Communications to the Editor
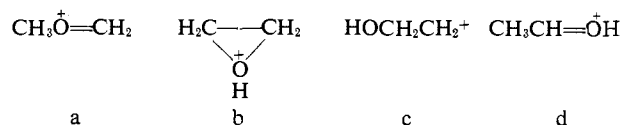
Identification of Gaseous Organic Ions by the Use of "Metastable Peaks"[1]

Sir:

Identification by comparison of physical and chemical properties is a basic tool for chemical investigations in most systems. In contrast, for gaseous organic ions few such properties are measurable; the exact mass and heat of formation are the main properties used to date. The former does not distinguish between isomers, and for the latter it is often impossible, or at least laborious, to make a determination with the accuracy necessary to distinguish between similar structures. Thus if two mass spectra exhibit particular ions which are identical within experimental error in mass and appearance potential, these ions do not necessarily have the same structure.

tively. Some of the m/e 18.7 peaks are "flat-topped," indicating formation with release of kinetic energy.[5]

The values found for compounds containing the moiety CH_3OCH_2 indicate that these $C_2H_5O^+$ ions have a unique structure, for which a is probably a favored canonical form. Loss of C_2H_2 from this

$$CH_3\overset{+}{O}\!=\!CH_2 \qquad \underset{\underset{H}{\overset{+}{O}}}{H_2C\!\!-\!\!-\!\!CH_2} \qquad HOCH_2CH_2^+ \quad CH_3CH\!=\!\overset{+}{O}H$$

a   b   c   d

structure should be unfavorable, consistent with the absence of the m/e 8.02 peak.

For the remaining compounds of Table I, the ion abundances at m/e 8.02 and 18.7 appear to be approximately the same with respect to each other, although not with respect to the mass 45 ion, and the energy re-

Table I. "Metastable Peaks" from the Decomposition of $C_2H_5O^+$ Ions

Structure	$\dfrac{[m/e\ 8.02]^e}{[m/e\ 45]}$	$\dfrac{[m/e\ 18.7]^e}{[m/e\ 45]}$	$\dfrac{[m/e\ 8.02]}{[m/e\ 18.7]}$	Kinetic energy, ev, of m/e 18.7^g
$CH_3OCH_2Y^a$	<0.1	12.3 ± 1.8^f	<0.01	<0.1
$HOCH_2CH_2Y^b$	55 ± 27	30 ± 14	1.8 ± 0.2	0.50 ± 0.04
$CH_3CH(OH)Y^c$	10.1 ± 2.6	5.3 ± 1.2	1.9 ± 0.1	0.44 ± 0.02
$CH_3CH_2OY^d$	13.7 ± 5.3	6.9 ± 2.3	2.0 ± 0.1	0.52 ± 0.05

^{a} Y = OCH_3, CH_2OH, CH_2CN, CH_2OCH_3. ^{b} Y = OH, CH_2OH, C_2H_4OH, CH_3, C_2H_5. ^{c} Y = H, CH_3, C_2H_5, C_3H_7, CH_2OH, C_2H_4OH, $COCH_3$. ^{d} Y = C_2H_4CN, $CONH_2$, CHO, C_2H_5. ^{e} Height of "metastable peak" × 10^4. ^{f} The ± signs indicate standard deviations. ^{g} Calculated according to ref 5. This energy appears to be independent of ionizing energy to within a few volts of the appearance potential.

Ions identical in structure and energy should exhibit identical decomposition reactions. Identification of such reactions in a complex mass spectrum is usually difficult because most secondary products can arise from more than one decomposition pathway. However, a "metastable peak" usually arises from a particular decomposition reaction. Rosenstock, Dibeler, and Harlee[2a] have reported recently that a series of n-hexyl derivatives give identical abundance ratios of two "metastable peaks" which result from decompositions of $C_6H_{13}^+$, and Muccini, Hamill, and Barker report[2b] that the "metastable peak" representing $C_3H_7^+ \rightarrow C_3H_5^+$ is found in the same abundance (relative to $C_3H_7^+$) in a series of n-alkanes. We now find that ions of the elemental composition $C_2H_5O^+$ from spectra of a wide variety of compounds can be classified in a few distinct structural types according to the mass, relative abundance, and shape of the peaks[3] resulting from the metastable decompositions of these ions.

