

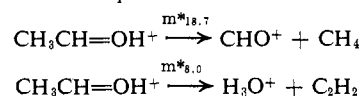
The abundance of the primary product ions, such as $C_2H_5O^+$ of Figure 1, *vs.* that of the molecular ions generally *increases* with an increase in the number of degrees of freedom; this could be due to multiple paths of formation and decomposition and to the effect of structure on bond strengths. This emphasizes the advantage of using the product ion yield of the same metastable decomposition reaction as a measure of internal energy distribution in the precursor.

Note in Figure 1 that the primary alcohols show different slopes than those of the secondary alcohols, despite the fact that the other "metastable ion characteristics" of their $C_2H_5O^+$ ions are identical.¹ A possible explanation is that the $C_2H_5O^+$ ions with sufficient energy to undergo metastable decomposition have rearranged to a common structure, such as the oxirane ion postulated previously,¹ but that the low-energy $C_2H_5O^+$ ions from the primary and secondary alcohols have the unrearranged structures $HOC_2H_4^+$ and $CH_3CH=OH^+$, respectively.¹¹

Thus the degree of freedom effect appears to offer a useful way to *correct for differences in energies* so that the abundances of "metastable ions" can be used to characterize the structure of the precursor. Also 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*, with the qualification that isomerization during the metastable decompositions can yield the same abundance ratios for precursor ions of different structure.

Acknowledgment. We are indebted to A. L. Wahrhaftig, T. W. Shannon, and H. W. Brown for very helpful discussions on many important aspects of this work.

(11) Dr. T. W. Shannon points out for the metastable transitions



that the heats of reaction involving ground-state species are $\Delta H_1 = 58$ and $\Delta H_2 = 66$ kcal/mole.¹² This agrees quite well with the observed kinetic energy released¹ of 10 and 0 kcal, respectively, for these reactions assuming that these kinetic energies represent the activation energies for the reverse process and that activation energies for the forward process are the same.

(12) Using heats of formation for CH_3CHOH^+ , CHO^+ , and H_3O^+ of 145,¹³ 122, and 157¹⁴ kcal/mole, respectively.

(13) A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966).

(14) D. Van Raalte and A. G. Harrison, *ibid.*, **41**, 3118 (1963).

(15) Postdoctoral Fellow, 1966-1967.

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Metastable Ion Characteristics. III.¹ Structures of $C_3H_6O^+$ Ions in the Mass Spectra of Aliphatic Ketones²

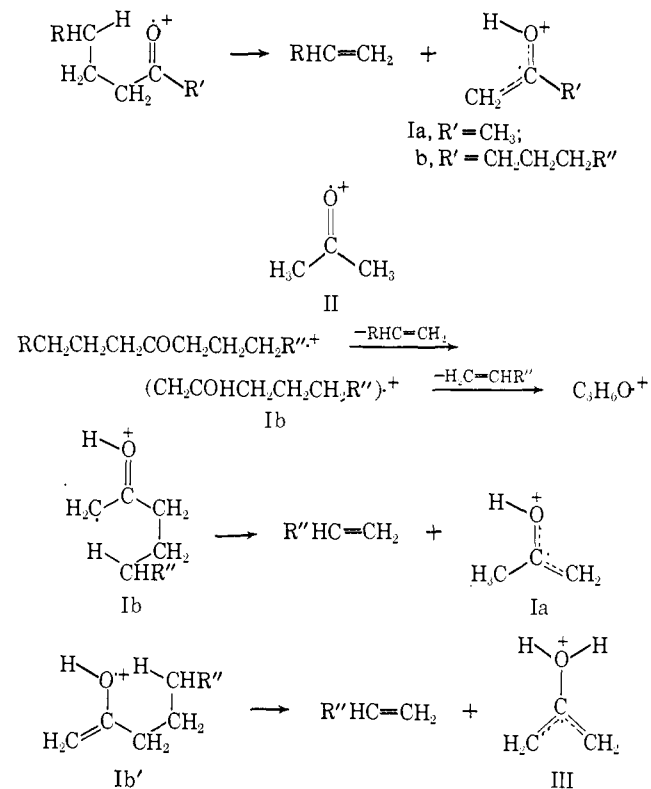
Sir:

For the electron-impact-induced rearrangement of carbonyl compounds involving migration of a γ -hy-

(1) Part II: F. W. McLafferty and W. T. Pike, *J. Am. Chem. Soc.*, **89**, 5951 (1967).

