and the determination of ionic enthalpies.[3] Speculations concerning a given ionic reaction will be on the firmest grounds when deductions made from these and other probes lead to the same conclusions.

Recently McLafferty and coworkers[4] have concluded from metastable abundance determinations that a substantial part of the C_8H_6O ions in the mass spectrum of coumarin does not correspond in structure to ions of the same composition in the mass spectrum of benzofuran. However, a study of the ion energetics of these compounds indicated that those C_8H_6O ions from the two compounds which eliminate a molecule of carbon monoxide, a substantial part of the reacting C_8H_6O ions, have similar structures. Because the metastable abundance probe primarily gives information regarding the nature of reacting ions, it appears that the conclusions arrived at by these two different methods are in conflict. To appreciate better the scope and limitations of the metastable abundance probe, it was decided to derive equations for the abundance of metastable ions and, where experimentally possible, confirm conclusions made therefrom.

The observation of two metastable peaks for two reactions of an ion of given composition may arise under two different circumstances.[5] The reactions may take place from the same state of the reacting ion, or the reactions may occur from different states of the reacting ion. Reactions of the first type, which are competitive, have been observed in the mass spectra of some alkanes,[5] while reactions of the second type, which are not necessarily competitive, have been observed in the mass spectra of ethanol and benzene.[5] In the analysis which follows, equations are derived which are applicable to each case. Some of the postulates of the quasi-equilibrium theory[5,6] of mass spectra are used; *viz.*, it is assumed that the rate of reaction of an ion is a function of its internal energy and that each ion constitutes an isolated system. Further, it is assumed[6] that the rate constant for a given reaction will be increasing very rapidly with increasing internal energy for internal energies just beyond the energy of activation; *e.g.*, excess energies of several tenths of an electron volt may correspond to reaction rates of about 10^6 sec^{-1}.

First Model

Consider the system



where M·+ represents those molecular ions having internal energy E which fragment with rate constant $k_1(E)$ to give a fragment ion F$^+$ which reacts from a single state (or structure) to give the fragments A$^+$ and B$^+$. For convenience, the mass spectrometer time scale derived by Chupka[7] is used, except, to avoid mathematical complexity, only ions spending 2 µsec in the ion source are considered. Thus, for a magnetic deflection mass spectrometer ions will spend 2 µsec in the ion source, 1 µsec in the accelerating and focusing regions, and 5 µsec in the first field-free region. Also, only those ions F$^+$ which are formed in the ion source and decompose in the first field-free region will give rise to metastable peaks.

Thus the number of F$^+$ leaving the ion source is

$$\mathrm{d}F = \frac{k_1(E)}{k_2(E) + k_3(E) - k_1(E)}\{\exp[-2 \times 10^{-6}k_1(E)] - \exp[-2 \times 10^{-6}(k_2(E) + k_3(E))]\}\,\mathrm{d}N \quad (1)$$

where dN is the number of molecular ions having internal energies in the range dE. The number of dF pro-

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(1) M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 529 (1966).

(2) T. W. Shannon and F. W. McLafferty, *ibid.*, **88**, 5021 (1966).

(3) For example, see J. L. Occolowitz and G. L. White, *Aust. J. Chem.*, 21, 997 (1968).

(4) W. T. Pike and F. W. McLafferty, *J. Amer. Chem. Soc.*, **89**, 5954 (1967).

(5) 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.

(6) R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, Chapter 7.

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

ducing metastables is

$$dF_M = dF\{\exp[-1 \times 10^{-6}(k_2(E) + k_3(E))] - \exp[-6 \times 10^{-6}(k_2(E) + k_3(E))]\} \quad (2)$$

Of the ions dF_M, $k_2(E)/(k_2(E) + k_3(E))$ will give rise to the metastable peak m_2^* and $k_3(E)/(k_2(E) + k_3(E))$ will give rise to m_3^*. Substituting eq 1 into eq 2, multiplying by the appropriate fraction of ions giving rise to each metastable, and integrating over the range of molecular ion internal energies give[8]

$$\frac{[m_2^*]}{[m_3^*]} = \frac{\int_0^{E_m}\left[\frac{k_2(E)}{k_2(E) + k_3(E)}\right]f(E)\,\frac{dN}{dE}dE}{\int_0^{E_m}\left[\frac{k_3(E)}{k_2(E) + k_3(E)}\right]f(E)\,\frac{dN}{dE}dE} \quad (3)$$

where

$$f(E) = \frac{k_1(E)}{k_2(E) + k_3(E) - k_1(E)}\{\exp[-1 \times 10^{-6} \times (k_2(E) + k_3(E))] - \exp[-6 \times 10^{-6}(k_2(E) + k_3(E))]\}\{\exp[-2 \times 10^{-6}k_1(E)] - \exp[-2 \times 10^{-6}(k_2(E) + k_3(E))]\} \quad (4)$$

and E_m is the maximum internal energy of the molecular ions, *i.e.*, the difference between the ionizing electron energy and the molecular ionization potential.

