The Structure of Decomposing \([C_7H_7O]^+\) Ions: Benzyl versus Tropylium Ion Structures

D. H. Russell
Department of Chemistry, Texas A & M University, College Station, Texas 77843, USA

B. S. Freiser
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA

E. H. McBay and D. C. Canada
Division of Analytical Chemistry, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA

The unimolecular dissociation reactions for \([C_7H_7O]^+\) ions generated by fragmentation of a series of precursor molecules have been investigated. The metastable kinetic energy values and branching ratios associated with decaconjugation and expulsion of a molecule of formaldehyde \((CH_2O)\) from the \([C_7H_7O]^+\) ions are interpreted as the hydroxybenzyl and hydroxytropylium \([C_7H_7O]^+\) not interconverting to a common structure on the microsecond time-scale. In addition, similar measurements on protonated benzylddehyde, methylyaryloxy and phenyl methylene ether \([C_7H_7O]^+\) ions are interpreted as the dominant fraction of these decomposing ions having unique structures on the microsecond time-scale. These results are supported by experimental heats of formation calculated from ionization/appearance energy measurements. The experimental heats of formation are determined as: hydroxybenzyl ions, 735 kJ mol\(^{-1}\); hydroxytropylium ions, 656 kJ mol\(^{-1}\); phenyl methylene ether ions, 640 kJ mol\(^{-1}\); methylyaryloxy ions 803 kJ mol\(^{-1}\). The combination of the results reported in this paper with previously reported experimental data for stable \([C_7H_7O]^+\) ions (see Ref. 1, C. J. Cassady, B. S. Freiser and D. H. Russell, Org. Mass Spectrom.) is interpreted as evidence that the relative population of benzyl versus tropylium \([C_7H_7O]^+\) ion structures from a given precursor molecule is determined by isomerization of the parent ion and not by structural equilibration of the \([C_7H_7O]^+\) ion.

Considerable effort has been directed toward elucidating the role of isomerization and/or rearrangement reactions of gas phase ionic systems which occur prior to or concurrent with dissociation. To probe such questions both stable (non-decomposing) and activated (decomposing) ions have been investigated. Re-}

ever, the relationship between structure of metastable ions and stable ions is not straightforward. That is, metastable ion techniques sample directly the reactive configuration or transition state leading to products, whereas stable ion techniques (ion-molecule reaction chemistry, photodissociation, or collisionally activated dissociation) sample ions which have a stable configuration and (presumably) vibrational energies near the ground state. Studies of stable ions may be complicated by the presence of ions which are vibrationally excited and the consequences of excess energy are not fully understood.

For many years mass spectroscopists have debated the question of ion structure for various \([C_7H_7]^+\) ions formed by fragmentation of higher molecular weight precursors, e.g. toluene or cycloheptatriene. Although a number of structures can be envisaged for \([C_7H_7]^+\), the basic issue addressed in these studies has been whether the \([C_7H_7]^+\) ions are formed as benzyl or tropylium ions, and whether these ion forms equilibrate at energies below the dissociation threshold. Although some experimental data has been presented to support the formation of other \([C_7H_7]^+\) ion structures, i.e. tolyl ions and bicyclic ions such as norbornadienyl and norcaradienyl ions, these forms are generally observed in low abundance or proposed as short-lived intermediates.

In Ref. 1 ion-molecule reaction chemistry, photodissociation spectroscopy and collisionally activated dissociation results are presented and interpreted as evidence that benzyl and tropylium structural forms represent minima on the \([C_7H_7O]^+\) ion potential

† Author to whom correspondence should be addressed.
energy surface, i.e. hydroxybenzyl \((a)\) and hydroxy-
tropylium \((b)\) ions. Although Ref. 1 presents convinc-
ing evidence for the formation of two stable structures of 
\([C_7H_7O]^+\) ions, i.e. \(a\) and \(b\), these results do not
address the question of the isomerization of these structural
forms, i.e. \(a \neq b\). That is, the previous data
do not distinguish whether \(a\) and \(b\) are formed as two
non-interconverting structural forms on whether the ions
are formed as a single structure which isomerizes
to the second structure. To address this latter question
we have investigated the unimolecular dissociation
reactions of a number of \([C_7H_7O]^+\) ions, employing
metastable ion techniques and thermochemical mea-
surements.

