

Letters to the Editor

Dear Sir

Loss of CO from 4,6-Dimethyl-2-pyrone and 2,6-Dimethyl-4-pyrone Radical Cations

The molecular ions of 2-pyrone and 4-pyrone and related compounds eliminate CO.¹ There has been considerable controversy about the mechanism and the structures of the product ions of this reaction,^{2,3} but the generation of furan ions as stable daughter ions seems *a priori* very reasonable. The formation of furan ions together with some vinylketene ions as stable products of CO loss from 2- and 4-pyrone has been proved by Holmes and Terlouw⁴ with the aid of collision-induced decompositions (CID) of the $[C_4H_4O]^+$ ions, but no firm structural assignment could be made for product ions with sufficient energy for unimolecular decomposition because the corresponding metastable ion (MI) spectra of the $[C_4H_4O]^+$ ions investigated were all different.

We have recently shown that the molecular ions of the isomeric dimethylfurans give rise to different MI spectra and different collisional activation (CA) spectra.⁵ Thus, in contrast to xylene ions, the dimethylfuran ions do not interconvert into the same ion structure or mixture of ion structures within the time-frame of a double focusing mass spectrometer. The loss of CO from the molecular ions of 4,6-dimethyl-2-pyrone (**1**) and 2,6-dimethyl-4-pyrone (**2**), respectively, should result in 2,4-dimethylfuran (**3**) and 2,5-dimethylfuran (**4**) ions if the fragmentation reaction occurs without skeletal rearrangement (Scheme 1). Hence, the MI and CA spectra of the $[M-CO]^+$ ions of **1** and **2** should make possible a structural assignment. The MI and CA spectra of the $[M-CO]^+$ ions in the 70 eV mass spectra of **1** and **2** and those of the molecular ions of 2,4-dimethylfuran (**3**), 2,5-dimethylfuran (**4**), 2,3-dimethylfuran (**5**), and 3,4-dimethylfuran (**6**) are reported in Table 1. It can be clearly seen that the MI and CA spectra of **3-6** are different and that the spectra of the $[M-CO]^+$ ion of **1** matches only those of

Table 1. MI and CA spectra of $[C_6H_8O]^+$ ions of 1-6

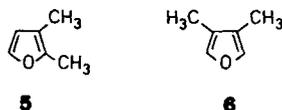
MI spectra ^a			
	m/z 95	m/z 81	m/z 68
1	88	6	6
2	96	4	—
3	85	7	8
4	94	6	—
5	82	16	2
6	76	7	17

CA spectra ^{a,b}													
	m/z 95	m/z 81	m/z 68	m/z 67	m/z 65	m/z 63	m/z 53	m/z 51	m/z 50	m/z 43	m/z 41	m/z 39	m/z 27
1 (166)	(26)	(25)	23	8	3	9	6	5	9	15	17	5	
2 (271)	(47)	—	3	2	1	12	12	9	39	7	7	8	
3 (108)	(20)	(20)	23	10	2	8	6	5	9	16	16	5	
4 (283)	(51)	—	5	3	1	14	11	5	41	5	5	8	
5 (163)	(44)	(5)	13	6	1	10	8	6	20	13	15	7	
6 (100)	(12)	(20)	27	8	2	8	7	5	2	17	18	7	

^a Intensities as percentage of total fragment ion intensity.

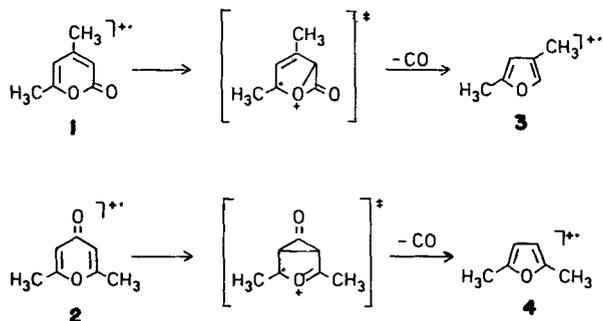
^b Unimolecular decompositions excluded from normalization and given in parentheses.

the molecular ions of **3** and that there is a similar correspondence between the spectra of the $[M-CO]^+$ ions of **2** and the molecular ions of **4**. These observations corroborate the results of Holmes and Terlouw⁴ with respect to a furan structure for the



stable product ions of the CO elimination from pyrone molecular ions. As the MI spectra are also very similar in our case, a furan structure of the *metastable* $[M-CO]^+$ ions is also very likely. It should be noted, however, that the present results prove only the same structures for the $[C_6H_8O]^+$ ions arising from **1** and **2** and the corresponding dimethylfurans. It cannot be excluded that some rearrangement does occur in the molecular ions of the dimethylfurans prior to unimolecular decomposition or CID in the second field-free region.

The loss of CO is the only unimolecular reaction of the metastable molecular ions of **1** and **2** observed in the second field-free region of a Vacuum Generator ZAB-2F mass spectrometer after ionization with 70 eV electrons. By analogy with the fragmentations of the unsubstituted pyrones,⁴ broad, dish-topped peaks are observed for the loss of CO in the MIKE spectra. The values of the kinetic energy T_{50} released during the CO loss and calculated from the peak width at 50% intensity are 31 kJ mol⁻¹ and 63 kJ mol⁻¹ for **1** and **2**, respectively. The large values of T_{50} and the non-statistical distribution clearly indicate a reverse critical energy for the CO elimination both from **1** and **2**. This is corroborated by a determination of the appearance energies (AE) of the $[M-CO]^+$ ions of **1** and **2** and by a calculation of the thermochemical threshold[†] for the formation of dimethylfuran ions **3** and **4**, respectively, from **1** and **2**. The heats of formation of the neutrals **1-6** are not known by experiment but can be calculated either by increments⁶ or by the MNDO program.⁷ From the results reported in Table 2 it is seen that the MNDO values are systematically lower by about 20 kJ mol⁻¹. However, as these deviations occur for the dimethylpyrones **1** and **2** (educt side of the reaction) and for the dimethylfurans (product side of the reaction), they cancel each other in the calculation of the heats of reaction. The ionization



Scheme 1

[†] The thermochemical threshold is the AE calculated from the enthalpy of reaction $M \rightarrow [F]^+ + N$; i.e. $AE([F]^+)_{th} = \Delta H_f([F]^+) + \Delta H_f(N) - \Delta H_f(M)$.

