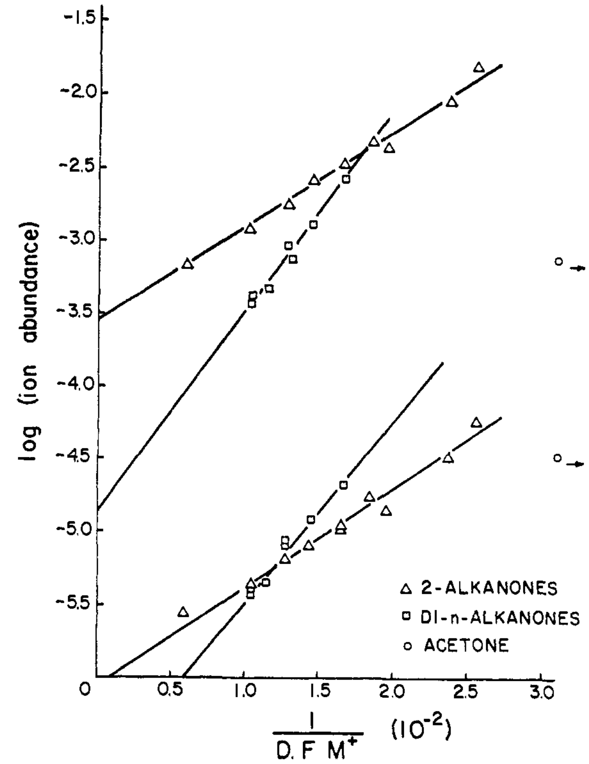

Figure 1. Correlation of "metastable ion" abundances, log ([m*]/[$C_3H_6O\cdot^+$]), with the number of vibrational degrees of freedom in acetone, 2-alkanones,[1] and the following di-*n*-alkanones: 4-heptanone, 4-octanone, 4- and 5-nonanone, 4-decanone, and 4- and 5-undecanones. The lower and upper 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 III[7] by specific rearrangement of γ-hydrogen atoms[6] 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 postulated[13] 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 $C_3H_4\cdot^+$.

(13) Reference 5a, p 132.

(14) Postdoctoral Fellow, 1966–1967.

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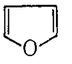
Received April 21, 1967

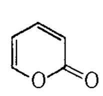
Metastable Ion Characteristics. IV.[1]
Structures of (M − CO) Ions from Pyrones

Sir:

A fundamental and difficult problem in mass spectrometric 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 characteristics[6] 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.


I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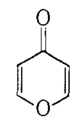
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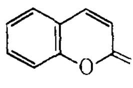
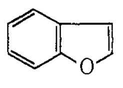

IV


V

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

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(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. Tatematsu, *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 for the 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).

to that of furan.[3,11] From this it could be inferred that the $C_4H_4O\cdot^+$ ions have the furan structure I.

Ions of formula $C_4H_4O\cdot^+$ in the spectra of I, II, and III decompose to yield two "metastable peaks" corresponding to the transitions

$$C_4H_4O\cdot^+ \xrightarrow{m^*_1} C_3H_4\cdot^+ + CO$$

$$C_4H_4O\cdot^+ \xrightarrow{m^*_2} C_2H_2O\cdot^+ + C_2H_2$$

Abundance ratios m^*_1/m^*_2 (Table I) of approximately 8.4, 3.7, and 2.3 are found for the $C_4H_4O\cdot^+$ metastables from furan, 2-pyrone, and 4-pyrone, respectively.

Table I

Compound	$[m_1^*]/[C_4H_4O\cdot^+]$	$[m_2^*]/[C_4H_4O\cdot^+]$
Furan	$(2.0 \pm 0.1) \times 10^{-3}$	$(2.4 \pm 0.2) \times 10^{-4}$
2-Pyrone	$(1.7 \pm 0.1) \times 10^{-2}$	$(4.6 \pm 0.2) \times 10^{-3}$
4-Pyrone	$(1.3 \times 0.1) \times 10^{-2}$	$(5.7 \pm 0.2) \times 10^{-3}$

Following arguments presented earlier,[6] these metastable ion characteristics indicate that a substantial part of the $C_4H_4O\cdot^+$ ions from the 2- and 4-pyrones must *not* correspond in structure to the $C_4H_4O\cdot^+$ ions from furan.[12]

Similarly coumarin (IV) on electron impact loses CO to yield abundant $C_8H_6O\cdot^+$ ions for which the benzofuran structure V has been inferred.[2b] Ions of formula $C_8H_6O\cdot^+$ in the spectra of IV and V decompose to give metastable peaks corresponding to the transitions

$$C_8H_6O\cdot^+ \xrightarrow{m^*_3} C_7H_6\cdot^+ + CO$$

$$C_8H_6O\cdot^+ \xrightarrow{m^*_4} C_6H_4O\cdot^+ + C_2H_2$$

Abundance ratios $[m^*_3]/[m^*_4]$ (Table II) of approximately 28 and 164 are found for the $C_8H_6O\cdot^+$ metastables from coumarin and benzofuran, respectively. These metastable ion characteristics indicate that a substantial part of the $C_8H_6O\cdot^+$ ions in the mass spectrum of coumarin must not correspond in structure to those of benzofuran.[12]