Inspection of eq 3 shows that $[m_2^*]/[m_3^*]$ will be independent of the origin of F^+ if $k_2(E)$ and $k_3(E)$ can be expressed in the form

$$k_n(E) = K_n g(E) \qquad n = 2 \text{ or } 3 \quad (5)$$

Under these circumstances, the right-hand side of eq 3 reduces to K_2/K_3 and $[m_2^*]/[m_3^*]$ is independent of the rate of formation of F^+, $k_1(E)$, and the energy distribution of the molecular ions from which F^+ is formed, dN/dE. It is necessary that both reactions of F^+ have the same energy of activation for eq 5 to be applicable to each.[9]

If eq 5 is not applicable, then the ratio of $[m_2^*]/[m_3^*]$ will be nearly independent of $k_1(E)$ and dN/dE only under the following conditions. Figure 1 shows $f(E)$ plotted against log $(k_2(E) + k_3(E))$ for $k_1(E)/(k_2(E) + k_3(E))$ in the range 10–1000. From the figure, $f(E)$ will be nearly independent of $k_1(E)$ for values of $k_1(E)/(k_2(E) + k_3(E))$ which exceed approximately 100, and is significant for a range of $k_2(E) + k_3(E)$ less than 2×10^6 sec^{-1}. Because the energy of activation for the formation of F^+ must be less than that for the formation of A^+ or B^+, it is to be expected generally that $k_1(E)$ will be much greater than $k_2(E) + k_3(E)$ when this sum is less than 2×10^6 sec^{-1}. Also, it is expected that dN/dE will be approximately constant over the relatively narrow range of E for which $f(E)$ is significant. Consequently, it is to be expected that usually the metastable abundance probe will return a nearly constant abundance ratio independent of the origin of F^+, and the experimental results of McLafferty and coworkers[1] indicate that this is true for a number of systems. Equation 3 shows that two circumstances can lead to variability in the metastable abundance ratio determined for different origins, *viz.* (1) where $k_1(E)$ is not large compared to the sum of $k_2(E)$ and $k_3(E)$ in the energy range for which $f(E)$ is significant,[10] *e.g.*, where the energy of activation for the formation of F^+ is close to the energy of activation for the formation of A^+ or B^+, or where the energy rate of change of $k_1(E)$ is small compared to the energy rate of change of $k_2(E)$ or $k_3(E)$; (2) where dN/dE is varying rapidly in the significant range of $f(E)$, or where the rate constant for the fragmentation of F^+ having the lower activation energy has a slow energy rate of increase resulting in a wider energy range for a significant $f(E)$.

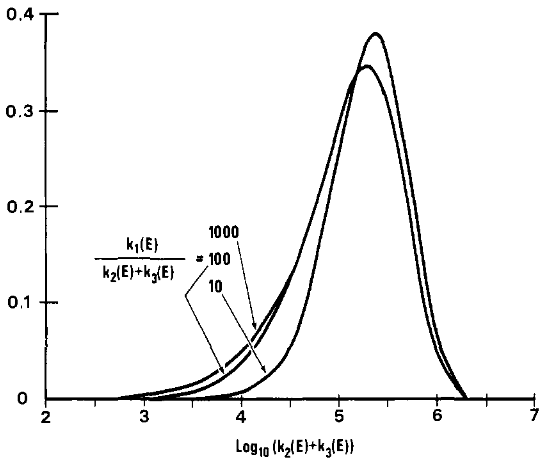
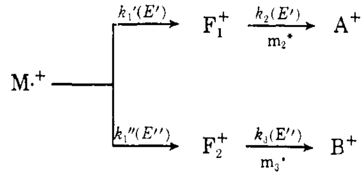


Figure 1. Variation of $f(E)$, see text, with the rate constant for fragment formation, $k_1(E)$, and rates of decomposition, $k_2(E)$ and $k_3(E)$.

Second Model

For the situation in which A^+ and B^+ arise from different states (F_1^+ and F_2^+) of a given fragment ion, consider the system



It is assumed that F_1^+ and F_2^+ are not in equilibrium and that there are two independent energy distributions for $M\cdot^+$: a distribution of internal energies represented by E' from which F_1^+ is derived, and a distribution of internal energies represented by E'' from which F_2^+ is derived.

