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Skeletal Rearrangements Preceding CO Loss from Metastable Phenoxymethylene Ions Derived from Phenoxyacetic Acid and Anisole†

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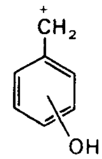
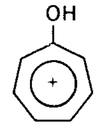
The loss of $CHO_2^{\cdot}$ from the molecular ion of phenoxyacetic acid and the expulsion of an $H^{\cdot}$ atom from ionized anisole lead to phenoxymethylene ions, which fragment predominantly by CO loss on the microsecond time-scale. Carbon-13 labelling reveals that ~90% of the CO molecules expelled from the metastable ions derived from phenoxyacetic acid incorporate the carbon atom from the 1-position of the phenyl group of the parent compound, whereas the residual CO molecules contain one of the other carbon atoms of the aromatic ring. The 2-fluoro- and 2-methylphenoxymethylene ions derived from the appropriate aryloxyacetic acids behave similarly, i.e. the carbon atom of the methylene group of the parent compound is not incorporated in the expelled CO molecules. In contrast, ~45% of the CO molecules eliminated from the metastable phenoxymethylene ions formed from ionized anisole contain the carbon atom of the methyl group, while the remaining part contains the carbon atom from the 1-position of the phenyl ring of the parent compound. This result is taken as evidence for the occurrence of a skeletal rearrangement of the anisole molecular ion leading to an interchange between the carbon atom of the methyl group and the carbon atom at the 1-position of the ring. The elimination of CO from the metastable ions generated from either phenoxyacetic acid or anisole gives rise to a composite metastable peak. Conclusive evidence as to the formation of $[C_7H_7O]^+$ isomers other than the phenoxymethylene ion is not obtained, indicating that the composite metastable peak is a result of two competing reactions both leading to CO loss. Possible mechanisms of these reactions are discussed together with the mechanism of the skeletal rearrangement of the molecular ion of anisole prior to $H^{\cdot}$ loss.

INTRODUCTION

The unimolecular reactions of gaseous (radical) cations derived from aromatic compounds often involve extensive skeletal rearrangements, which may precede or occur concomitant with product formation.[1-6] Pertinent examples include the formation of tropylium ions in the dissociations of the molecular ions of alkylbenzenes[1,2,4,7-11] and the loss of the identity of the cyano-function in metastable benzonitrile ions leading to prevalent loss of hydrogen cyanide molecules with a carbon atom originating from the aromatic ring.[12] With respect to the tropylium ion, numerous studies[4,13] have been concerned with the generation and stability of this ion as well as the benzyl ion and similar questions have been addressed to the substituted species, e.g. the hydroxybenzyl (**a**) and the hydroxytropylium (**b**) cations.[14-19] According to experimental[14,15] and theoretical[17-19] studies, these $[C_7H_7O]^+$ ions are stable species in the gas phase, which can be distinguished from other isomers such as methyl-substituted phenoxy cations (**c**), oxygen-protonated benzaldehyde (**d**) and the phenoxymethylene ion (**e**).



a



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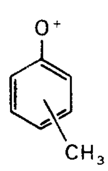

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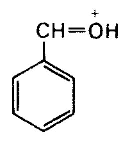

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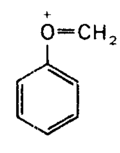

e

The different metastable $[C_7H_7O]^+$ ions, **a**–**e**, are known to react by competing eliminations of CO and CH_2O.[15] The loss of a CO molecule is the predominant process and it is evident that this reaction of, for example, the phenoxymethylene ion requires a structural reorganization before the reactant configuration is reached.

The phenoxymethylene ion is known to be formed by fragmentation of the molecular ions of 1-phenoxypropan-2-one[14,15] and the methyl ester of phenoxyacetic acid.[16] The loss of CO from metastable phenoxymethylene ions is reported to give rise to a composite metastable peak in contrast to CO elimination from the metastable **a**–**d** ions, which leads to a broad peak only.[15] In general terms, a composite peak for a given dissociation of a metastable frgment ion indicates (i) the existence of two different reaction channels, (ii) the generation of two isomeric non-

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interconverting species in the reaction of the primary ion or (iii) the formation of ions in different isolated electronic states.[20,21] With respect to $[C_7H_7O]^+$ ions, previous reports concerned with the reactions of metastable phenoxymethylene ions have not provided insight into the origin of the carbon atom, which is incorporated in the expelled neutral species. In order to achieve this insight and shed some light on the mechanism of CO elimination from phenoxymethylene ions, we have examined this process by ^{13}C-labelling and metastable peak analysis.

Phenoxyacetic acid was selected as the precursor of phenoxymethylene ions since the molecular ion of this compound readily expels $CHO_2^{\bullet}$ with formation of abundant $[C_7H_7O]^+$ ions. Similarly, we used methyl and fluorine containing phenoxyacetic acids as precursors for substituted phenoxymethylene ions with the purpose of determining the influence of these substituents on the CO loss. Further, loss of a hydrogen atom from the methyl group in ionized anisole may be thought to give rise to phenoxymethylene ions as well. To examine this possibility, we studied the behaviour of the appropriate species generated from the molecular ions of deuterium and/or ^{13}C-labelled anisoles.

EXPERIMENTAL

The electron impact (EI) and mass-analyzed ion kinetic energy (MIKE)[20] spectra were recorded with a Fisons ZAB-2HFqQ reverse-geometry double-focusing quadrupole hybrid mass spectrometer. The compounds were introduced into the combined EI–chemical ionization (CI) source through a septum inlet system heated to 150 °C or with a heated direct insertion probe. The ion-source conditions were: ionization energy 10–70 eV, acceleration voltage 8 kV, ion repeller potential 0 V with respect to the ion source chamber and temperature 150–190 °C.

Materials

Aryloxyacetic acids. Phenoxyacetic acid was prepared by reaction of sodium phenolate with chloroacetic acid.[22] The methyl- and fluorine-substituted compounds were prepared likewise by reaction of the appropriate phenolate anion with chloroacetic acid. The $C_6H_5O^{13}CH_2CO_2H$ (95% ^{13}C) compound was synthesized by first preparing $^{13}CH_3CO_2H$ by reaction of the Grignard reagent of $^{13}CH_3I$ with carbon dioxide and then converting the labelled acetic acid into bromoacetic acid before the reaction with sodium phenolate. Phenoxyacetic acid labelled with a ^{13}C atom at the 1-position of the ring was prepared from [1-^{13}C]phenol (90% ^{13}C) and bromoacetic acid. The [1-^{13}C]phenol compound was synthesized by first preparing [1-^{13}C]-4-nitrophenol from [2-^{13}C]acetone and nitromalonaldehyde monohydrate and subsequently removing the nitro group by reduction with $NaBH_4$ followed by diazotization and reaction with hypophosphorous acid.[23] The $C_6D_5OCH_2CO_2H$ (>98% d_5) compound was prepared from C_6D_5OH and chloroacetic acid, while $C_6H_5OCD_2CO_2H$ (98% d_2) was synthesized from phenol and $BrCD_2CO_2D$. All compounds were purified by recrystallization from water and their identity was confirmed by mass spectrometry and NMR.

Anisoles. The $C_6D_5OCH_3$ (90% d_5 and 10% d_4) compound was prepared from deuterium-labelled phenol and CH_3I, whereas $C_6H_5OCD_3$ (99% d_3 and 1% d_2) was prepared from unlabelled phenol and CD_3I.[22] Anisole labelled with a ^{13}C atom at the 1-position of the aromatic ring (99% ^{13}C) was synthesized by reaction of the appropriately labelled phenol (see Acknowledgements) with dimethyl sulphate, whereas $C_6H_5O^{13}CH_3$ (98% ^{13}C) was synthesized from unlabelled phenol and $^{13}CH_3I$. The $C_6D_5O^{13}CH_3$ (75% d_5 and 25% d_4) compound was prepared by reaction of deuterium-labelled phenolate anions with $^{13}CH_3I$. The $C_6H_5O^{13}CD_3$ (99% ^{13}C and 99.5% d_3) compound was prepared from unlabelled phenol and $^{13}CD_3I$. The compounds were purified by preparative gas chromatography prior to use (column, Reoplex 400; temperature, 100 °C) and their identity was ascertained by mass spectrometry.

RESULTS

Aryloxyacetic acids

The molecular ions of the aryloxyacetic acids, $YC_6H_4OCH_2CO_2H$ (Y = H, CH_3 and F), dissociate readily by loss of $CHO_2^{\bullet}$ with formation of $[YC_7H_6O]^+$ ions. The molecular ions of the deuterium-labelled compounds $C_6H_5OCD_2CO_2H$ and $C_6D_5OCH_2CO_2H$ expel in the ion source only $CHO_2^{\bullet}$, indicating that hydrogen atom interchange is not occurring prior to this reaction.