Table 2. Calculated heats of formation and experimental ionization energies and appearance energies of 1-5

	$\Delta H_f(M)^a$		IE(M) ^{a,b}	AE([M-CO] ⁺) ^{a,b}
	Incr. ⁶	MNDO ⁷		
1	-257	-285	821	950
2	-235	-255	871	988
3	-102	-113	810	—
4	-106	-126	796	—
5	-102	-121	796	—
CO	-111 ⁸			

^a kJ mol⁻¹.
^b ±10 kJ mol⁻¹.

energies of **3-5** of 796-810 kJ mol⁻¹ (Table 2) are slightly larger than the value of 773 kJ mol⁻¹ reported in the literature for **5**.⁸ Using the IEs of **3** and **4** and the average of the values of $\Delta H_f(h)$ obtained by increments and MNDO, a thermochemical threshold of 863 kJ mol⁻¹ and 814 kJ mol⁻¹ (±10 kJ mol⁻¹) is obtained for the formation of **3** and **4** from **1** and **2**, respectively, by CO elimination. This is considerably below the experimental AEs of 950 kJ mol⁻¹ for **1** and 988 kJ mol⁻¹ for **2**.

It is of interest to note that the larger AE is obtained for **2** in spite of the lower thermochemical threshold. A similar difference has been observed for the CO elimination from 2- and 4-pyrone.⁴ The data reported in Table 2 indicate a reverse critical energy ϵ_r^\ddagger of 88 ± 10 kJ mol⁻¹ and 174 ± 10 kJ mol⁻¹ for the CO elimination from **1** and **2**, respectively. Thus, the higher AE

and the lower thermochemical threshold for the reaction of **2** results in an increase of ϵ_r^\ddagger . This difference in ϵ_r^\ddagger is also reflected by the larger value of T_{50} observed for the CO loss from **2**. However, in both the reaction of **1** and **2** about 36% of ϵ_r^\ddagger is released as kinetic energy. Hence, with respect to the partition of ϵ_r^\ddagger between internal energy and kinetic energy of the products, both reactions behave identically. In addition, the critical energy of the forward reaction ϵ_f^\ddagger (= AE - IE) is very similar for the CO elimination from the molecular ions of **1** and **2**. Therefore, the mechanism of the CO elimination from these molecular ions appears to be identical and gives rise to the corresponding dimethylfuran ions without skeletal rearrangements.

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Yours

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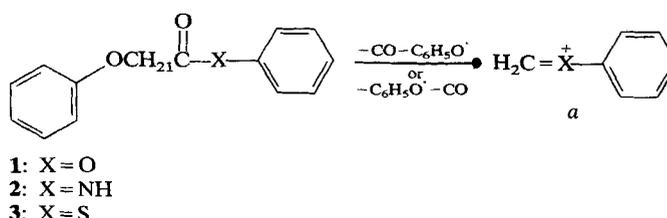
Dear Sir

Rearrangement in the Mass Spectra of Phenoxyacetyl Derivatives

An interesting observation in the mass spectra of alkyl phenoxythioacetates¹ and thiophenoxythioacetates² is the simultaneous or rapid successive elimination of phenoxy or thiophenoxy radical and CO. Tomer and coworkers¹ postulated that the d orbitals on sulphur may be responsible for this kind of unusual phenomenon. With a view to understanding the mechanism of the rearrangement the present study of the mass spectra of phenyl phenoxyacetate (**1**), *N*-phenylphenoxyacetamide (**2**) and *S*-phenyl phenoxythioacetate (**3**) (Scheme 1) was undertaken.

It can be seen from Table 1 that ion *a* (Scheme 1) is the most intense peak for all three compounds. The formation of ion *a* in **1** and **2** clearly shows that the S atom is not essential for such a rearrangement. Though the ion at *m/z* 107 in **1** could arise by a simple α -cleavage, a similar process in **2** and **3** does not give rise to very intense ions. This also shows that in **1** the rearrangement is a dominant process.

Analysis of the daughter ion spectra of the molecular ions of **1**, **2** and **3** by linked



Scheme 1

Table 1. Partial mass spectra of **1**, **2** and **3** taken at 70 eV on VG Micromass 7070-H

Ions	Intensities Σ_{36}		
	1	2	3
[M] ⁺	3.0	7.1	1.4
[M-CO] ⁺	3.2	—	—
[M-C ₆ H ₅ O] ⁺	0.3	1.4	—
[M-CO-C ₆ H ₅ O] ⁺ (<i>a</i>)	24.7	16.6	16.3
<i>m/z</i> 107	24.7	4.3	4.3

scan in the first field-free region (FFR) shows that ion *a* is formed directly from the molecular ion (Table 2) in addition to the other stepwise processes. The intensity of *a* is enhanced under CAD in **1** and **2**. This

suggests that the direct formation of *a* is an energetic process in **1** and **2** whereas in **3** it is a low-energy process. Rapid successive elimination of CO and C₆H₅O[•] (or C₆H₅O[•] and CO) must be occurring in these com-