It is important to consider the rationale for employ-
ing metastable ion measurements to probe the
question of \(a \neq b\). Using a potential energy surface
concept Bowen and Williams have discussed the
criteria implicating isomer equilibration and non-
equilibration prior to unimolecular dissociation. The
criteria proposed are (i) branching ratios for compet-
ing reaction channels \((k(E) = 10^6 \text{ } s^{-1})\): for common
decomposing structures any differences will be small
and can be attributed to small differences in internal
energy; (ii) metastable kinetic energy release values,
the partitioning of internal energy into translational
degrees-of-freedom, will be similar independent of the
mode of preparation; (iii) appearance energies for
each unimolecular dissociation channel must be the
same; and (iv) isotopic labeling results will be the
same in terms of label retention and/or isotope effects.

Thus, if the \([C_7H_7O]^+\) ions generated from different
precursors have the same structure or mixture of
structures \((a \neq b)\) the measured quantities cited above
will be the same or similar. On the other hand, if these
ions do not isomerize to a common structure, this
should be reflected in at least one (or more) of these
criteria.

RESULTS

The \([C_7H_7O]^+\) ions investigated in this study are
derived from a relatively large variety of precursor
molecules. For example, model ions for the hy-
droxybenzyl cation \((a)\) are generated by dissociative
ionization of methylphenols, ring-substituted methyl-
phenols and alkylphenols (reactions (1) and (2)),

\[
\begin{align*}
\text{R}+\text{H}, \text{CH}_3, \text{C}_6\text{H}_5 & \rightarrow \text{R}^+ + \text{CH}_2\text{R} + \text{CH}_3 \quad (1) \\
\text{X}=\text{Cl}, \text{CH}_4 & \rightarrow \text{OH} + \text{CH}_2\text{R} + \text{CH}_3 \quad (2)
\end{align*}
\]

whereas the model hydroxytropylium ions \((b)\) are
formed by dissociation of cycloheptadienone molecular
ions (reaction (3)) and gas phase protonation of
2,4,6-cycloheptatrienone (reaction (4)). There are pit-
falls associated with such an approach, e.g. the ring-
substituted methylenophenols could, and probably do,
produce initially a tolyl \([C_7H_7O]^+\) ion structure, which
could isomerize to hydroxybenzyl ions \((a)\) via hy-
drogen rearrangement or ring expand to hydroxyt-
ropylium ion \((b)\). Likewise, the \([C_7H_7O]^+\) ion formed
by the loss of \(\text{H}^+\) from the methylphenols can arise by
expulsion of a methyl, ring or oxygen-bonded hy-
drogen. The observed randomization of hydrogen/ deuterium atoms prior to elimination of \(\text{H}^+ / \text{D}^+\)
from isotopically labeled methylenophenol molecular
ions \((\text{H}^+ \text{ ring-substituted 4-methylphenol, a,a,a}^-\text{H}_3-
methylenophenol and } \text{H}^+ \text{ O-4-methylphenol})\) indicates
that hydrogen atom rearrangement is facile; however,
this does not necessarily imply rearrangement of the
carbon skeleton. For example, experimental re-
sults have shown that hydrogen and carbon randomi-
zation in other aromatic systems, viz. benzene, occurs
by separate processes.

