$C_2H_5O^+$ 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
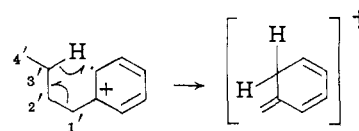
gen rearrangement takes place from the 3' position. However, MacLeod and Djerassi[8] present convincing evidence that the hydrogen rearrangement in phenyl alkyl ethers (oxygen at position 1') does *not* proceed in this fashion, in contrast to previous postulations.[9] In the *n*-butyl ether there is substantial transfer of hydrogen atoms from all four alkyl positions; this method is consistent with Scheme II.[8]

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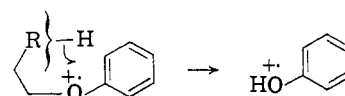
In a further investigation of the applicability of the techniques of metastable ion characteristics[10] and substituent effects,[1,11] we find that both Schemes I and II describe this rearrangement inadequately. Both phenol and phenetole exhibit flat-topped "meta-

(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).

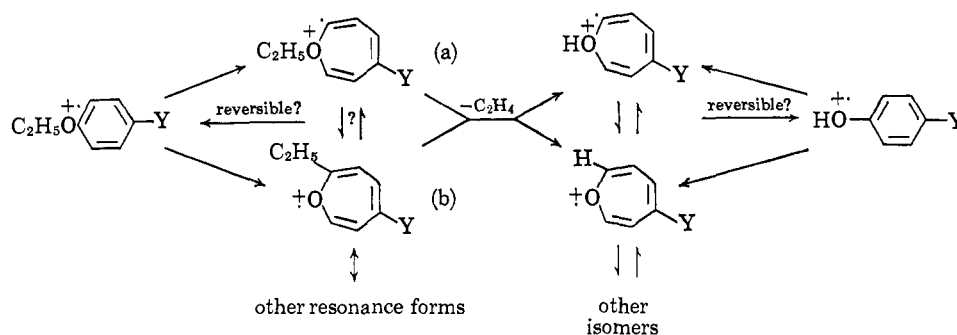(8) J. K. MacLeod and C. Djerassi, *ibid.*, **88**, 1840 (1966).

(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).
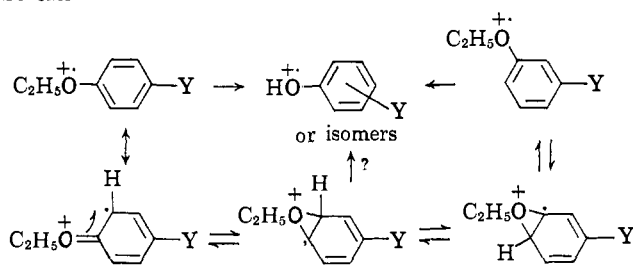
Scheme III

other resonance forms

other
isomers

stable ions" at m/e 46.4 ($94^+ \rightarrow 66^+$) of 0.23 ± 0.02 ev width[12] and of identical abundance. This indicates[10] that most of the $C_6H_6O \cdot^+$ ions in the spectra of these compounds have the same structure. For all but the CH_3, NO_2, $COOH$, and CHO derivatives, Table I shows[13] that the effect of a particular substituent on the rate of formation and rates of subsequent decompositions of $(M - C_2H_4) \cdot^+$ is independent of the ring position (*meta* or *para*) of that substituent.

Schemes III and IV are possible rationalizations for

Scheme IV

or isomers

these data. In Scheme III the oxepin ring is similar to the cycloheptatriene isomer proposed by Meyer and Harrison[14] to explain the partial equilibration of α- and ring-methyl groups in methylethylbenzenes.[15] Other bridged or nonclassical isomers are also possible;[16] a further study to include $C_2D_5OC_6H_4C_2H_5$, $(C_2H_5O)_2$-C_6H_4, $C_2D_5OC_6H_4Y$, and DOC_6H_4Y may yield evidence to support a particular mechanism.

The spectra of *m*- and *p*-bromophenetole and *m*- and *p*-bromophenol all show the same (in m/e, relative abundance, and shape) "metastable peak" for the reaction $XC_6H_5O \cdot^+ \rightarrow C_6H_5O^+$, as do the corresponding iodo derivatives. These data show that loss of ring position identity can also occur in decompositions of phenols; again, possible rationalizations include isomerizations of M^+ similar to those of Schemes III and IV (replacing C_2H_5 by H). The

(12) T. W. Shannon, F. W. McLafferty, and C. R. McKinney, *Chem. Commun.*, 478 (1966).

(13) At 15 ev further decomposition of $(M - C_2H_4) \cdot^+$ is negligible, except where noted. Thus the 15-ev values correspond to substituent effects on the rates of formation of $(M - C_2H_4) \cdot^+$.[1,11]

(14) F. Meyer and A. G. Harrison, *J. Am. Chem. Soc.*, **86**, 4757 (1964).

(15) Form b should provide better stabilization of the unpaired electron and a better opportunity of randomizing the ring positions than a, but requires the usually unfavorable step of migration of an alkyl group. Possible routes for scrambling include insertion of the oxygen atom into other than the adjacent ring position,[14] reversible contraction of the new seven-membered ring to yield another six-membered ring isomer, and exchange of ring substituents in the seven-membered ring.

(16) Similar formulations have been used to explain the spectra of benzyl alcohol: H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 169.

spectra of *p*-nitrophenol and *p*-nitrophenetole show the same "flat-topped metastable peak,"[12,17] but this is *not* present for the corresponding *meta* compounds.[18]

For the methylphenetoles an additional ring-expansion isomerization[14] may be possible to yield an ethoxycycloheptatriene ion which can also undergo rearrangement loss of C_2H_4 at a different rate. The data of Table I would be explained if this isomerization is favored in one of the isomers.

These results suggest that the similarity in mass spectra of many *ortho*, *meta*, and *para* isomers may be due to randomizing isomerizations of the molecular ions and not just to similarities in decomposition rates of different bonds.

Acknowledgment. The authors are indebted to Drs. F. A. L. Anet and H. A. Morrison for valuable discussions.

(17) This "metastable peak" is also found in the spectrum of *p*-nitrophenyl acetate.

(18) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5023 (1966).

(19) National Institute of Health Undergraduate Summer Research Program, 1965.

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Rearrangements and "Flat-Topped Metastable Ions" in the Mass Spectra of Substituted Nitrobenzenes[1]

Sir:

The mass spectra of nitroaromatic compounds have been studied extensively.[2] Of special interest is the loss of NO from the molecular ion, for which a rearrangement mechanism involving a three-center isomerization to a nitrite structure has been proposed.[2] For some nitroaromatics this NO loss also produces "flat-topped metastable ions,"[3] an unusual and little understood phenomenon. Our observation that the rearrangement loss of C_2H_4 from phenetole is accompanied by the unexpected loss of ring position identity[1] has prompted us to extend our studies of substituent effects to this nitroaromatic rearrangement.

Intensity ratios of the M − 30 ion with respect to the molecular ion at 75 and at 13.8 v, and for the M −

(1) Substituent Effects in Unimolecular Ion Decompositions. VI. Paper V: F. W. McLafferty, M. M. Bursey, and S. M. Kimball, *J. Am. Chem. Soc.*, **88**, 5022 (1966).

(2) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, **29**, 311 (1964), and references cited therein.

(3) 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).