The $[YC_7H_6O]^+$ ions derived from the aryloxyacetic acids fragment further on the microsecond time-scale by the competing losses of CO and CH_2O as indicated in Table 1 and Eqns (1) and (2).

$$YC_6H_4OCH_2CO_2H^{+\bullet} \xrightarrow[-CHO_2^{\bullet}]{}$$

$$[YC_7H_6O]^+ \longrightarrow [YC_6H_6]^+ + CO \qquad (1)$$

$$[YC_7H_6O]^+ \longrightarrow [YC_6H_4]^+ + CH_2O \qquad (2)$$

$$Y = H,\ CH_3 \text{ and } F$$

The elimination of formaldehyde is a minor reaction of the metastable $[YC_7H_6O]^+$ ions. This process involves only the atoms of the oxygen–methylene function in the parent compound as indicated by the exclusive loss of CD_2O from the $[C_7H_5D_2O]^+$ ions generated from ionized $C_6H_5OCD_2CO_2H$ and the exclusive elimination of $^{13}CH_2O$ from the $[C_7{}^{13}CH_9O]^+$ ions derived from 2-methylphenoxyacetic acid labelled with a ^{13}C atom in the methylene group (Table 2). Introduction of a methyl group at the 2- and the 6-position results in predominant elimination of formaldehyde, as disclosed by the results obtained for the metastable ions generated by $CHO_2^{\bullet}$ loss from ionized 2,6-dimethylphenoxyacetic

Table 1. Reactions of the metastable ions formed by loss of $CHO_2^{\bullet}$ from the molecular ions of aryloxyacetic acids[a]

Parent compound	Reactant ion	Loss (%) CO	CH_2O	H_2O	$CH_3^{\bullet}$	HF	CHFO
$C_6H_5OCH_2CO_2H$	$[C_7H_7O]^+$	96	4	—	—	—	—
$2\text{-}CH_3C_6H_4OCH_2CO_2H$	$[C_8H_9O]^+$	86	14	—	—	—	—
$3\text{-}CH_3C_6H_4OCH_2CO_2H$	$[C_8H_9O]^+$	85	7	8	—	—	—
$4\text{-}CH_3C_6H_4OCH_2CO_2H$	$[C_8H_9O]^+$	91	7	2	—	—	—
$2,6\text{-}(CH_3)_2C_6H_3OCH_2CO_2H$	$[C_9H_{11}O]^+$	3	93	—	4	—	—
$2\text{-}FC_6H_4OCH_2CO_2H$	$[C_7H_6FO]^+$	95	2	—	—	3	—
$3\text{-}FC_6H_4OCH_2CO_2H$	$[C_7H_6FO]^+$	93	2	—	—	5	—
$4\text{-}FC_6H_4OCH_2CO_2H$	$[C_7H_6FO]^+$	90	7	—	—	3	—
$2,6\text{-}F_2C_6H_3OCH_2CO_2H$	$[C_7H_5F_2O]^+$	39	—	—	—	5	56
$C_6F_5OCH_2CO_2H$	$[C_7F_5H_2O]^+$	85	—	—	—	—	15

[a] See also text.

acid (Table 1). Loss of a formaldehyde molecule is not observed if the 2- and 6-positions are substituted with fluorine atoms. Instead, the metastable $[C_7H_5F_2O]^+$ ions formed from 2,6-difluorophenoxyacetic acid eliminate CHFO in addition to CO loss [Eqn (3)]. The former process is favoured over CO loss and observed only if a fluorine atom is introduced at the 2- and 6-positions, i.e. the metastable $[C_7H_6FO]^+$ ions derived from 2-fluorophenoxyacetic acid do not expel CHFO (Table 1).

$$\underset{m/z\ 143}{[C_7H_5F_2O]^+} \longrightarrow \underset{m/z\ 95}{[C_6H_4F]^+} + CHFO \qquad (3)$$

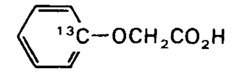
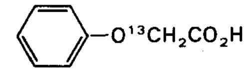
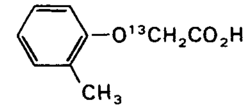
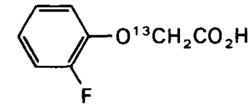
Loss of $CHO_2^{\bullet}$ from the molecular ion of phenoxyacetic acid containing a ^{13}C atom in the methylene group yields $[C_6{}^{13}CH_7O]^+$ ions, which expel exclusively unlabelled carbon monoxide [Eqn (4) and Table 2]. A similar result is obtained for the metastable ions generated by $CHO_2^{\bullet}$ loss from the molecular ions of 2-fluoro- and 2-methylphenoxyacetic acids labelled with a ^{13}C atom at the methylene position. The metastable $[C_6{}^{13}CH_7O]^+$ ions derived from phenoxyacetic acid containing a ^{13}C atom at the 1-position of the ring eliminate ~90% ^{13}CO and ~10% CO (Table 2).

$$\underset{m/z\ 153}{\left.C_6H_5\text{-}O\text{-}{}^{13}CH_2CO_2H\right]^{+\bullet}} \xrightarrow[-CHO_2^{\bullet}]{}$$

$$\begin{tikzcd} & \underset{m/z\ 80}{[C_5{}^{13}CH_7]^+ + CO} \quad (4a) \\ \underset{m/z\ 108}{[C_6{}^{13}CH_7O]^+} \arrow[ur] \arrow[dr, "/\!/"] & \\ & \underset{m/z\ 79}{[C_6H_7]^+ + {}^{13}CO} \quad (4b) \end{tikzcd}$$

Loss of CO from the metastable $[C_7H_7O]^+$ ions derived from phenoxyacetic acid gives rise to a composite metastable peak (Fig. 1), as reported previously.[15]

Table 2. Relative importance of CO and CH_2O elimination from the metastable ions generated by CHO_2 loss from the molecular ions of deuterium and ^{13}C-labelled aryloxyacetic acids[a]

Parent compound	Reactant ion	Loss (%) CO	^{13}CO	CH_2O	$^{13}CH_2O$	CD_2O
$C_6H_5OCD_2CO_2H$	$[C_7D_2H_5O]^+$	98	—	—	—	2
$C_6D_5OCH_2CO_2H$	$[C_7D_5H_2O]^+$	96	—	4	—	—
 $^{13}C\text{—}OCH_2CO_2H$	$[C_6{}^{13}CH_7O]^+$	10	80	10	—	—
 $\text{—}O^{13}CH_2CO_2H$	$[C_6{}^{13}CH_7O]^+$	99	—	—	1	—
 $\text{—}O^{13}CH_2CO_2H$, CH_3	$[C_7{}^{13}CH_9O]^+$	85	—	—	15	—
 $\text{—}O^{13}CH_2CO_2H$, F	$[C_6{}^{13}CH_6FO]^+$	>99	—	—	<1	—

[a] See also Table 1 and text.

The relative importance of the broad and narrow component is independent of the electron energy, indicating that the metastable $[C_7H_7O]^+$ ions generated from phenoxyacetic acid by ionization with 10 eV electrons behave as the ions formed by 70 eV ionization. Moreover, the metastable peak associated with ^{13}CO loss from the ions derived from phenoxyacetic acid labelled with a ^{13}C atom at the 1-position of the phenyl ring is composite and indistinguishable from the peak corresponding to this reaction of the unlabelled ions. This holds also for the loss of CO from the $[C_6{}^{13}CH_7O]^+$ ions derived from $C_6H_5O^{13}CH_2CO_2H$.

Elimination of CO from the $[C_8H_9O]^+$ ions derived from the methyl-substituted phenoxyacetic acids gives rise also to a composite metastable peak. The relative contributions of the broad and narrow components to the peaks are dependent on the position of the methyl group in the parent compound, as can be seen by comparing Figs 2(a)–(c). For example, the broad component is particularly pronounced for CO loss from the metastable $[C_8H_9O]^+$ ions derived from 2-methylphenoxyacetic acid, whereas the peak for CO loss from the ions generated from the 3-methyl-substituted acid is dominated by the narrow component.

The introduction of a fluorine atom causes the narrow component to disappear and only a broad, flat-topped metastable peak is observed for the loss of CO from the $[C_7H_6FO]^+$ ions derived from the 2-, 3- and 4-fluorophenoxyacetic acids. The values of the kinetic energy released (as determined from the width at half-height of the peaks)[20] during CO loss from the $[C_7H_6FO]^+$ ions are given in Table 3 together with the values for CO loss from metastable $[C_7H_7O]^+$ ions generated from different precursors.