The number of F_1^+ leaving the ion source is

$$dF_1 = \frac{k_1'(E')}{k_2(E') - k_1'(E')}\{\exp[-2 \times 10^{-6}k_1'(E')] - \exp[-2 \times 10^{-6}k_2(E')]\}\,dN \quad (6)$$

The number of dF_1 decomposing in the first field-free region is

$$dF_{1M} = dF_1\{\exp[-1 \times 10^{-6}k_2(E')] - \exp -6 \times 10^{-6}k_2(E')]\} \quad (7)$$

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(8) For reactions of a molecular ion $[m_2^*]/[m_3^*]$ may be obtained from eq 3 by letting $k_1(E)$ approach infinity.

(9) The difference in activation energy which will permit the observation of two metastable peaks will be relatively small, say several tenths of an electron volt.

(10) For a system where $k_2(E) = 10^{13}(1 - 4.00/E)^6$, $k_3(E) = 10^{13} \cdot (1 - 4.10/E)^6$, and dN/dE is constant, the metastable abundance ratio will be 32.8 for the case where $k_1(E)$ is ten times the sum $k_2(E) + k_3(E)$ and 34.9 where $k_1(E)$ is very large compared to the sum $k_2(E) + k_3(E)$. The change is more marked if $k_2(E) = 10^{13}(1 - 2.00/E)^6$ and $k_3(E) = 10^{13}(1 - 2.10/E)^6$; for this system the ratios are 7.71 and 4.41, respectively.

Substituting eq 6 into eq 7 and integrating over the appropriate range of molecular ion internal energy give

$$[\mathrm{m_2}^*] = \int_0^{E_\mathrm{m}'} \frac{k_1'(E')}{[k_2(E') - k_1'(E')]}\{\exp[-2 \times 10^{-6}k_1'(E')] - \exp[-2 \times 10^{-6}k_2(E')]\}\{\exp[-1 \times 10^{-6}k_2(E')] - \exp[-6 \times 10^{-6}k_2(E')]\}\frac{\mathrm{d}N}{\mathrm{d}E'}\,\mathrm{d}E' \quad (8)$$

For reasons similar to those presented in the first model, $k'_1(E')$ will usually be much greater than $k_2(E')$ over the range in which the third term of the integrand is significant ($k_2(E') < 7 \times 10^6$ sec^{-1}) and eq 8 reduces to

$$[\mathrm{m_2}^*] \approx \int_0^{E_\mathrm{m}'} \{\exp[-3 \times 10^{-6}k_2(E')] - \exp[-8 \times 10^{-6}k_2(E')]\}\frac{\mathrm{d}N}{\mathrm{d}E'}\,\mathrm{d}E' \quad (9)$$

Similarly, the expression for [m$_3$*] can be written

$$[\mathrm{m_3}^*] \approx \int_0^{E_\mathrm{M}''} \{\exp[-3 \times 10^{-6}k_3(E'')] - \exp[-8 \times 10^{-6}k_3(E'')]\}\frac{\mathrm{d}N}{\mathrm{d}E''}\,\mathrm{d}E'' \quad (10)$$

If dN/dE' and dN/dE'' are approximately constant near ϵ_0' and ϵ_0'', the minimum internal energies of the molecular ions capable of producing A$^+$ and B$^+$, respectively, division of eq 9 by eq 10 gives

$$\frac{[\mathrm{m_2}^*]}{[\mathrm{m_3}^*]} \approx \left\{\left[\left(\frac{\mathrm{d}N}{\mathrm{d}E'}\right)_{\epsilon_0'}\Big/\left(\frac{\mathrm{d}N}{\mathrm{d}E''}\right)_{\epsilon_0''}\right] \times \int_0^{E_\mathrm{m}'}\{\exp[-3 \times 10^{-6}k_2(E') - \exp[-8 \times 10^{-6}k_2(E')]\}\,\mathrm{d}E'\right\}\Big/\left\{\int_0^{E_\mathrm{M}''} \times \{\exp[-3 \times 10^{6}k_3(E'')] - \exp[-8 \times 10^{-6}k_3(E'')]\}\,\mathrm{d}E''\right\} \quad (11)$$

Inspection of eq 11 shows that, unlike the first case, the metastable abundance ratio for reactions arising from two separate states of a given fragment will always be dependent on the nature of the distribution of energy of the molecular ions. For fragments having the same composition derived from different origins, there are three situations where [m$_2$*]/[m$_3$*] will be different, *viz.*, (i) where F$_1^+$ and F$_2^+$ are common to all spectra but $(\mathrm{d}N/\mathrm{d}E')_{\epsilon_0'}/(\mathrm{d}N/\mathrm{d}E'')_{\epsilon_0''}$ is different for each origin, (ii) where F$_1^+$ is common to each origin but F$_2^+$ is different, and (iii) where both F$_1^+$ and F$_2^+$ are different for each origin.