For the sake of completeness we have also charac-
terized the unimolecular dissociation reactions of
\([C_7H_7O]^+\) ions formed by dissociation of phenoxal-
kyl compounds and substituted benzyl alcohols. These
\([C_7H_7O]^+\) ion precursors are employed as model sys-
tems for phenyl methylene ether \((c)\) and protonated
benzaldehyde \((d)\) \([C_7H_7O]^+\) ions (reactions (5) and
(6), respectively). In addition, the \([C_7H_7O]^+\) ion

\[
\begin{align*}
\text{R}+\text{H}, \text{CH}_3, \text{C}_6\text{H}_5 & \rightarrow \text{R}^+ + \text{OH} + \text{CH}_2\text{R} + \text{CH}_3 \quad (5) \\
\text{R}+\text{H}, \text{CH}_3, \text{C}_6\text{H}_5 & \rightarrow \text{OH} + \text{CH}_3 + \text{CH}_2\text{R} + \text{CH}_3 \quad (6)
\end{align*}
\]

formed by loss of \(\text{NO}^+\) from 2-, 3- and 4-nitrotoluene
and \(\text{CH}_3\) loss from 4,4-dimethylcyclohexadiene are
employed as model systems for methylarlyloxy \((e)\)
\([C_7H_7O]^+\) ions, i.e. the keto form of the hydroxyben-
zyl cation (reactions (7) and (8), respectively). Both
isotopic labeling data and metastable kinetic energy
release measurements for the nitrotoluenes support
the assignment of this \([C_7H_7O]^+\) ion as a keto ion
structure, specifically for 4-nitrotoluene precursors. On
the other hand, the previous experimental data do
not preclude the subsequent isomerization of this ion
to some other structure, e.g. hydrogen rearrangements
such as reaction (9).
The dominant unimolecular dissociation reactions for \([\text{C}_7\text{H}_7\text{O}]^+\) ions investigated in this study, i.e. ions decomposing with rate constants of approximately \(10^6 \text{s}^{-1}\), are loss of CO and CH\(_2\text{O}\) to give \([\text{C}_6\text{H}_5]^+\) and \([\text{C}_6\text{H}_5]^+\), respectively (reactions (10) and (11)). In all cases more than 95% of the total metastable ion current is carried by these two reaction channels. A weak signal corresponding to loss of H\(_2\) was observed for the \([\text{C}_7\text{H}_7\text{O}]^+\) ion generated by dissociation of benzyl alcohol and the substituted benzyl alcohols (reaction (12)). However, in no case was the unimolecular loss of H\(_2\) (reaction (13)) observed, as previously reported by Meyerson et al.\(^\text{13}\) Both the loss of H\(_2\) and H\(_2\) appear to arise exclusively by a collisionally activated dissociation process. For example, at a source pressure of c. \(5 \times 10^{-6}\) Torr, the loss of H\(_2\) in the first field free region accounts for approximately 2–3% of the total metastable ion current. As the source pressure is increased by admitting air to the source region the metastable signal intensity for H\(_2\) loss increases linearly, increasing to a maximum of c. 7% (total metastable ion current). At relatively high pressures, c. \(5 \times 10^{-5}\) Torr, a weak signal (1–2% total metastable ion current) is observed corresponding to loss of H\(_2\).

Owing to the fact that the loss of H\(_2\) and H\(_2\) arise primarily, if not exclusively, by a collisionally activated process, no attempt was made to characterize further these reaction channels. Also, for deuterium-labeled precursor molecules, e.g. \(\alpha,\alpha-^2\text{H}_2\)-benzyl alcohol, the loss of H\(_2\) and H\(_2\) are preceded by extensive atom randomization. For example, the observed ratio for loss of \(^1\text{H}\) versus \(^2\text{H}\) is approximately 5:2 as predicted for statistical randomization.

Similar pressure dependent reactions for loss of H\(_2\) and H\(_2\) are observed for \([\text{C}_7\text{H}_7\text{O}]^+\) ions derived from the alkylphenols and the phenylmethylen ether ions. Since the reactions also appear to be collisionally activated no attempt has been made to characterize these reaction channels.