Anisoles

The molecular ion of anisole reacts in the ion source to a minor extent by loss of $H^\bullet$ with formation of $[C_7H_7O]^+$ ions. The relative intensity of the signal corresponding to these ions in the 70 eV spectrum of anisole is about 1.6% of that of the molecular ion peak, which is the base peak in the spectrum. Deuterium labelling reveals that the $H^\bullet$ may originate either from the methyl or the phenyl group, but an accurate estimate of the relative extents of $H^\bullet$ and $D^\bullet$ loss in the ion-source reactions of the deuterium-labelled anisole ions is hampered by the presence of ~1% of $C_6H_5OCD_2H$ in the sample of $C_6H_5OCD_3$ and ~10% of $C_6D_4HOCH_3$ in the sample of $C_6D_5OCH_3$ (see Experimental).

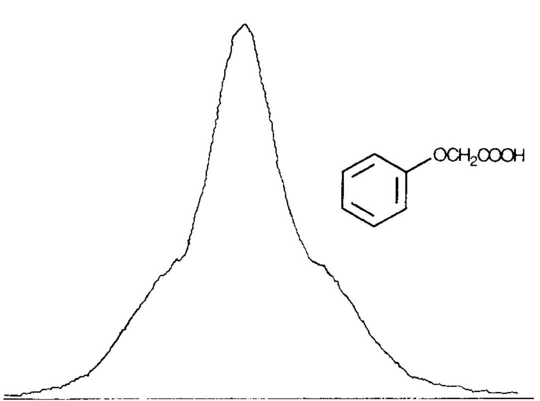


Figure 1. Composite metastable peak associated with the elimination of CO from the metastable $[C_7H_7O]^+$ ions generated by $CHO_2^\bullet$ loss from the molecular ion of phenoxyacetic acid (see text).

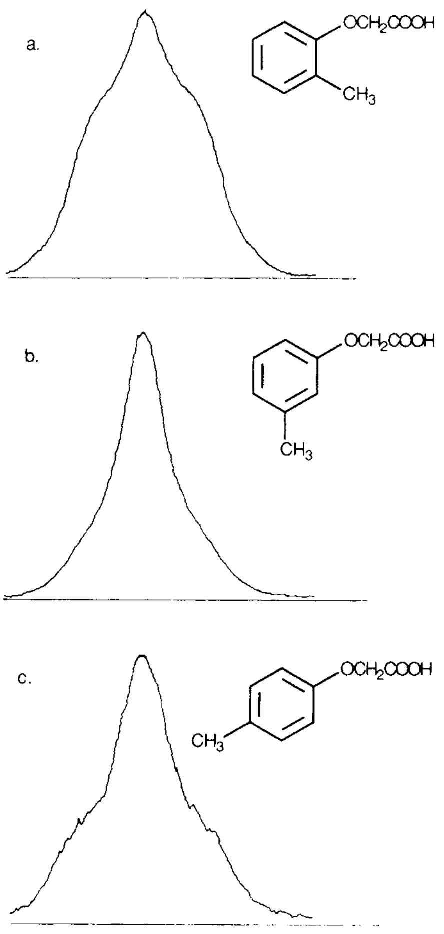


Figure 2. Composite metastable peaks associated with the elimination of CO from the metastable $[C_8H_9O]^+$ ions generated by $CHO_2^\bullet$ loss from the molecular ions of (a) 2-methylphenoxyacetic acid, (b) 3-methylphenoxyacetic acid and (c) 4-methylphenoxyacetic acid (see text).

The metastable molecular ions of anisole react by the competing losses of $H^\bullet$, $CH_3^\bullet$, $HCO^\bullet$, CH_2O and CO.[24–26] Elimination of CH_2O is the main process and is associated with a composite metastable peak, as discussed in detail previously.[24] The losses of $CH_3^\bullet$, $HCO^\bullet$ and CO are of minor importance, whereas $H^\bullet$ loss is a pronounced reaction of the metastable ions, as indicated in Table 4.

Introduction of deuterium atoms at either the methyl or the phenyl groups leads to the competing losses of $D^\bullet$ and $H^\bullet$ from the metastable molecular ions. The relative intensities of the peaks corresponding to $H^\bullet$ and $D^\bullet$ loss from ionized $C_6H_5OCD_3$ and $C_6D_5OCH_3$ are 80:20 and 70:30, respectively. These ratios are significantly different from those expected for the occurrence of non-selective loss of $H^\bullet$ and $D^\bullet$ from the 2- and 6-positions of the ring and the methyl group or complete loss of positional identity of the $H^\bullet$ and $D^\bullet$ prior to dissociation (see Table 5).

The occurrence of partial interchange between the hydrogen atoms of the methyl and phenyl groups is

Table 3. Kinetic energy released ($T_{0.5}$) during CO loss from metastable $[C_7H_7O]^+$ and $[C_8H_9O]^+$ ions together with the values for some fluorine substituted analogues[a]

Parent compound	Reactant ion	Proposed structure	$T_{0.5}$ (meV)
$C_6H_5OCH_2CO_2H$	$[C_7H_7O]^+$	$C_6H_5OCH_2{}^+$	34/290[b]
$C_6H_5OCH_3$	$[C_7H_7O]^+$	$C_6H_5OCH_2{}^+$	28/275
$2\text{-}CH_3C_6H_4OCH_2CO_2H$	$[C_8H_9O]^+$	$2\text{-}CH_3C_6H_4OCH_2{}^+$	–/287[c]
$3\text{-}CH_3C_6H_4OCH_2CO_2H$	$[C_8H_9O]^+$	$3\text{-}CH_3C_6H_4OCH_2{}^+$	41/–[c]
$4\text{-}CH_3C_6H_4OCH_2CO_2H$	$[C_8H_9O]^+$	$4\text{-}CH_3C_6H_4OCH_2{}^+$	22/292[c]
$2\text{-}FC_6H_4OCH_2CO_2H$	$[C_7H_6FO]^+$	$2\text{-}FC_6H_4OCH_2{}^+$	268
$3\text{-}FC_6H_4OCH_2CO_2H$	$[C_7H_6FO]^+$	$3\text{-}FC_6H_4OCH_2{}^+$	270
$4\text{-}FC_6H_4OCH_2CO_2H$	$[C_7H_6FO]^+$	$4\text{-}FC_6H_4OCH_2{}^+$	266
$2,6\text{-}F_2C_6H_3OCH_2CO_2H$	$[C_7H_5F_2O]^+$	$2,6\text{-}F_2C_6H_3OCH_2{}^+$	316
$C_6F_5OCH_2CO_2H$	$[C_7F_5H_2O]^+$	$C_6F_5OCH_2{}^+$	288
$2\text{-}CH_3C_6H_4OCD_3$	$[C_7H_7O]^+$	$2\text{-}CH_3C_6H_4O^+$	274
$2\text{-}C_2H_5C_6H_4OH$	$[C_7H_7O]^+$	$HOC_6H_4CH_2{}^+$	345[d]
$C_6H_5CH_2OH$	$[C_7H_7O]^+$	$C_6H_5CH{=}OH^+$	200[d]
2-Methylcyclohepta-3,5-dienone	$[C_7H_7O]^+$	Hydroxytropylium	195[d]
$CH_2{=}CHCH_2CH_2CH{=}CHCO_2CH_3$	$[C_7H_7O]^+$	$CH_2{=}CHCH{=}CHCH{=}CHCO^+$	~50

[a] See also text.
[b] Values of 20/280 meV are given in Ref. 15.
[c] See also Fig. 2a–c.
[d] Taken from Ref. 15.

revealed in the loss of a methyl radical and a formaldehyde molecule. For example, the metastable molecular ions of $C_6H_5OCD_3$ expel $CD_3{}^\bullet$ and $CHD_2{}^\bullet$ in a ratio of 58:42 and CD_2O, CHDO and CH_2O in a ratio of 73:21:6. As indicated in Table 5, these results differ from those predicted for equilibration between the hydrogen atoms of the methyl group and all five hydrogen atoms of the phenyl ring or only the hydrogen atoms at the 2- and 6-positions.