In Table I the "metastable peaks" at m/e 8.02 and 18.7 correspond to the decompositions $C_2H_5O^+ \rightarrow H_3O^+ + C_2H_2$[4] and $C_2H_5O^+ \rightarrow CHO^+ + CH_4$, respec-

leased in the transitions giving rise to the 18.7 peaks is also approximately the same. These observations indicate that these m/e 8.02 and 18.7 peaks have a common precursor. For this the protonated oxirane structure, b, is the most probable, as b has been demonstrated by Van Raalte and Harrison[4] on the basis of energetics and isotopic label retention to be the $C_2H_5O^+$ ion structure yielding the H_3O^+ ion (m^* 8.02) in the spectra of 2-propanol and 2-butanol. For any compound of Table I, formation of b requires isomerization either of the molecular ion, during decomposition, or of the $C_2H_5O^+$ ion. Ions of structure c may well be present in the spectra of compounds of the type $HOCH_2$-CH_2Y. However, the high values of the ratio of "metastable ion" abundances to $C_2H_5O^+$ abundances indicate that isomerization of these compounds is relatively rapid compared to the remaining compound types, a fact consistent with the $HOCH_2CH_2Y$ structure.[5a]

For $CH_3CH(OH)Y$ compounds the much lower abundance of the "metastable peaks," relative to the

(2) (a) H. M. Rosenstock, V. H. Dibeler, and F. N. Harlee, J. Chem. Phys., **40**, 591 (1964); (b) G. A. Muccini, W. H. Hamill, and R. Barker, J. Phys. Chem., **68**, 261 (1964).

(3) The rate constant for the metastable decomposition reaction should also be a useful characteristic.

(4) D. Van Raalte and A. G. Harrison, Can. J. Chem., **41**, 3118 (1963).

(5) J. H. Beynon, R. A. Saunders, and A. E. Williams, Z. Naturforsch., **20a**, 180 (1965); T. W. Shannon, F. W. McLafferty, and C. R. McKinney, Chem. Commun., 478 (1966).

(5a) Note Added in Proof. In another system studied recently in this laboratory by Dr. W. T. Pike the abundance of the "metastable peak" relative to its precursor ion appears to decrease with increasing size of the ejected neutral fragment; the data for the $HOCH_2CH_2Y$ compounds of Table I are consistent with this. Thus the structure of the neutral fragment may also influence the metastable transition appreciably in particular cases.

$C_2H_5O^+$ ion, shows that the predominant m/e 45 ion species in these spectra must have a structure other than a or b; formula d is expected from the structures of the parent molecules.[6] Isomerization of this predominant $C_2H_5O^+$ isomer appears to produce consistent abundance ratios of masses 8.02/45 and 18.7/45; no "metastable peak" from the direct decomposition of structure d could be found. The data for the C_2H_5OY compounds indicate an intermediate rate of isomerization to structure b; this could be due in part to initial isomerization to structure d or its precursor. The "metastable peaks" of the other molecules studied indicate varying proportions of $C_2H_5O^+$ ion structures.

These data have interesting implications for the quasi-equilibrium theory of mass spectra.[7] The identity of the energy released in the metastable decomposition of the $C_2H_5O^+$ ion, as well as the consistency of the metastable intensities, may indicate that this ion is formed with the same energy and that this energy is rapidly randomized over the available degrees of freedom to form a common electronic state. It must be noted however, that metastable transitions occur with a relatively narrow range of rate constants of 10^5 to 10^6 sec^{-1}. For systems of moderate complexity the rate constants in this range are changing rapidly with energy, so that the measurements of the metastable reactions represent only a small sample of the total internal energy distribution of the m/e 45 ion. Only further experiments and theoretical calculations can reveal whether this remarkable agreement among the data reported here is due to the formation of common electronic states or is a consequence of the experimental techniques used.

In this technique an ion of a particular structure and energy content is identified from its characteristic fragmentation pattern as shown by its metastable decompositions. The accompanying communications describe applications of this technique.

(6) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, p 316.
(7) H. M. Rosenstock and M. Krauss in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 1.
(8) To whom requests for reprints should be sent.