It should be possible to find systems where a fragment undergoes three or more reactions, and the metastable abundance probe will return apparently different conclusions depending on the pair of reactions chosen. Three such systems are studied here, and experimentally determined metastable abundance ratios for these systems are presented in Tables I–III.

Table I. Metastable Intensity Ratios for Reactions of $C_2H_4O_2\cdot^+$ (*m/e* 60)

Origin	[60 → 43]/ [60 → 45]	[60 → 42]/ [60 → 43]
n-Butyric acid	4.1 ± 10%	2.9 ± 10%
n-Valeric acid	5.1	2.9
n-Hexanoic acid	5.5	2.6
4-Phenylbutyric acid	3.9	3.0
4-Phenyl-3-methylbutyric acid	3.2	3.3
5-Phenylvaleric acid	4.1	2.9

Table II. Metastable Intensity Ratios for Reactions of $C_6H_{10}\cdot^+$ (*m/e* 82)

	Origin	
	Cyclohexene	Cyclohexylacetate
[82 → 67]/[82 → 81]	28 ± 10%	35 ± 10%
[82 → 67]/[82 → 80]	40	252
[82 → 67]/[82 → 66]	63	78
[82 → 67]/[82 → 54]	256	365
[82 → 66]/[82 → 54]	4.1	4.7

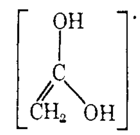
Table III. Metastable Intensity Ratios for Reactions of $C_8H_6O\cdot^+$ (*m/e* 118)

Origin	[118 → 90]/ [118 → 92]	[118 → 90]/ [118 → 89][a]
Coumarin	24 ± 10%	160
Benzofuran	304	162
o-Ethynylphenol	51	159

[a] For determination of this ratio, the electrostatic analyzer potential was reduced to 89.5/118 of its normal value and the accelerating voltage kept constant. By scanning the magnet, 118 → 89 could be resolved from 117 → 89.

Experimental Results

For the reactions of $C_2H_4O\cdot^+$ presented in Table I, the [60 → 42]/[60 → 43], which is constant within the reproducibility of the results, indicates that the elimination of OH· and H_2O from $C_2H_4O_2\cdot^+$ proceeds from a common state. Probably this state is a vibrationally excited form of



which can arise from all of the molecular ions by a McLafferty rearrangement.[11,12] The variability in [60 → 43]/[60 → 45], which is outside the experimental error, can arise either because the approximations which result in a constant metastable abundance ratio do not hold for the reaction

$$C_2H_4O_2\cdot^+ \longrightarrow CHO_2^+ + CH_3\cdot$$

or else the elimination of $CH_3\cdot$ proceeds from a state different from that arising by the McLafferty rearrangement, *e.g.*, $CH_3COOH\cdot^+$. Because the variation is relatively small, the former alternative is preferred here.

Tables II and III illustrate instances where there are marked differences in some metastable abundance ratios for reactions of a given fragment derived from different molecules where other reactions of the same fragment give nearly identical ratios. For the cyclohexene–cyclohexyl acetate system, it appears that all reactions of

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(11) F. W. McLafferty, *Anal. Chem.*, 28, 306 (1956).

(12) The molecular ion of acetic acid gives abundance ratios of 29 and 0.2, respectively, indicating that it reacts from a state different from the $C_2H_4O_2$ fragment ions.

the C_6H_{10} ions except the elimination of H_2 take place from a similar state. If the elimination of $CH_3\cdot$ and H_2 were the only reactions considered for the metastable abundance probe, it would be concluded that the reacting C_6H_{10} ions in each spectrum were different.

The results for the coumarin–benzofuran system in Table III may be used to clarify the contradictory results[3,4] obtained previously. The results show that the elimination of CO and $CHO\cdot$ from the C_8H_6O ions occurs from reacting states common to both coumarin and benzofuran, but the elimination of C_2H_2[13] occurs from dissimilar states. Thus, both the consideration of ion energetics[3] and the metastable abundance probe indicate that the elimination of CO occurs from the same state of the C_8H_6O ion in each spectrum. The postulation that those C_8H_6O ions which eliminate a molecule of CO in the spectra of coumarin, benzofuran, and *o*-ethynylphenol are similar is also supported by the results presented in Table III.