Table 4. Relative importance of the reactions of the metastable molecular ions of anisole and its isotopomers[a]

Loss of	$C_6H_5OCH_3$	$C_6H_5O^{13}CH_3$	$C_6H_5OCD_3$	$C_6D_5OCH_3$
$H^\bullet$	20	30	18	15
$D^\bullet$	—	—	5	6
$CH_3{}^\bullet$	3	—	—	2
$^{13}CH_3{}^\bullet$	—	2	—	—
$CDH_2{}^\bullet$	—	—	—	~1
$CD_2H^\bullet$	—	—	~2	≤1
$CD_3{}^\bullet$	—	—	~3	—
CO	2	2	2	2
^{13}CO	—	—	—	—
$HCO^\bullet$	5	—	—	7
$H^{13}CO^\bullet$	—	6	—	—
$DCO^\bullet$	—	—	4	(—)[b]
CH_2O	70	—	(—)[b]	52
$H_2{}^{13}CO$	—	60	—	—
CHDO	—	—	12	14
CD_2O	—	—	54	1

[a] See also Table 5 and text.
[b] The losses of $DCO^\bullet$ and CH_2O give rise to product ions with the same nominal mass.

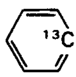
Table 5. Occurrence of hydrogen–deuterium atom interchange in the metastable molecular ions of the labelled anisoles[a]

	$C_6H_5OCD_3$			$C_6D_5OCH_3$		
		Statistical			Statistical	
Loss of	Exptl	A[b]	B[c]	Exptl	A[b]	B[c]
$H^\bullet$	80	40	62.5	73	60	37.5
$D^\bullet$	20	60	37.5	27	40	62.5
$CH_3{}^\bullet$	—	—	17.8	53	10	1.8
$CDH_2{}^\bullet$	—	30	53.6	34	60	26.8
$CD_2H^\bullet$	42	60	26.8	13	30	53.6
$CD_3{}^\bullet$	58	10	1.8	—	—	17.8
CH_2O[d]	6	10	35.7	82	30	10.7
CDHO	21	60	53.6	18	60	53.6
CD_2O	73	30	10.7	1	10	35.7

[a] Normalized abundances of the product ions of the given reaction.
[b] Estimated on the assumption that complete interchange occurs between the $H^\bullet$ and $D^\bullet$ of the methyl and the 2- and 6-positions of the phenyl ring. For $H^\bullet/D^\bullet$ loss this is equivalent to non-selective expulsion of an $H^\bullet$ or $D^\bullet$ from the methyl group and the 2- and 6-positions (see also text).
[c] Estimated on the assumption that complete interchange between all hydrogen and deuterium atoms occurs prior to dissociation. For $H^\bullet/D^\bullet$ loss this is equivalent to a non-selective process (see also text).
[d] The losses of $DCO^\bullet$ and CH_2O give rise to ions with the same nominal mass (see Table 4 and text).

The metastable $[C_7H_7O]^+$ ions derived from anisole eliminate CO, CH_2O and to some extent $H^\bullet$. The loss of CO from these ions is associated with a composite metastable peak, which is almost identical with the peak for the $[C_7H_7O]^+$ ions from phenoxyacetic acid (see Fig. 1). This is reflected in the kinetic energy released ($T_{0.5}$) during CO loss, which for the ions generated from anisole is determined to be 28 meV for the process leading to the narrow component and 275 meV for the reaction giving rise to the broad component. These values are close to those obtained for CO loss from the $[C_7H_7O]^+$ ions from phenoxyacetic acid (see Table 3) and, in addition, the relative importance of the narrow and broad component is essentially the same in the two instances. Notwithstanding these findings, the $[C_6{}^{13}CH_7O]^+$ ions formed by $H^\bullet$ loss from the molecular ion of anisole labelled with a ^{13}C atom in the methyl group eliminate ~55% CO and ~45% ^{13}CO [Eqn (5) and Table 6]. The complementary result is obtained if anisole is labelled with a ^{13}C atom at the 1-position of the ring, i.e. the metastable $[C_6{}^{13}CH_7O]^+$ ions derived

Table 6. Relative importance of CO and ^{13}CO loss from the metastable ions derived from ^{13}C-labelled anisoles[a]

Anisole	Reactant ion	Elemental composition of reactant ion	Loss (%) CO	Loss (%) ^{13}CO
$C_6H_5OCH_3$	$[M-H^\bullet]^+$	$[C_7H_7O]^+$	100	—
$C_6H_5O^{13}CH_3$	$[M-H^\bullet]^+$	$[C_6{}^{13}CH_7O]^+$	55	45
 $^{13}COCH_3$	$[M-H^\bullet]^+$	$[C_6{}^{13}CH_7O]^+$	45	55
$C_6H_5O^{13}CD_3$	$[M-H^\bullet]^+$	$[C_6{}^{13}CD_3H_4O]^+$	~20	~80
	$[M-D^\bullet]^+$	$[C_6{}^{13}CD_2H_5O]^+$	~75	~25
$C_6D_5O^{13}CH_3$	$[M-H^\bullet]^+$ [b]	$[C_6{}^{13}CD_5H_2O]^+$	≥80	≤20
	$[M-D^\bullet]^+$ [c]	$[C_6{}^{13}CD_4H_3O]^+$	~23	~77

[a] See also text.

[b] The sample of $C_6D_5O^{13}CH_3$ contained ~25% $C_6D_4HO^{13}CH_3$. The molecular ion of the latter isotopomer of anisole has the same nominal mass as the ion formed by $H^\bullet$ loss from ionized $C_6D_5O^{13}CH_3$. The loss of CO from metastable molecular ions of anisole is insignificant, however, and the carbon atom incorporated in the CO molecules originate entirely from the 1-position of the ring (Table 4).

[c] The loss of a $D^\bullet$ from $C_6D_5O^{13}CH_3$ yields ions with the same elemental composition as the ions formed by $H^\bullet$ loss from ionized $C_6D_4HO^{13}CH_3$. The ions formed by $H^\bullet$ loss from ionized $C_6D_4HO^{13}CH_3$ may eliminate mainly unlabelled carbon monoxide as observed for the species generated by $H^\bullet$ loss from ionized $C_6D_5O^{13}CH_3$. The pronounced loss of ^{13}CO can be ascribed, therefore, to the ions formed by $D^\bullet$ loss from ionized $C_6D_5O^{13}CH_3$.

from the ring-labelled anisole eliminate ~45% CO and ~55% ^{13}CO.

$$\underset{m/z\ 109}{C_6H_5O^{13}CH_3{}^{+\bullet}} \xrightarrow[-H^\bullet]{}$$

$$\underset{m/z\ 108}{[C_6{}^{13}CH_7O]^+} \begin{cases} \xrightarrow{\sim 55\%} \underset{m/z\ 80}{[C_5{}^{13}CH_7]^+} + CO & (5a) \\ \xrightarrow{\sim 45\%} \underset{m/z\ 79}{[C_6H_7]^+} + {}^{13}CO & (5b) \end{cases}$$

The results given in Table 6 for the $C_6H_5O^{13}CD_3$ and $C_6D_5O^{13}CH_3$ compounds reveal that the relative extent of CO and ^{13}CO loss depends on the origin of the $H^\bullet/D^\bullet$ expelled from the ionized molecules. For example, the metastable ions formed by loss of $H^\bullet$ from the molecular ion of the former anisole eliminate mainly ^{13}CO, whereas the ions formed by $D^\bullet$ loss fragment predominantly by CO loss [Eqn (6)].

$$\underset{m/z\ 112}{C_6H_5O^{13}CD_3{}^{+\bullet}} \xrightarrow[-H^\bullet]{}$$

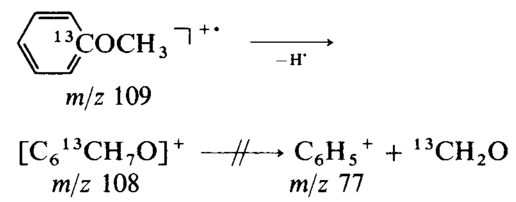
$$\underset{m/z\ 111}{[C_6{}^{13}CD_3H_4O]^+} \begin{cases} \xrightarrow{\sim 20\%} \underset{m/z\ 83}{[C_5{}^{13}CD_3H_4]^+} + CO & (6a) \\ \xrightarrow{\sim 80\%} \underset{m/z\ 82}{[C_6D_3H_4]^+} + {}^{13}CO & (6b) \end{cases}$$

Elimination of formaldehyde is more significant for the ions generated by $H^\bullet$ loss from ionized anisole than for the $[C_7H_7O]^+$ ions from phenoxyacetic acid, as can be seen by comparing the results summarized in Eqns (7) and (8) with those in Table 1.

$$\underset{m/z\ 108}{C_6H_5OCH_3{}^{+\bullet}} \xrightarrow[-H^\bullet]{}$$

$$\underset{m/z\ 107}{[C_7H_7O]^+} \begin{cases} \xrightarrow{\sim 18\%} \underset{m/z\ 77}{C_6H_5{}^+} + CH_2O & (7) \\ \xrightarrow{\sim 82\%} \underset{m/z\ 79}{[C_6H_7]^+} + CO & (8) \end{cases}$$