Branching ratios for loss of CO and CH\(_2\text{O}\)

As pointed out previously, the dominant unimolecular dissociation reactions for \([\text{C}_7\text{H}_7\text{O}]^+\) ions are loss of CO and CH\(_2\text{O}\) (reactions (10) and (11)). However, the relative branching ratios for these two reactions vary significantly depending on the ion precursor (see Tables 1 and 2). For example, the \([\text{C}_7\text{H}_7\text{O}]^+\) ions formed via dissociation of benzyl alcohol decompose primarily by loss of CO (>99% relative abundance). Also, for the phenyl methylene ether \([\text{C}_7\text{H}_7\text{O}]^+\) ions (ions formed via reaction (5)) the dominant unimolecular reaction is loss of CO (c. 95% relative abundance).\(^\text{14}\)

On the other hand, the \([\text{C}_7\text{H}_7\text{O}]^+\) ions derived from the methylenophenols, substituted methylenophenols and related precursors (see Table 1) decompose competitively via both reaction channels, i.e. loss of CO and CH\(_2\text{O}\). However, the relative branching ratios are strongly precursor ion dependent (see Table 1). For example, the \([\text{C}_7\text{H}_7\text{O}]^+\) ion generated from 2-methylphenol favors CO expulsion (~90%), whereas the \([\text{C}_7\text{H}_7\text{O}]^+\) ions formed by dissociation of 3-methylphenol and substituted 3-methylphenols show a considerable enhancement for the loss of CH\(_2\text{O}\) (ranging from ~15% to 35% relative abundance). The loss of CH\(_2\text{O}\) is greatest for the \([\text{C}_7\text{H}_7\text{O}]^+\) ions formed from 4-methyl and related precursors.

For the 3-methyl- and 4-methyl-phenol \([\text{C}_7\text{H}_7\text{O}]^+\) ions, the relative branching ratios for loss of CO and CH\(_2\text{O}\) show a strong precursor dependence. We believe these variations in relative branching ratios are dependent on the average internal energy of the decomposing ion rather than a structural effect. This point will be discussed in greater detail in the following sections.

The branching ratio for \([\text{C}_7\text{H}_7\text{O}]^+\) ions generated from the methylenophenol precursors contrast markedly with the branching ratio for \([\text{C}_7\text{H}_7\text{O}]^+\) ions formed by fragmentation of nitrotoluene and 4,4-dimethylcyclohexadiene. These latter \([\text{C}_7\text{H}_7\text{O}]^+\) ions, with the exception of 2-nitrotoluene, dissociate exclusively by expulsion of CO (>99%).

Kinetic energy release for decomposing \([\text{C}_7\text{H}_7\text{O}]^+\) ions

The kinetic energy release data for decomposing \([\text{C}_7\text{H}_7\text{O}]^+\) ions are contained in Tables 1 and 2. These data are similar to the metastable branching ratios in that a strong precursor ion dependence is observed. For example, the phenyl methylene ether \([\text{C}_7\text{H}_7\text{O}]^+\) ions which decompose via CO loss show two distinctive kinetic energy release (T) profiles (T(FWHM) = 20 meV and 290 meV). The \([\text{C}_7\text{H}_7\text{O}]^+\) ion formed by
THE STRUCTURE OF DECOMPOSING \([C,H,O]^+\) IONS

