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Structures of $[C_4H_4O]^{+\cdot}$ Ions Produced from 2- and 4-Pyrone

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Abstract: Contrary to earlier conclusions, the nonfragmenting $[C_4H_4O]^{+\cdot}$ ions generated by loss of CO from 2- and 4-pyrone mainly have the $[\text{furan}]^{+\cdot}$ structure; some $[\text{vinylketene}]^{+\cdot}$ ions are also generated. This conclusion was drawn from examination of the collisional activation spectra of $[C_4H_4O]^{+\cdot}$ ions of known structure and from measurements of the heats of formation of the molecular ions of 11 isomeric $[C_4H_4O]^{+\cdot}$ species. It was further concluded that no firm structural assignment can be made for the $[C_4H_4O]^{+\cdot}$ ions having sufficient internal energy to fragment on the microsecond time scale.

Introduction

The elucidation of molecular and ionic structures by mass spectrometry has greatly benefitted from simple rationalizations derived from organic chemistry. However, an intriguing and longstanding exception concerns the loss of CO from 2- and 4-pyrone molecular ions.[2a] The proposed generation of $[\text{furan}]^{+\cdot}$ as a stable daughter ion seems a priori very reasonable. McLafferty and Pike[2b] cautiously concluded, from a study of relative metastable peak abundances for the fragmenting $[C_4H_4O]^{+\cdot}$ ions derived from furan and 2- and 4-pyrones, that a substantial fraction of the decomposing ions cannot have the furan structure.

Shortly thereafter, Pirkle and Dines,[3] in their second detailed study, concluded that the majority of further decomposing $[C_4H_4O]^{+\cdot}$ ions could confidently be excluded from having the structure of $[\text{furan}]^{+\cdot}$.

We here present evidence that, for the nondecomposing (lifetimes > 5 μs) $[C_4H_4O]^{+\cdot}$ ions from both pyrones, the $[\text{furan}]^{+\cdot}$ structure is the *predominant* species and that no firm deductions concerning the structures of either the reacting or the nonreacting ions can be made from metastable peak characteristics.

Results and Discussion

The heats of formation, ΔH_f, of the *m/z* 68, $[C_4H_4O]^{+\cdot}$ daughter ions from 2- and 4-pyrones were estimated to be $\ngtr 217$ and $\ngtr 222$ kcal mol^{-1}, respectively. (From appearance energy (AE), *m/z* 68, for 2-pyrone AE = 10.34 ± 0.05 eV, and for 4-pyrone AE = 10.64 ± 0.05 eV, both measured with energy selected electrons;[4] $\Delta H_f(\text{2-pyrone}) = -43 \pm 2$ kcal mol^{-1} and $\Delta H_f(\text{4-pyrone}) = -34 \pm 2$ kcal mol^{-1} from group additivity,[5] whence $\Delta H_f([C_4H_4O]^{+\cdot})$ from 2-pyrone = 222 ± 2 kcal mol^{-1} and $\Delta H_f([C_4H_4O]^{+\cdot})$ from 4-pyrone = 237 ± 2 kcal mol^{-1}. However, both fragmentations are associated with appreciable reverse activation energies (E_{rev}) whose *minimum* values, calculated from the widths of the dish-topped metastable peaks across their maxima,[6,7] were $E_{\text{rev}}(\text{2-pyrone}) \geq 4.5$ kcal mol^{-1} and $E_{\text{rev}}(\text{4-pyrone}) \geq 14.5$ kcal mol^{-1} [8].) Thus, the above ΔH_f values represent *upper limits* for the $[C_4H_4O]^{+\cdot}$ daughter ions. Comparing these values with representative thermochemical data (Table I) permits the elimination of all structures proposed earlier[3] and leaves but three feasible structures for *threshold* $[C_4H_4O]^{+\cdot}$ (i.e., ions having *insufficient energy* to fragment further), $[\text{vinylketene}]^{+\cdot}$, $[\text{furan}]^{+\cdot}$, and $[\text{buta-1,2-dienone}]^{+\cdot}$.