In conclusion, changing the origin of an ion, either by changing the compound from which it is derived or by changing the energy distribution of the molecular ions by using a different ionizing energy, can result in changes in the metastable abundance ratios even though the structure of the ion is the same for each origin. Insufficient data on energy distribution functions and the dependence of rate constants with excess energy preclude calculation of the magnitude of the change, but the experimental results presented here indicate that a variation of 30–50% is not unusual. In those cases where the metastable abundance probe shows that two reactions of an ion occur from different states, it is advisable to determine a second ratio in order to find which reactions occur from states common to all origins.

Experimental Section

All metastable abundance data were obtained from a CEC 21-110 mass spectrometer using the defocusing method[14,15] for detecting metastable ions. To minimize changes in abundance ratio due to changes in instrumental operating conditions, all data for a given ionic species were determined in the shortest practicable time, 2 hr or less for the full range of precursor compounds. A four-figure digital voltmeter, which measured a fixed fraction of the ion accelerating voltage, was used to check the mass of the reacting ions.

Except for *o*-ethynylphenol, which was prepared from benzofuran, all compounds studied were commercially available samples. The mass spectra of the samples indicated some diethyl ether in the *o*-ethynylphenol but no impurities in the other compounds.

Acknowledgment. The author wishes to thank D. W. Smith for the numerical calculations presented in this paper.

(13) The relative concentration of *m/e* 92 is low both in the first field-free region and at the collector; it is a minor species in each of the three spectra.

(14) M. Barber and R. M. Elliott, ASTM Conference on Mass Spectrometry, Montreal, June 1964.

(15) For metastable ions observed under normal conditions, the time for a metastable ion to travel from the ion source exit to a point in the first field-free region will be independent of the mass of the daughter ion. For metastable ions observed by the defocusing method, this time can be shown to be proportional to the square root of the mass of the daughter ion. Consequently, there may be differences in the metastable abundance ratios determined by the two methods; however, the general conclusions presented in this paper are applicable to metastable ions observed by either method.

Thermomagnetic Analysis of Hemin and Related Compounds

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Abstract: The magnetic susceptibility from 2.2 to 200°K was measured for hemin and the related $\alpha,\beta,\gamma,\delta$-tetraphenylporphiniron(III) chloride, thiocyanate, bromide, and iodide. All were found to be high-spin with the $^6A_1$ ground state predominating over the temperature range studied. An analytical expression for the susceptibility as a function of temperature and zero-field splitting, *D*, could not describe the data with reasonable values of *D* in all cases. At 2.2 and 4.2°K, and varying values of the applied field, the compounds approached 90% of paramagnetic saturation. A compound which has been formulated to date as the hydroxide derivative of $\alpha,\beta,\gamma,\delta$-tetraphenylporphiniron(III) was found to be diamagnetic at low temperatures.

Hemin, protoporphyrin(IX)iron(III) chloride, is a pentacoordinate complex formed by oxidizing heme, the prosthetic part of hemoglobin, during the removal of globin. Monovalent anions other than chloride can occupy the fifth coordination position, *e.g.*, Br^-, I^-, SCN^-, etc. Structural data[1] reveal that the coordinating nitrogens lie nearly in a plane with the iron ion displaced from this plane by about 0.5 Å. The microstructure about the iron ion in $\alpha,\beta,\gamma,\delta$-tetraphenylporphiniron(III) chloride, a synthetic analog of the naturally occurring hemin, is similar.[2]

Static magnetic susceptibility measurements have indicated that the iron in these pentacoordinate complexes is trivalent and high-spin, necessitating the assignment of a $^6S_{5/2}$ ground state.[3] Electron spin resonance (esr) studies on hemin[4,5] and the related myoglobin fluoride[6,7] have shown that the degeneracy of this symmetrical ground state is removed by the axial crystalline

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(1) D. F. Koenig, *Acta Cryst.*, **18**, 663 (1965).

(2) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Am. Chem. Soc.*, **89**, 1992 (1967).

(3) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964.

(4) G. Schoffa, O. Ristau, and F. Jung, *Naturwissenschaften*, 10, 227 (1960).

(5) G. Schoffa, *Nature*, **203**, 640 (1964).

(6) J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discussions Faraday Soc.*, **26**, 72 (1958).

(7) H. Morimoto and M. Kotani, *Biochim. Biophys. Acta*, **126**, 176 (1966).