Table 1. Metastable ion branching ratio and kinetic energy release data for \([C,H,O]^+\) ions from phenols and related compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Branching ratio [^a^]</th>
<th>Kinetic energy release [^b^]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>([107]^+ \rightarrow [79]^+)</td>
<td>([107]^+ \rightarrow [77]^+)</td>
</tr>
<tr>
<td>2-Methylphenol</td>
<td>0.91 (0.08)</td>
<td>0.09 (0.10)</td>
</tr>
<tr>
<td>4-Chloro-2-methylphenol</td>
<td>0.86 (0.90)</td>
<td>0.14 (0.10)</td>
</tr>
<tr>
<td>Bis(2-hydroxyphenyl)methane</td>
<td>0.32</td>
<td>0.08</td>
</tr>
<tr>
<td>m-Cresyl acetate</td>
<td>0.90</td>
<td>0.10</td>
</tr>
<tr>
<td>o-Cresyl acetate</td>
<td>0.90</td>
<td>0.10</td>
</tr>
<tr>
<td>3-Methylphenol</td>
<td>0.65 (0.90)</td>
<td>0.35 (0.10)</td>
</tr>
<tr>
<td>2-Chloro-5-methylphenol</td>
<td>0.70</td>
<td>0.30</td>
</tr>
<tr>
<td>4-Chloro-3-methylphenol</td>
<td>0.65 (0.86)</td>
<td>0.35 (0.15)</td>
</tr>
<tr>
<td>m-Cresyl acetate</td>
<td>0.85</td>
<td>0.15</td>
</tr>
<tr>
<td>4-Methylphenol</td>
<td>0.60 (0.86)</td>
<td>0.40 (0.15)</td>
</tr>
<tr>
<td>4-Ethylphenol</td>
<td>0.35 (0.86)</td>
<td>0.65 (0.15)</td>
</tr>
<tr>
<td>Bis(4-hydroxyphenyl)methane</td>
<td>0.40 (0.90)</td>
<td>0.60 (0.10)</td>
</tr>
<tr>
<td>p-Cresyl acetate</td>
<td>0.65 (0.80)</td>
<td>0.35 (0.20)</td>
</tr>
<tr>
<td>2,3-Xylenol</td>
<td>0.80</td>
<td>0.20</td>
</tr>
<tr>
<td>2,4-Xylenol</td>
<td>0.78</td>
<td>0.22</td>
</tr>
<tr>
<td>2,5-Xylenol</td>
<td>0.85</td>
<td>0.15</td>
</tr>
<tr>
<td>2,6-Xylenol</td>
<td>0.90</td>
<td>0.10</td>
</tr>
<tr>
<td>3,4-Xylenol</td>
<td>0.70</td>
<td>0.30</td>
</tr>
<tr>
<td>3,5-Xylenol</td>
<td>0.80</td>
<td>0.20</td>
</tr>
<tr>
<td>3,5-Cycloheptadienone</td>
<td>0.90</td>
<td>0.10</td>
</tr>
<tr>
<td>2-Methyl-3,5-cycloheptadienone</td>
<td>0.92</td>
<td>0.08</td>
</tr>
<tr>
<td>2-Phenyl-3,5-cycloheptadienone</td>
<td>0.91</td>
<td>0.09</td>
</tr>
</tbody>
</table>

[^a^]: Expressed as a fraction of the total metastable ion current using the integrated peak areas.
[^b^]: Expressed in millielectron volts (meV).
[^c^]: Obtained on a triple analyser MIKE spectrometer (see experimental section).

The structure of decomposing \([C,H,O]^+\) ions is influenced by the presence of substituents on the aromatic ring. The kinetic energy release values for loss of 
H\(^+\) from benzyl alcohol or fragmentation of the substituted benzyl alcohols decomposing via CO loss are accompanied by an estimated average kinetic energy release value of 200 meV (FWHM). However, the \([C,H,O]^+\) ions formed by fragmentation of the 
methylenophenols and substituted methylenophenols have a large variation in average kinetic energy release values for loss of CO (300-550 meV). The kinetic energy release accompanying decarbonylation appears to be sensitive to the position of the hydroxyl group. For example, the \([C,H,O]^+\) ion formed by dissociation of 2-methylphenol molecular ions and related precursors have an average kinetic energy release of 345 ± 25 meV (FWHM) (average of all ions investigated), whereas a kinetic energy release value (FWHM) of 400 ± 20 meV and 490 ± 40 meV is obtained for the 3- and 4-methylphenol \([C7H7O]^+\) ion precursors, respectively. These values are the average energy distribution for all the 3- and 4-methylphenol and related precursors. The average kinetic energy release values for decarbonylation of \([C,H,O]^+\) ions formed by dissociation of 2-, 3- and 4-nitrotoluene and 4,4-dimethylcyclohexadienone show a characteristic precursor dependence. In addition, the estimated average kinetic energy release values for those ions derived from 3- and 4-

Table 2. Metastable ion kinetic energy release and branching ratio data for \([C,H,O]^+\) ions derived from anisoles, benzyl alcohols and related precursors