Structural information for nondecomposing ions can also be obtained from their collisional activation (CA) mass spectra. These spectra represent the intensity distribution of the ionic products of decomposition from the fast dissociations which a mass selected stable ion is forced to undergo upon collision with an inert gas in the field free region between the magnetic and electric sector of the mass spectrometer. The high energy imparted to the ion by the collision precludes extensive isomerization before fragmentation and so fast reactions characteristic of ion structure are normally observed.[13]

The $[C_4H_4O]^{+\cdot}$ ions from the pyrones display only three important peaks in their collisional activation (CA) mass spectra, *m/z* 39, 40, and 42. The complete spectra are shown in Table II. The CA mass spectrum of 4-pyrone is closely similar to that of furan but significantly different from that of vinylketene. We conclude that loss of CO from $[\text{4-pyrone}]^{+\cdot}$ indeed produces $[\text{furan}]^{+\cdot}$ as the nonfragmenting daughter ion. We propose that loss of CO from $[\text{2-pyrone}]^{+\cdot}$ generates mainly $[\text{furan}]^{+\cdot}$ ions together with $[\text{vinylketene}]^{+\cdot}$.

The generation of $[\text{vinylketene}]^{+\cdot}$ from 2-pyrone can be rationalized by invoking a 1,4- or a 1,2-hydrogen shift prior to the loss of CO from a molecular ion which has undergone a ring-opening analogous to the photochemical behavior of the neutral molecule.[14–16] Isomerization of $[\text{2-pyrone}]^{+\cdot}$ into the molecular ion of bicyclo[2.2.0]pyran-2-one can be ruled out on the basis of their mass spectra.[17]

We suggest that the possible third isomer, $[\text{buta-1,2-dienone}]^{+\cdot}$ is an unlikely $[C_4H_4O]^{+\cdot}$ daughter ion because its CA mass spectrum would be expected to display appreciable loss

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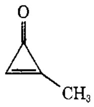
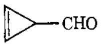
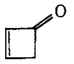
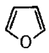
Table I. Heats of Formation of $[C_4H_4O]^{+\cdot}$ Ions

structure	ΔH_f (neutral),[a] kcal mol^{-1}	IE, eV	$\Delta H_f[C_4H_4O]^{+\cdot}$, kcal mol^{-1}
$CH_3C{\equiv}CCHO$	+15	10.25 ± 0.05[b,c]	251
$CH_3COC{\equiv}CH$	+12	10.25 ± 0.05[b]	249
$CH_2{=}CHOC{\equiv}CH$	+36	>8.9[d]	>241
	+29	9.15 ± 0.05[b]	240
$CH_2{=}C(OH)C{\equiv}CH$	+33	>9.0[e]	>240
$CH_2{=}C{=}CHCHO$	+18	≥9.5[f]	≥237
	+14	~9.6[g]	~235
	+15	~9.3[h]	~231
$CH_3CH{=}C{=}C{=}O$	+13[i]	~8.3[j]	~203
	−8.3[k]	8.88 ± 0.05[b,c]	197
$CH_2{=}CHCH{=}C{=}O$	+4[i]	8.30 ± 0.05[b,c]	194[i]

[a] Estimated by group additivity,[5] ±2 kcal mol^{-1} (unless referenced). [b] Photoelectron (HeI) spectra.[11] [c] Energy selected electrons.[4] [d] Compare 8.93 eV for $CH_2{=}CHOCH_3$.[9] [e] Compare 9.0 eV for $CH_2{=}CHOH$.[10] [f] Compare 9.5 eV for $CH_2{=}C{=}CH_2$, 9.5 eV for C_6H_5CHO.[9] [g] Compare 9.6 eV for cyclopropene.[9] [h] Compare 9.3 eV for cyclohexene-2-one.[11] [i] Reference 12. [j] Assuming same the IE as vinylketene.[12] [k] Reference 9.

Table II. 70-eV Collisional Activation Spectra of Some $[C_4H_4O]^{+\cdot}$ Ions

	m/z daughter ion												
compd	54	53	51	59	49	42	40	39	38	37	29	26	25
furan	1	1	1	4	2	11	20	100	29	17	14	6	1.5
4-pyrone	1	1	4	2	2	11	25	100	31	17	15	6	1.5
2-pyrone	1	1	1	5	3	14	37	100	32	19	12	8	2.5
vinylketene	1	2	1	6	3	18	45	100	33	20	7	7	2.5

of $CH_3\cdot$ (*m/z* 53). Note that it is expected that m/z 53 ions of the same structure ($HC{\equiv}C\ C^+{=}O$) are generated upon loss of $CH_3\cdot$ from the C_4H_4O isomer 3-butyn-2-one, where this process gives rise to the base peak in the CA mass spectrum.