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Skeletal and Hydrogen Rearrangements in Aryl Alkyl Ether Ions[1,2]

Sir:

In the mass spectra of several types of aromatic compounds a common hydrogen-transfer reaction, Scheme I, appears to be due to a McLafferty rearrangement.[3] The spectra of deuterium-labeled benzyl ethers,[4]

(1) Substituent Effects in Unimolecular Ion Decompositions. V. Paper IV: M. M. Bursey and F. W. McLafferty, submitted for publication.
(2) Generous financial support by the National Institutes of Health (Grant GM 12755) is gratefully acknowledged. Purchase of the Hitachi RMU 6A mass spectrometer was made possible by National Science Foundation Grant GP 4335.
(3) F. W. McLafferty, *Anal. Chem.*, **28**, 306 (1956); **31**, 82 (1959).
(4) J. K. MacLeod and C. Djerassi, *Tetrahedron Letters*, 2183 (1966).

Table I. Substituent Effects on the Abundance of $YC_6H_5O \cdot {}^+$
$YC_6H_4OC_2H_5 \cdot {}^+ \longrightarrow YC_6H_5O \cdot {}^+ + C_2H_4$
$Z = [YC_6H_5O \cdot {}^+]/[YC_6H_4OC_2H_5 \cdot {}^+]$

Y	Z/Z_0, 15 v	Z/Z_0, 75 v
H	1.00	1.00
p-NH$_2$	0.52	0.50
m-NH$_2$	0.49	0.53
p-OH	0.91	0.85
m-OH	0.89	0.84
p-OCH$_3$	0.63	0.42
m-OCH$_3$	0.60	0.38
p-F	1.09	1.06
m-F	1.13	1.00
p-Cl	1.26	1.16
m-Cl	1.24	1.12
p-Br	1.09	0.73
m-Br	1.12	0.78
p-I[a]	0.46	0.27
m-I[a]	0.45	0.26
p-CN	1.28	1.16
m-CN	1.36	1.07
p-CH$_3$[a]	1.57	0.97
m-CH$_3$[a]	0.78	0.63
p-COOH[a]	0.80	0.38
m-COOH[a]	4.1	1.15
p-CHO[a]	0.38	0.20
m-CHO[a]	0.53	0.28
p-NO$_2$[a]	0.54	0.22
m-NO$_2$[a]	0.79	0.43

[a] Further decomposition of the $(M - 28) \cdot {}^+$ indicated at 15 v.

β-phenylethyl alcohol,[5] and γ-phenylpropyl ethers[4,6] (oxygen atoms at positions 2′, 3′, and 4′, respectively) as well as alkylbenzenes[7] show that hydro-

Scheme I
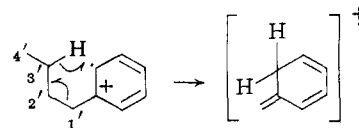
gen rearrangement takes place from the 3′ position. However, MacLeod and Djerassi[8] present convincing evidence that the hydrogen rearrangement in phenyl alkyl ethers (oxygen at position 1′) does *not* proceed in this fashion, in contrast to previous postulations.[9] In the *n*-butyl ether there is substantial transfer of hydrogen atoms from all four alkyl positions; this method is consistent with Scheme II.[8]

Scheme II
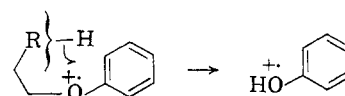
In a further investigation of the applicability of the techniques of metastable ion characteristics[10] and substituent effects,[1,11] we find that both Schemes I and II describe this rearrangement inadequately. Both phenol and phenetole exhibit flat-topped "meta-

(5) J. A. Gilpin, *J. Chem. Phys.*, **28**, 521 (1958).
(6) J. D. McCollum and S. Meyerson, unpublished results quoted in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 510.
(7) J. D. McCollum and S. Meyerson, *J. Am. Chem. Soc.*, **81**, 4116 (1959).
(8) J. K. MacLeod and C. Djerassi, *ibid.*, **88**, 1840 (1966).
(9) F. W. McLafferty, *Anal. Chem.*, **31**, 2072 (1959).
(10) T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5021 (1966).
(11) M. M. Bursey and F. W. McLafferty, *ibid.*, **88**, 529 (1966); (b) *ibid.*, **88**, 4484 (1966).