The study of formaldehyde elimination from the ions derived from the ^{13}C-labelled anisoles proved to be hampered by the presence of minor amounts of insufficiently or unlabelled anisole molecules in the samples (see Experimental). For example, the loss of $H^\bullet$ is a very minor process for the molecular ions of the ^{13}C-labelled anisoles and yields $[C_6{}^{13}CH_7O]^+$ ions, which have the same nominal mass as ionized unlabelled anisole. The presence of the latter ion prevented the determination of whether the $[C_6{}^{13}CH_7O]^+$ ions from $C_6H_5O^{13}CH_3$ react on the microsecond time-scale by elimination of CH_2O in addition to $^{13}CH_2O$ loss, which gives rise to ions in an abundance of ~13% relative to the ions generated by carbon monoxide loss. However, loss of $^{13}CH_2O$ is not observed for the metastable $[C_6{}^{13}CH_7O]^+$ ions from the molecular ion of anisole labelled with a ^{13}C atom at the 1-position [Eqn (9)], implying that the formaldehyde molecules contain only the carbon atom from the methyl group.



$$\underset{m/z\ 108}{[C_6{}^{13}CH_7O]^+} \not\longrightarrow \underset{m/z\ 77}{C_6H_5{}^+} + {}^{13}CH_2O \qquad (9)$$

A similar complication was encountered in the experiments with the sample of $C_6H_5OCD_3$, which contained about 1% $C_6H_5OCHD_2$. The loss of $H^\bullet$ from the molecular ion of the former compound yields a $[C_7H_4D_3O]^+$ ion, which has the same nominal mass as ionized $C_6H_5OCHD_2$, also generated in the ion source. Both of these ions may decompose by loss of CD_2O on the microsecond time-scale, thus leading to product ions of the same nominal mass. However, the metastable ions generated by $D^\bullet$ loss do not eliminate a formaldehyde molecule, i.e. only CO loss is observed for the $[C_7H_5D_2O]^+$ ions generated from $C_6H_5OCD_3$ [Eqns (10) and (11)].

$$\underset{m/z\ 111}{C_6H_5OCD_3{}^{+\bullet}} \xrightarrow[-D^\bullet]{}$$

$$\underset{m/z\ 109}{[C_7H_5D_2O]^+} \begin{cases} \not\longrightarrow \underset{m/z\ 77}{C_6H_5{}^+} + CD_2O & (10) \\ \longrightarrow \underset{m/z\ 81}{[C_6H_5D_2]^+} + CO & (11) \end{cases}$$

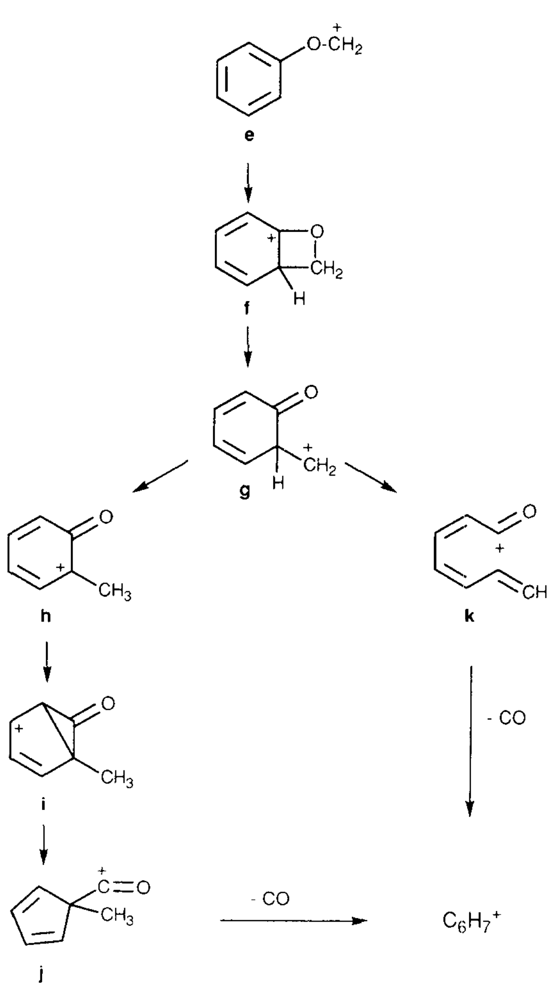
DISCUSSION

Mechanistic aspects of CO loss from phenoxymethylene ions

The composite metastable peak for CO elimination from the metastable $[C_7H_7O]^+$ ions derived from phenoxyacetic acid can arise, in principle by the occurrence of two different mechanisms for this process and/or the formation of two non-interconverting species in the loss of $CHO_2^{\bullet}$.[20,21] Structural reorganization of the molecular ion of phenoxyacetic acid seems unlikely in view of the result that the $CHO_2^{\bullet}$ species consist entirely of the atoms of the *original* carboxylic acid group in the parent compound. The possibility for isomerization of part of the $[C_7H_7O]^+$ ions prior to leaving the ion source is indicated by the reported observation that ~20% of the $[C_7H_7O]^+$ ions generated by 70 eV ionization of 1-phenoxypropan-2-one[14] or the methyl ester of phenoxyacetic acid[16] are unreactive towards the parent compound, whereas the main part of the ions reacts by a formal methylene cation transfer, in agreement with a phenoxymethylene structure. With respect to the metastable $[C_7H_7O]^+$ ions derived from phenoxyacetic acid, the eliminated formaldehyde molecules (see Table 1) consist only of the atoms of the oxygen–methylene function of the parent compound. This does not preclude that part of the ions which expel CO has rearranged to another structure prior to reaching the second field-free region (FFR) of the instrument. However, the shape of the composite metastable peak for CO loss is not affected by a decrease in the electron energy from 70 to 10–12 eV (see Results and Fig. 1). Based on these findings, it can be concluded that the metastable $[C_7H_7O]^+$ ions from phenoxyacetic acid have predominantly, if not exclusively, the phenoxymethylene structure. In other words, the composite metastable peak for CO loss arises as a result of two competing reactions.

The results of the ^{13}C-labelling experiments (Table 2) reveal clearly that the ions from phenoxyacetic acid eliminate CO molecules which contain predominantly the carbon atom from the 1-position of the ring and only to a minor extent CO molecules with one of the other carbon atoms of the phenyl group. A mechanistic proposal in agreement with the result that the bond between the oxygen atom and the carbon atom at the 1-position is retained in both of the reactions leading to CO loss is depicted in Scheme 1.

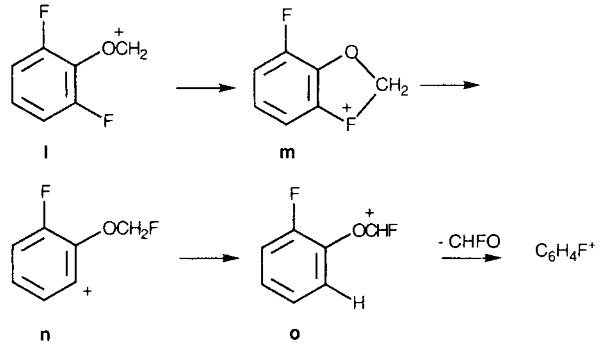
The initial step involves attack of the methylene group on the 2- or 6-position of the ring with formation of ion *f*. Cleavage of the bond between the oxygen atom and the methylene carbon atom in *f* yields ion *g*, which may isomerize to the 2-methyl phenoxy cation (*h*). This species can expel CO after rearranging to ion *j* in analogy with the mechanism often advanced for the loss of CO from the phenoxy cation. (The CO molecules expelled from metastable phenoxy cations incorporate only the carbon atom to which the oxygen atom is bonded in the initial structure, as revealed by the exclusive loss of ^{13}CO from the metastable ions generated by $CH_3^{\bullet}$ expulsion from the molecular ion of anisole labelled with a ^{13}C atom at the 1-position of the ring.)[27] The second route in Scheme 1 involves cleavage of the ring in ion *g* with formation of an acyclic acylium ion (*k*), which then dissociates by CO loss.



Scheme 1. Proposed reaction mechanism for the loss of CO from metastable phenoxymethylene cations.

The attack at the 2- or 6-position as the initial step is supported by the result that the ions derived from 2,6-dimethylphenoxyacetic acid eliminate predominantly formaldehyde and is further corroborated by the finding that the ions from 2,6-difluorophenoxyacetic acid expel CFHO (Table 1). The mechanism advanced for CHFO loss (Scheme 2) involves initial attack on a fluorine atom with formation of a fluoronium ion (*m*) followed by cleavage of the bond between the appropriate carbon atom of the ring and the fluorine atom leading to ion *n*. Subsequently a hydride shift may occur in *n* yielding ion *o*, which then eliminates CHFO.