It remains to consider $[C_4H_4O]^{+\cdot}$ ions which have sufficient internal energy to fragment. Work on the structures of $[C_7H_7]^+$ [18] clearly illustrates that the structures of nondecomposing ions need not be the same as the structures of corresponding ions with sufficiently high internal energies to cause fragmentation. In agreement with the results of McLafferty and Pike,[2] we find that the relative abundances of the only two significant metastable peaks (loss of CO or C_2H_2) for fragmentations of the $[C_4H_4O]^{+\cdot}$ ions generated from the pyrones are different from furan: furan, 100:19; 2-pyrone, 100:26; 4-pyrone, 100;53. The ratios are also different from that observed for vinylketene: 100:5. Moreover, and contrary to an earlier report,[19] the metastable peak shapes for both losses are also significantly different. The metastable peaks for the loss of CO from the four compounds and the kinetic energy release distributions[20] derived therefrom are shown in Figure 1.

The kinetic energy releases calculated from the half-height width of the metastable peaks, $T_{0.5}$, and the average energy releases, T_{Av}, obtained from the distributions of released energies are the following: furan, $T_{0.5} = 16$, $T_{Av} = 87$; vinylketene, $T_{0.5} = 20$, $T_{Av} = 60$; 2-pyrone, $T_{0.5} = 50$, $T_{Av} = 147$; 4-pyrone, $T_{0.5} = 80$, $T_{Av} = 237$ meV. Of these, the metastable peak for the loss of CO from $[\text{vinylketene}]^{+\cdot}$ is characterized by a small energy release and a Gaussian shape, indicating that the rearranged form of the ion (from which dissociation occurs by simple bond rupture) is produced by a route which requires less energy than its dissociation. The appearance energy for loss of CO from this isomer (measured with energy selected electrons) is indeed compatible with threshold generation of the most stable $[C_3H_4]^{+\cdot}$ product ion, $[\text{allene}]^{+\cdot}$,[12]

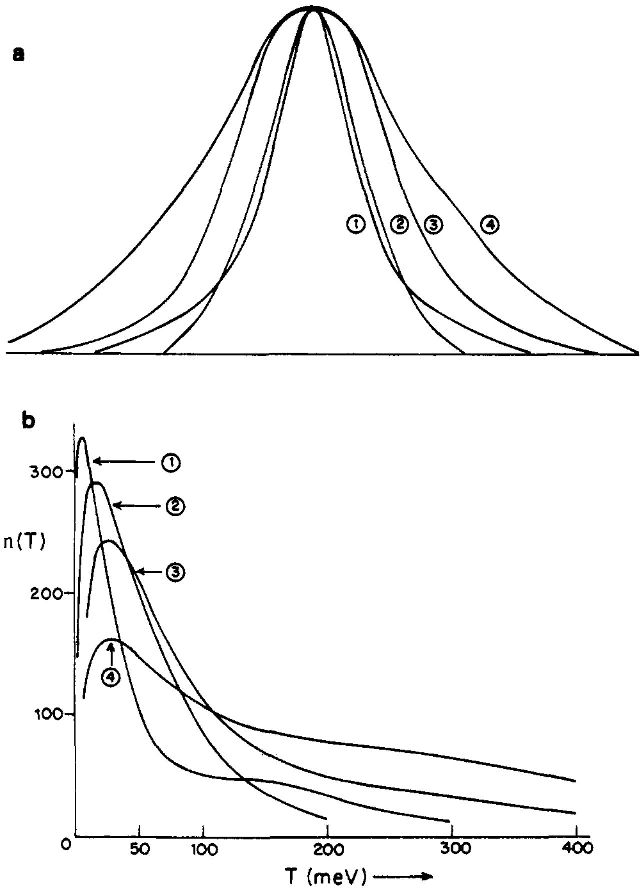


Figure 1. Metastable peak shapes (a) and the associated kinetic energy release distributions (b) for the loss of CO from $[C_4H_4O]^{+\cdot}$ ions derived from (1) furan, (2) vinylketene, (3) 2-pyrone, and (4) 4-pyrone.