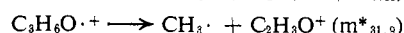
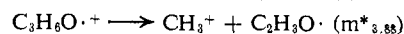
(2) The generous financial support of the National Institutes of Health (GM 12755 and FR 00354) is gratefully acknowledged. The Hitachi RMU-6D mass spectrometer used in this work was purchased through National Science Foundation Grant GP 4335.

drogen atom³ there is ample evidence⁴ in favor of the formation of the enol radical ion I rather than the keto form (such as II, the molecular ion of acetone). However, when two such rearrangements^{5,6} of γ -hydrogen



atoms occur from both alkyl chains of a higher alkanone (reaction 1), structures Ia or III are possible,⁵⁻⁷ depending on whether the second hydrogen atom migrates to the carbon or oxygen atom, respectively. The driving forces for such rearrangements have been of considerable interest recently because of their importance in applying mass spectrometry to molecular structure determination. We report here evidence from metastable ion characteristics^{1,8} in support of the formation of the allylic-radical oxonium-ion structure III.

Ions of the formula $C_3H_6O^+$ in the spectra of acetone, 2-alkanones, and 4- and 5-alkanones decompose to yield two metastable peaks, $m^*_{3,88}$ and $m^*_{31,9}$, whose abundances relative to that of $C_3H_6O^+$ are shown in Figure 1. Abundance ratios, $[m^*_{31,9}]/[m^*_{3,88}]$, of ap-



proximately 23,⁹ 280, and 110 are found for $C_3H_6O^+$

(3) A McLafferty rearrangement: F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

(4) S. Meyerson and J. D. McCollum, "Advances in Analytical Chemistry and Instrumentation," Vol. 2, C. N. Reilley, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 179, and references cited therein.

(5) Termed "consecutive rearrangements": (a) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966; or "double rearrangements": ref 3 or H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964. The former name will be used here to avoid confusion with reactions in which two hydrogen atoms are rearranged in a single step.

(6) H. Budzikiewicz, C. Fenselau, and C. Djerassi, *Tetrahedron*, **22**, 1391 (1966).

(7) J. H. Beynon, *Endeavour*, **25**, 79 (1966).

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

(9) Because of the interference of the m/e 32 peak, the $m^*_{31,9}$ value for acetone is a maximum; therefore this ratio is also a maximum value.

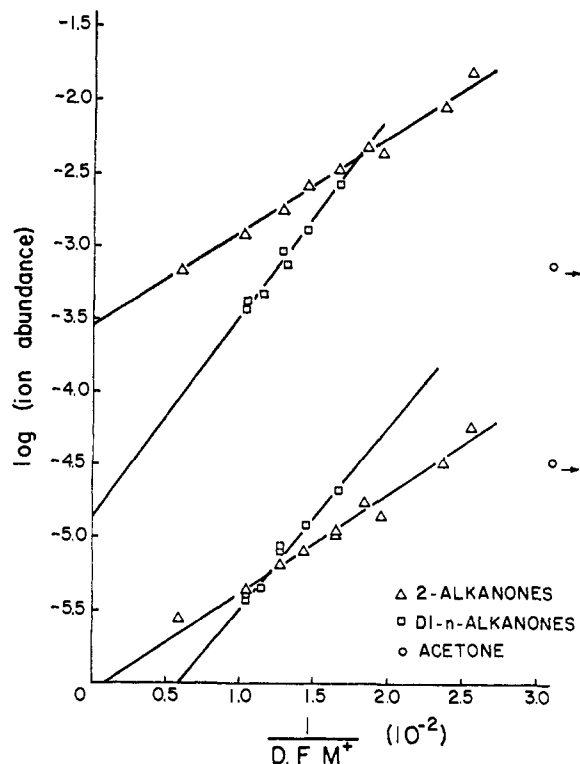


Figure 1. Correlation of "metastable ion" abundances, $\log ([m^*]/[C_3H_6O \cdot^+])$, with the number of vibrational degrees of freedom in acetone, 2-alkanones,¹ and the following di-*n*-alkanones: 4-heptanone, 4-octanone, 4- and 5-nonanone, 4-decanone, and 4- and 5-undecanones. The lower and upper values of each pair correspond to $m_{3.88}^*$ and $m_{31.9}^*$, respectively. The abscissa value for acetone is 4.17.

metastables from acetone, the single rearrangement, and the consecutive rearrangement reactions, respectively, and the effect of the number of degrees of freedom of the molecular ion on the latter two classes is also markedly different. Following the arguments presented earlier,^{1,8} these metastable ion characteristics indicate that a substantial part of the $C_3H_6O \cdot^+$ ions from the 4- and 5-alkanones must *not* correspond to structures Ia or II.