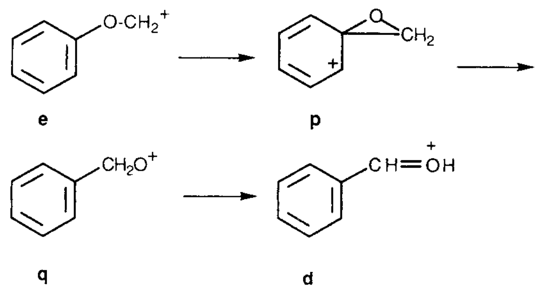
An unequivocal assignment of the broad and narrow components of the metastable peak for CO loss from the phenoxymethylene ions is not possible. Tentatively, the broad component may be associated with the pathway involving the 2-methylphenoxy cation (*h*) and the narrow component with the sequence involving ring opening of ion *g*. This is in keeping with the observation that CO elimination from the metastable ions generated by $CD_3^{\bullet}$ loss from the molecular ion of 2-$CH_3C_6H_4OCD_3$ gives rise to a non-composite broad metastable peak and a kinetic energy release, which is



Scheme 2. Proposed mechanism for the elimination of CHFO from metastable 2,6-difluorophenoxymethylene cations generated by $CHO_2^{\cdot}$ loss from the molecular ion of 2,6-difluorophenoxyacetic acid.

close to that obtained for the process leading to the broad component of the peak for CO loss from phenoxymethylene ions (see Table 3). The involvement of ion *k* in the reaction leading to the narrow component is less certain since suitable precursors for metastable ions with structure *k* are not readily accessible or easily prepared. It may be noted, however, that the $[C_7H_7O]^+$ ions generated by CH_5O loss from the molecular ion of the methyl ester from hepta-2,6-dienoic acid eliminate CO with a kinetic energy release ($T_{0.5}$) of ~50 meV (Table 3). Although this value is larger than the kinetic energy released in the reaction giving rise to the narrow component of the composite metastable peak, such a dissimilarity may be a result of a difference in the internal energy of the reactant ions if formed by different routes and, hence, not necessarily invalidate the proposed ring opening of ion *g*.

It should be emphasized that other $[C_7H_7O]^+$ isomers eliminate CO with a broad non-composite peak, e.g. the hydroxybenzyl (*a*) and hydroxytropylium (*b*) ions.[15] The $T_{0.5}$ value for CO loss from the former ions is reported to be 345 meV, whereas the latter ion expels CO with a kinetic energy release of 195 meV. Elimination of CO from protonated benzaldehyde (*d*) is likewise associated with a kinetic energy release, which is significantly smaller than the value for the process leading to the broad component of the peak for the phenoxymethylene ion (see Table 3). Even though it is not possible to exclude that species such as *a*, *b* or *d* can be involved as intermediates in the CO loss from the phenoxymethylene ion, the results of the ^{13}C-labelling experiments place restrictions as to the mechanistic proposals which can be put forward. For example, ion *d* could be formed by the reaction sequence shown in Scheme 3, involving initial attack on the 1-position of the ring in ion *e* giving *p*, followed by ring opening to a benzyloxy ion (*q*) and a subsequent 1,2-hydride shift. However, the ions formed by H$^{\cdot}$ loss from the molecular ion of $C_6H_5{}^{13}CH_2OH$ eliminate only ^{13}CO on the microsecond time-scale,[27] indicating that the rearrangement in Scheme 3 leads to loss of CO molecules containing only the carbon atom of the methylene function in the phenoxymethylene ion, in contrast to observation.



Scheme 3. Proposed mechanism for the rearrangement of metastable phenoxymethylene cations to protonated benzaldehyde.

Other considerations in assigning mechanistic possibilities to CO loss from phenoxymethylene ions concern the thermodynamics of the overall processes in relation to the elimination of formaldehyde. The latter reaction represents a simple cleavage of an oxygen–carbon bond, implying that the critical energy is close to the endothermicity of the process. Based on the published heat of formation of the phenoxymethylene ion (640 kJ mol^{-1}),[14,15,28] the endothermicity of formaldehyde elimation is estimated to be ~378 kJ mol^{-1} (see Fig. 3), suggesting that the critical energies for the processes leading to CO loss should be lower than this value, in keeping with the observation that the metastable ions expel preferentially CO (Table 1). Further, the barrier towards formation of the 2-methylphenoxy cation should be lower than the critical energy for formaldehyde loss for this species to be involved as an intermediate in the reaction leading to the broad component of the composite peak for formation of the $C_6H_7{}^+$ ions.

The reaction sequences in Scheme 1 indicate that

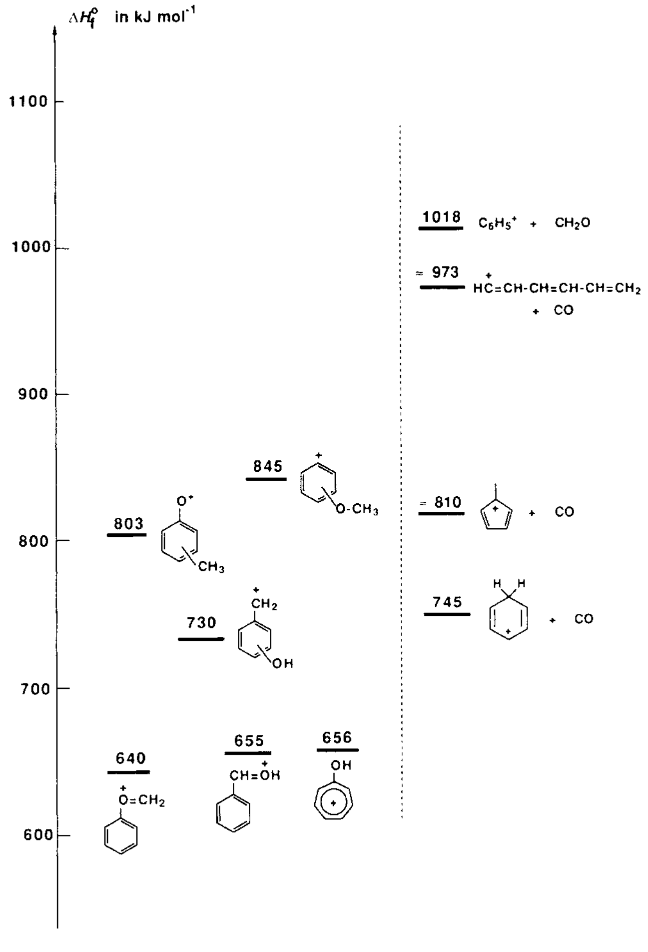
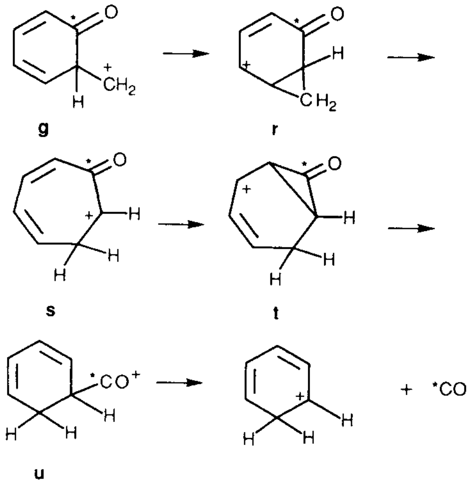


Figure 3. Heats of formation of isomeric $[C_7H_7O]^+$ ions and possible reaction products (see also text and Appendix).

methyl-substituted cyclopentadiene ions may arise initially in the reaction leading to the broad component, whereas CO loss from *k* yields an acyclic $C_6H_7^+$ isomer, i.e. $CH_2{=}CH{-}CH{=}CHCH{=}CH^+$. The heat of formation of the former $C_6H_7^+$ isomer is reported to be 890–955 kJ mol^{-1} (see also Appendix),[29] giving an enthalpy change of the process leading to its formation from ion *e* of roughly 170 kJ mol^{-1}. Accurate thermodynamic data on acyclic $C_6H_7^+$ isomers are not available, but on the basis of the reported proton affinity of hexa-1-yne-3,5-diene (~811 kJ mol^{-1}),[29] the heat of formation of the acyclic ion can be estimated to be ~1083 kJ mol^{-1}. The enthalpy change for the reaction leading to the formation of this ion from ion *e* thus becomes ~45 kJ mol^{-1} lower than the value for formaldehyde elimination (see Fig. 3). In conclusion, these considerations indicate that the barrier towards the reverse reaction of CO loss from ion *k* may be lower than the barrier for the reverse reaction of CO loss from ion *h*, which is inclined, therefore, to dissociate with a larger kinetic energy release than *k*.[20,21]