In contrast, the kinetic energy release distributions for the loss of CO from furan and the two pyrones show that a wide range of kinetic energies is released upon fragmentation. This implies that considerable excess energy is required for these $[C_4H_4O]^{+\cdot}$ ions to rearrange to the transition state for the dissociation step. Indeed, the loss of CO from $[\text{furan}]^{+\cdot}$ has such a high activation energy[21] that the energy level of the transition state (~280 kcal mol^{-1}) makes thermochemically feasible the participation of many isomeric $[C_4H_4O]^{+\cdot}$ structures (cf. Table I).

Therefore, for these isomeric $[C_4H_4O]^{+\cdot}$ ions no firm deductions can be made from metastable peak characteristics concerning the structures of either the reacting or the nonreacting ions. Pirkle and Dine's deuterium labeling experiments[3] elegantly demonstrate that the metastably fragmenting (but energy rich) $[C_4H_4O]^{+\cdot}$ ions from 2-pyrone do not undergo reversible ring closure. However, this conclusion may not be extrapolated to the structure of the ions which give rise to the intense peaks at m/z 68 in the normal 70-eV mass spectra of both pyrones. These peaks largely consist of $[\text{furan}]^{+\cdot}$ ions.

Experimental Section

The collisional activation and the metastable ion (MI) spectra were measured on a Vacuum Generators ZAB-2F double-focussing mass spectrometer of reversed Nier–Johnson geometry. A 100-μA ionizing electron beam of 70 eV and an accelerating potential of 7920 V were used; sample reservoir and ion source temperatures were ~130 °C. The magnetic field was set to select the m/z 68 $[C_4H_4O]^{+\cdot}$ precursor ions; ionic products of their metastable decompositions (the MI spectrum) occurring in the field free drift region between the magnetic and electrostatic analyzers were measured by scanning the electrostatic analyzer (ESA) potential under conditions of good energy resolution. (Main beam width was 0.10 V at an ESA voltage of 422.1 V.) Kinetic energy releases were calculated in the usual way and corrected for limiting half-height width of the main beam. CA spectra were obtained in the same way after introduction of helium as a collision gas in the collision chamber near the β focal point. An external voltage (−320 V) was applied on the chamber to separate the normal metastable peaks from the CA peaks.

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(21) AE ($[C_3H_4]^{+\cdot}$) from furan = 11.80 eV, measured with energy selected electrons.[4] Note that this energy lies above the calculated thermochemical thresholds for production of CO ($\Delta H_f = -26.4$ kcal mol^{-1})[9] and AE($[CH_2{=}C{=}CH_2]^{+\cdot}$) = 10.88[9] or $[CH_3C{\equiv}CH]^{+\cdot}$ = 11.48 eV[9]—and even AE($[\text{cyclopropene}]^{+\cdot}$) = 11.74 eV.[9] The discontinuity in the energy release distribution (Figure 1) may reflect the co-generation of two different product ion structures. The large activation energy may represent that required for ring opening.

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 34. Rate Constants for Spin Trapping. 2. Secondary Alkyl Radicals[1]

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Abstract: The cyclization of the secondary 6-hepten-2-yl radical to form the primary 2-methylcyclopentylcarbinyl radical has been studied by kinetic EPR spectroscopy. The rate constant for this cyclization, k_c, can be represented by $\log (k_c/s^{-1}) = (9.8 \pm 0.3) - (6.4 \pm 0.3)/\theta$ where $\theta = 2.303RT$ kcal/mol. This cyclization has been used as a standard to measure the absolute rate constants for the spin trapping of secondary alkyls in benzene at 40 °C by a few of the more commonly employed spin traps. These results are compared with the previously determined[4] k^T values for trapping primary alkyl radicals under the same conditions. Relative k^T values for trapping of the tertiary 2-phenylprop-2-yl radical have also been measured.

Spin trapping[3] is an EPR spectroscopic technique that has proved immensely valuable in studies of reaction mechanisms because it allows transient radicals, R·, to be "visualized" by reacting them with a spin trap, T, to form a persistent spin adduct, RT·:

$$R\cdot + T \xrightarrow{k^T} RT\cdot$$

As we have pointed out previously,[4] spin trapping will only achieve its full potential when quantitative data on the rate constants, k^T, for trapping of all types of R· radicals become available. In our initial studies of spin-trapping rates[4,5] we worked with primary alkyl radicals. In the present paper, we report an extension of this work to secondary alkyls. Our experimental procedure is almost unchanged. In the earlier

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