Table II

Compound	$[m^*_3]/[C_8H_6O\cdot^+]$	$[m^*_4]/[C_8H_6O\cdot^+]$
Coumarin	$(9.7 \pm 0.2) \times 10^{-3}$	$(3.4 \pm 0.2) \times 10^{-4}$
Benzofuran	$(1.4 \pm 0.1) \times 10^{-2}$	$(8.5 \pm 0.2) \times 10^{-5}$

These results raise questions concerning the structures of other $(M - CO)\cdot^+$ ions in which formation by expulsion of CO has been assumed to be accompanied by ring closure.[2] We are presently extending our studies to such systems.

Metastable ion abundances were determined in the first drift region of a CEC 21-110 double-focusing mass spectrometer using the defocusing technique.[13]

Acknowledgment. We thank Dr. William H. Pirkle, Dr. Peter Beak, and Dr. George Van Lear, University of Illinois, for furnishing us purified samples of the pyrones, and the National Institutes of Health (GM 12755 and FR 00354) for generous support of this work.

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[11] P. Beak, T. H. Kinstle, and G. A. Carls, *J. Am. Chem. Soc.*, **86**, 3833 (1964).

[12] Dr. Nakata has kindly informed us prior to publication of evidence that some of the (M − CO) ions from substituted 2-pyrones do have the furan-type structure. However, Dr. M. M. Bursey, University of North Carolina, has also informed us prior to publication of independent evidence for nonfuran type structures for similar (M − CO) ions: M. M. Bursey and L. R. Dusold, *Chem. Commun.*, 712 (1967).

[13] M. Barber and R. M. Elliott, ASTM E-14 Conference on Mass Spectrometry, Montreal, Canada, June 1964; T. W. Shannon, T. E. Mead, C. G. Warner, and F. W. McLafferty, *Anal. Chem.*, **39**, 1748 (1967).

[14] Postdoctoral Fellow, 1966–1967.

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Received June 16, 1967

Hydrogen Bonding. I. Two Approaches to Accurate Heats of Formation[1]

Sir:

Despite the crucial role of hydrogen bonding in chemical and biochemical theory,[2] relatively few determinations of heats of hydrogen-bond formation (ΔH_f) have been described previously for well-characterized systems. Most of these have employed a temperature variation of equilibrium constant, a procedure which is usually less reliable than calorimetry.[3] Hydrogen-bond energies (ΔG_f and ΔH_f) commonly fall in the 3–7-kcal/mole range.[2] Cited error limits are often close to ±1 kcal/mole, and discrepancies between published results may exceed 100%.

In the hope of developing a definitive collection of reliable values suitable for testing or refuting theories, we have pooled our resources[4] to study well-characterized hydrogen-bonding systems by several independent methods (infrared, ^{19}F nmr, and solution calorimetry).

Described below are direct calorimetric measurements of molar enthalpies of formation ($\Delta H_f°$) for 1:1 hydrogen-bonded complexes between phenol and *p*-fluorophenol (PFP) with three typical bases in carbon tetrachloride solution. $\Delta H_f°$ is defined as the standard enthalpy change for the reaction $A(CCl_4) + B(CCl_4) \rightarrow C(CCl_4)$, where A is the hydrogen-bonding acid, B is the acceptor base, and C is their 1:1 adduct. These results and those in the accompanying communication[4] will be extended to other bases and correlated with related thermodynamic and spectral properties in a complete article which will also contain experimental details and documentation of results. Here we will demonstrate two independent calorimetric methods for determining ΔH_f which give mutually consistent values. We will also show that the ΔH_f for a given hydrogen-bonded complex is rather insensitive to the medium in

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[1] Supported at Pittsburgh by a National Institutes of Health Grant, GM-10872, and (in part) at Princeton University by a grant from the Petroleum Research Fund, administered by the American Chemical Society. From doctoral theses of T. S. S. R. Murty, University of Pittsburgh, 1967, and L. Joris, Princeton University, 1967. L. J. was a National Institutes of Health Predoctoral Fellow, 1967.

[2] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman & Co., San Francisco, Calif., 1960.

[3] (a) E. J. King, "Acid–Base Equilibria," The Macmillan Co., New York, N. Y., 1965, p 192 ff; (b) J. W. Larson and L. Hepler in "Solvent–Solute Interactions," Interscience Publishers, Inc., New York, N. Y., in press.

[4] D. Gurka, R. W. Taft, L. Joris, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 5957 (1967).