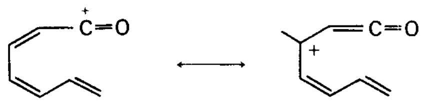
The methyl-substituted cyclopentadiene ion and the acyclic species are both likely to isomerize into protonated benzene, which is thermodynamically the more stable isomer (see Fig. 3).[28] Formation of protonated benzene as the initial product ion in the process leading to the broad component of the composite metastable peak cannot be excluded *a priori* and a mechanism for the generation of this ion by CO loss from the phenoxymethylene ion is shown in Scheme 4. This sequence of structural reorganization preceding dissociation involves ring expansion of *g* to ion *s*. Subsequently, ring contraction to *u* can occur in such a way that the oxygen atom remains bonded to the carbon atom at the 1-position of the aromatic ring in the reactant ion as indicated by the ^{13}C-labelling experiments. The seven-membered ring intermediate in Scheme 4 may be expected to rearrange relatively easily into the hydroxytropylium ion (*b*) and, in addition, ion *u* in Scheme 4 may represent the reactant configuration for the loss of CO from protonated benzaldehyde (*d*). However, metastable *b* and *d* ions expel CO with a kinetic energy release which is significantly lower than the energy released in the reaction giving rise to the broad component of the peak associated with CO loss from the phenoxymethylene ion (see Table 3). Initial formation of protonated benzene is less likely to occur, therefore, than generation of methyl-substituted cyclopentadiene ions in the reaction leading to the broad component of the peak.



Scheme 4. Proposed mechanism for the formation of protonated benzene as the initial product ion in the loss of CO from metastable phenoxymethylene ions (see text).

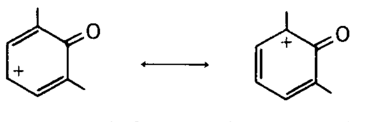
Loss of CO from substituted phenoxymethylene ions

The ^{13}C-labelling experiments with the 2-fluoro- and 2-methylphenoxyacetic acids reveal that the metastable ions from these compounds eliminate formaldehyde molecules consisting entirely of the atoms of the original oxygen–methylene function and CO molecules, which do not contain the carbon atom of the methylene group in the parent species (Table 2). These findings indicate that substituted phenoxymethylene ions are generated from the methyl- or fluorine-containing aryloxyacetic acids, implying that CO loss can be discussed on the basis of the reaction sequences shown in Scheme 1. The relative contributions of the broad and narrow components to the metastable peaks associated with CO loss from the methyl-substituted ions (Fig. 2) may thus be ascribed to a change in the competition between the 1,2-hydride shift in ion *g* and ring opening of this species (see Fig. 2 and Tables 2 and 3). For example, a methyl group at the 3-position in the reactant ion could stabilize *k* as indicated in Eqn (12), whereas the introduction of a methyl group at this position is expected to have little influence on the stabilization of the charge in *h*. This may favour formation of an acyclic acylium ion and lead to the observed preference for the process giving rise to the narrow component (Fig. 2).



(12)

The reverse may be true for the ions derived from 2-methylphenoxyacetic acid, since the presence of a methyl group at the 2-position can stabilize the charge in ion **h** [Eqn (13)]. As a result, CO is expelled preferentially by the pathway leading to the broad component in agreement with observation (Fig. 2).



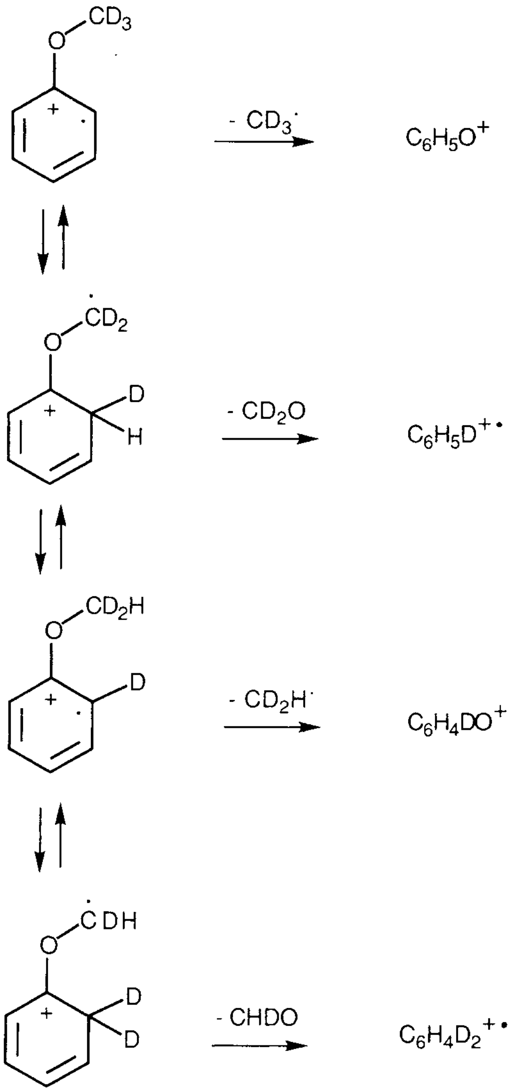
(13)

Other factors may influence the competition between the processes leading to the narrow and broad components. For example, formaldehyde loss is a more pronounced process of the metastable ions derived from 2-methylphenoxyacetic acid than of the ions from the 3- and 4-methyl-substituted compounds (Table 1). Formaldehyde elimination may be preferred over CO loss for that part of the metastable ion population, which has a relatively high internal energy. In keeping with the assignment of the narrow component to the process with a relatively high critical energy (see above), this may result in fewer ions undergoing CO loss by this pathway and cause the process leading to the broad component to dominate.

The presence of a fluorine atom causes the narrow component to disappear (see Results and Table 3), implying that a fluorine atom may destabilize *k* with respect to *h*. The initial position of the fluorine atom has no effect on the shape of the metastable peak, indicating that *k* is destabilized relative to *h* irrespective of the position of the fluorine atom and/or the positional identity of the fluorine atom is lost during the initial steps of the reaction leading to CO loss.

Loss of CO from the $[M - H^\cdot]^+$ ions from anisole

The elimination of formaldehyde from the metastable molecular ions of anisole represents a classical example of a process which gives rise to a composite metastable peak. As discussed in detail, the broad component of the peak can be associated with a process involving an H-shift from the methyl group to the 1-position of the aromatic ring, whereas the narrow component can arise by a reaction initiated by an H-shift to the 2- or 6-position.[24] The present results provide evidence that reversible H-shifts from the methyl group to the 2- or 6-position to some extent precede the expulsion of a methyl radical or a formaldehyde molecule (see Table 4 and Scheme 5).



Scheme 5. Proposed pathway for interchange between the hydrogen atoms of the methyl group and the hydrogen atoms at the 2- and 6-positions of the phenyl ring prior to loss of a methyl radical or a formaldehyde molecule from the metastable molecular ions of anisole.

The interchange between the hydrogen atoms of the methyl and phenyl groups may also precede H· loss, although direct loss of an H· from the methyl group and the aromatic ring may occur in the ion source. The former reaction with formation of the phenoxymethylene ion is estimated to be ~205 kJ mol⁻¹ less endothermic than formation of a methoxy-substituted phenyl ion [Fig. 3 and Eqns (14) and (15)].[28]