The formation of structure III⁷ by specific rearrangement of γ -hydrogen atoms⁶ is consistent with the known tendency for hydrogen rearrangement to both saturated and unsaturated oxygen atoms.⁵ Such rearrangement to a C=C double bond is also common;¹⁰ unfortunately the data do not allow a determination of [Ia]/[III]. It has been postulated that an important driving force for such specific rearrangements is the presence of the radical site as distinguished from the site of positive charge.¹¹ These data are consistent with this postulate, if the canonical form Ib' is an important contributor to the reacting species.¹²

(10) F. W. McLafferty, *Anal. Chem.*, **31**, 2072 (1959).

(11) F. W. McLafferty, *Chem. Commun.*, 78 (1966).

(12) The apparent stability of III may be somewhat surprising in view of its similarity to $\cdot CHRCH_2CH_2CH_2OH_2^+$ which is postulated¹³ as the intermediate in the loss of H_2O from primary alcohols. However, the analogous loss of H_2O from III would involve the formation of the comparatively high energy ion $C_3H_4^+$.

(13) Reference 5a, p 132.

(14) Postdoctoral Fellow, 1966-1967.

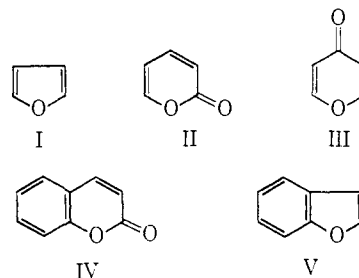
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Metastable Ion Characteristics. IV.¹ Structures of (M - CO) Ions from Pyrones

Sir:

A fundamental and difficult problem in mass spectro-metric investigations is the assignment of structures to the various ions encountered. One method is to infer the structure of a particular product ion from a correlation between peaks of lower m/e values with corresponding peaks in the spectrum of a known molecule whose elemental composition is identical with that of the product ion studied. This method has found wide use in the assignment of structure to ions formed by direct loss of CO from various aromatic systems on electron impact.²

Recently the application of this technique in the assignment of a cyclic furan structure (I) to the (M - CO) species produced in the fragmentation of 2-pyrone (II) has been questioned by Pirkle and rejected on the grounds of labeling evidence.³ However, Pirkle's conclusions have recently been challenged by Brown and Green,⁴ who point out that in view of the mechanism proposed by Nakata, *et al.*,⁵ for the formation of the $C_3H_3^+$ ion in the mass spectra of 2-pyrones, Pirkle has only established that an important alternative pathway exists for the formation of the $C_3H_3^+$ ion and not that the $C_4H_4O \cdot^+$ ion has, or has not, any particular structure. We report here that metastable ion characteristics⁶ clearly show that the loss of CO from compounds containing the pyrone moiety produces (M - CO) ions of which a substantial proportion do not have the structure of the molecular ion from the corresponding furan derivative.



2-Pyrone (II) and 4-pyrone (III) on electron impact lose $CO^{7,8}$ to yield abundant $C_4H_4O \cdot^+$ ions whose subsequent fragmentation leads to mass spectra similar

(1) Part III: F. W. McLafferty and W. T. Pike, *J. Am. Chem. Soc.*, **89**, 5953 (1967).

(2) J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959); (b) C. S. Barnes and J. L. Occolowitz, *Australian J. Chem.*, **17**, 975 (1964); (c) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 2, Holden-Day Inc., San Francisco, Calif., 1964, Chapter 29.

(3) W. H. Pirkle, *J. Am. Chem. Soc.*, **87**, 3022 (1965).

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

(5) H. Nakata, Y. Hirota, and A. Tatamatsu, *Tetrahedron Letters* **123** (1965).

(6) T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5021 (1966); F. W. McLafferty and W. T. Pike, *ibid.*, **89**, 5951 (1967).

(7) The metastable ion transition is observed.

(8) It appears that it is the carbonyl which is expelled. While no direct evidence of this is presently offered, there is ample precedent for it.^{2a,9,10}

(9) J. D. McCollum and S. Meyerson, *J. Am. Chem. Soc.*, **85**, 1739 (1963).

(10) J. M. Wilson, M. Ohashi, H. Budzikiewicz, C. Djerassi, S. Ito, and T. Nozoe, *Tetrahedron*, **19**, 2247 (1963).