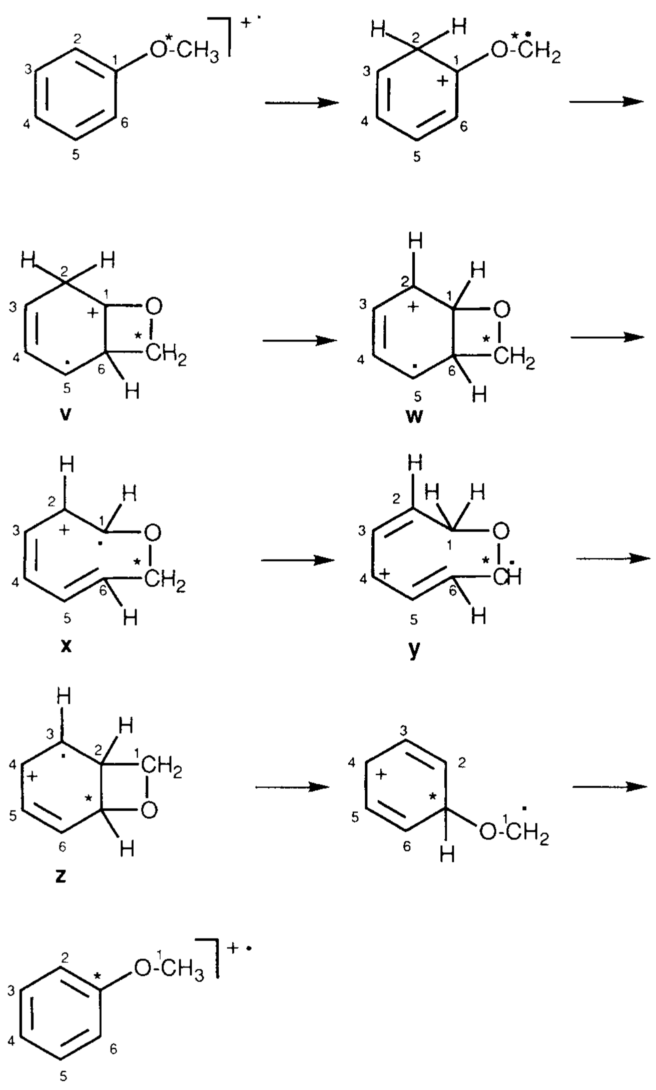
$$C_6H_5OCH_3^{\rceil +\cdot} \longrightarrow \begin{cases} C_6H_5OCH_2^{+} + H^{\cdot} \quad \Delta H_r^{\circ} = 134\ \text{kJ mol}^{-1} & (14) \\ {}^{+}C_6H_4OCH_3 + H^{\cdot} \quad \Delta H_r^{\circ} = 339\ \text{kJ mol}^{-1} & (15) \end{cases}$$

Irrespective of the origin of the expelled H·, the metastable $[C_7H_7O]^+$ ions from anisole eliminate CO with a composite metastable peak, which is almost identical with the peak for CO loss from the ions derived from phenoxyacetic acid, indicating that phenoxymethylene ions are generated in both instances.

A significant part of the metastable ions from anisole eliminates formaldehyde [Eqns (7) and (8)], indicating that relatively more ions are formed with a sufficient internal energy for reaction through this pathway than if generated from phenoxyacetic acid. The loss of a $^{\cdot}CO_2H$ radical from the molecular ion of phenoxyacetic acid is only ~35 kJ mol⁻¹ less endothermic [Eqn (16); see also Appendix] than direct loss of H· from the methyl group in ionized anisole [Eqn (14)].[28] Further, the $[M - D^\cdot]^+$ ions from ionized $C_6H_5OCD_3$ do not eliminate formaldehyde to any significant extent [Eqns (10) and (11)] on the microsecond time-scale. The pronounced loss of formaldehyde from the ions from unlabelled anisole can be ascribed, therefore, to direct expulsion of a phenyl hydrogen atom with subsequent rearrangement of the methoxy-substituted phenyl ions to the phenoxymethylene structure and/or to the interchange of the methyl and phenyl ring hydrogen atoms prior to cleavage of a C—H bond in the former group. This suggests that the interchange occurs mainly in ions with relatively more internal energy than the ions which expel an H· directly from the methyl group.

$$C_6H_5OCH_2CO_2H^{\rceil +\cdot} \longrightarrow C_6H_5OCH_2^{+} + {}^{\cdot}CO_2H \qquad \Delta H_r^{\circ} = 100\ \text{kJ mol}^{-1} \quad (16)$$

A striking dissimilarity between the phenoxymethylene ions from anisole and phenoxyacetic acid manifests itself in the results of the ^{13}C-labelling experiments. In particular, the ions from anisole eliminate CO molecules containing the carbon of the methyl group in the parent compound, whereas the methylene carbon atom is not incorporated in CO molecules expelled from the ions generated from the acid. In keeping with the conclusion that phenoxymethylene ions are formed from both precursors, these results reveal the occurrence of a skeletal rearrangement of the anisole molecular ion. This rearrangement is likely to involve an interchange between the carbon atoms of the methyl group and 1-position in view of the complementary results obtained for the anisoles labelled with a ^{13}C atom in the methyl group and at the 1-position of the ring (Table 6). A pos-



Scheme 6. Proposed mechanism for the reaction leading to interchange of the methyl carbon atom and the carbon atom at the 1-position in ionized anisole.

sible mechanism leading to this interchange is shown in Scheme 6.

The initial step is proposed to be an H-shift from the methyl group to the 2-position followed by attack of the methylene group on the 6-position leading to ion *v*. An H-shift from C-2 to C-1 yields *w*, which can ring open to an eight-membered cyclic ion (*x*) before an H-shift from the methylene group to C-1 gives ion *y*. Bond formation between the carbon atom carrying the radical in *y* and C-2 leads to *z*. After ring opening and an H-shift the anisole structure is restored.

The rearrangement of the carbon skeleton leads also to a methyl group containing one or more of the hydrogen atoms of the original phenyl group. This may explain the observation that mainly ^{13}CO is expelled from the $[M - H^{\bullet}]^+$ ions derived from $C_6H_5O^{13}CD_3$ and from the $[M - D^{\bullet}]^+$ ions of ionized $C_6D_5O^{13}CH_3$ (Table 6). The proposed rearrangement of the molecular ion of anisole prior to $H^{\bullet}$ loss may compete with direct formation of phenoxymethylene ions by cleavage of a C—H bond of the original methyl group as revealed by the predominant loss of CO from the metastable ions formed by $D^{\bullet}$ loss from ionized $C_6H_5O^{13}CD_3$ and from the ions generated by $H^{\bullet}$ loss from the molecular ion of $C_6D_5O^{13}CH_3$.

CONCLUSIONS

Metastable phenoxymethylene ions are generated by electron impact-induced dissociation of phenoxyacetic acid and anisole. These ions expel CO through two different reaction channels as manifested in a composite metastable peak. The broad component of the peak is ascribed to a reaction involving isomerization to the 2-methylphenoxy cation, which eliminates CO with the formation of a methyl-substituted cyclopentadiene cation as the initial product ion. The narrow component of the peak is suggested to be a result of formation of an open chain acylium ion, which eliminates CO leading to an acyclic $C_6H_7^+$ ion. The CO molecules expelled by either pathway incorporate the carbon atom originally at the 1-position of the ring if generated from phenoxyacetic acid. In contrast, the metastable phenoxymethylene ions from anisole eliminate CO molecules containing either the methyl carbon atom or the carbon atom at the 1-position in the parent compound. This finding is taken as evidence for the occurrence of an unprecedented skeletal rearrangement of the molecular ion of anisole leading to an interchange of the carbon atoms of the methyl group and position 1 prior to the loss of an $H^{\bullet}$.

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APPENDIX

The thermodynamic data used in this study were taken from Refs 14, 15, 28 and 29, with the exception of the heat of formation of the molecular ion of phenoxyacetic acid. The heat of formation of this ion was estimated to be 331 kJ mol^{-1} based on an ionization energy of 8.1 eV determined from the onset of the first band in the photoelectron spectrum of phenoxyacetic acid. The heat of formation of phenoxyacetic acid was placed at -449 kJ mol^{-1} on the basis of the assumption that the difference in $\Delta H_f{}^{\circ}$ of *n*-propylbenzene (8 kJ mol^{-1})^{28} and ethyl phenyl ether (-102 kJ mol^{-1})^{28} is the same as the difference in the $\Delta H_f{}^{\circ}$ of 3-phenylpropionic acid (-339 kJ mol^{-1})^{28} and the compound of interest. The $\Delta H_f{}^{\circ}$ of the methyl-substituted cyclopentadiene cation is placed between 890 and 955 kJ mol^{-1} in Ref. 29. It should be noted that the heat of formation of this ion is estimated to be ~1018 kJ mol^{-1} on the basis of the assumption that the difference between the heats of formation of cyclopentadiene ($\Delta H_f{}^{\circ} = 131$ kJ mol^{-1})^{28} and the cyclopentadiene cation ($\Delta H_f{}^{\circ} = 1052$ kJ mol^{-1})^{28} is similar to the difference between the $\Delta H_f{}^{\circ}$ of 2-methylcyclopentadiene ($\Delta H_f{}^{\circ} = 97$ kJ mol^{-1})^{28} and the methyl-substituted cyclopentadiene ion. This leads to an endothermicity of about 270 kJ mol^{-1} for the formation of the methyl-substituted cyclopentadiene cation by CO loss from the phenoxymethylene ion instead of the value of ~170 kJ mol^{-1} given in the text. This does not invalidate, however, any of the conclusions reached in the present study.