<table>
<thead>
<tr>
<th>Compound</th>
<th>Branching ratio [^a^]</th>
<th>Kinetic energy release [^b^]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>([107]^+ \rightarrow [79]^+)</td>
<td>([107]^+ \rightarrow [77]^+)</td>
</tr>
<tr>
<td>2-Chloroanisole</td>
<td>0.95 (0.05)</td>
<td>0.05 (0.05)</td>
</tr>
<tr>
<td>3-Chloroanisole</td>
<td>0.94 (0.06)</td>
<td>0.06 (0.06)</td>
</tr>
<tr>
<td>4-Chloroanisole</td>
<td>0.75 (0.26)</td>
<td>0.26 (0.26)</td>
</tr>
<tr>
<td>2-Phenoxylethanol</td>
<td>0.95 (0.05)</td>
<td>0.05 (0.05)</td>
</tr>
<tr>
<td>1-Phenoxy-2-propanone</td>
<td>0.95 (0.05)</td>
<td>0.05 (0.05)</td>
</tr>
<tr>
<td>Phenoxyacetic acid</td>
<td>0.94 (0.06)</td>
<td>0.06 (0.06)</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>&gt;0.99</td>
<td>&gt;0.99</td>
</tr>
<tr>
<td>2-Chlorobenzyl alcohol</td>
<td>&gt;0.99</td>
<td>&gt;0.99</td>
</tr>
<tr>
<td>3-Chlorobenzyl alcohol</td>
<td>&gt;0.99</td>
<td>&gt;0.99</td>
</tr>
<tr>
<td>4-Chlorobenzyl alcohol</td>
<td>&gt;0.99</td>
<td>&gt;0.99</td>
</tr>
<tr>
<td>1-Phenylethanol</td>
<td>&gt;0.99</td>
<td>&gt;0.99</td>
</tr>
<tr>
<td>1,2-Diphenylethanol</td>
<td>&gt;0.99</td>
<td>&gt;0.99</td>
</tr>
<tr>
<td>2-Nitrotoluene</td>
<td>0.85 (0.15)</td>
<td>0.15 (0.15)</td>
</tr>
<tr>
<td>3-Nitrotoluene</td>
<td>0.99 (0.01)</td>
<td>0.01 (0.01)</td>
</tr>
<tr>
<td>4-Nitrotoluene</td>
<td>0.99 (0.01)</td>
<td>0.01 (0.01)</td>
</tr>
<tr>
<td>4,4-Dimethylcyclohexadienone</td>
<td>0.98 (0.02)</td>
<td>0.02 (0.02)</td>
</tr>
</tbody>
</table>

[^a^]: Expressed as a fraction of the total metastable ion current using the integrated peak areas.
[^b^]: Expressed in millielectron volts (meV).
[^c^]: Signal intensity is too weak to measure reliably.
Table 3. Thermochemical data for [C,H,O] ions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Δ Hf(M)</th>
<th>IE (M)</th>
<th>Δ Hf(M)</th>
<th>AE ([C,H,O])</th>
<th>Δ Hd(C,H,O)</th>
<th>AE ([C,H,O])</th>
<th>Δ Hd(C,H,O)</th>
<th>AE ([C,H,O])</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylphenol</td>
<td>-128</td>
<td>785</td>
<td>657</td>
<td>1081</td>
<td>735</td>
<td>1093</td>
<td>868</td>
<td></td>
</tr>
<tr>
<td>3-Methylphenol</td>
<td>-132</td>
<td>794</td>
<td>662</td>
<td>1078</td>
<td>728</td>
<td>1097</td>
<td>858</td>
<td></td>
</tr>
<tr>
<td>4-Methylphenol</td>
<td>-125</td>
<td>784</td>
<td>658</td>
<td>1074</td>
<td>731</td>
<td>1110</td>
<td>877</td>
<td></td>
</tr>
<tr>
<td>4-Ethylphenol</td>
<td>-150</td>
<td>756</td>
<td>606</td>
<td>1002</td>
<td>710</td>
<td>1087</td>
<td>905</td>
<td></td>
</tr>
<tr>
<td>3,5-Cycloheptadieneon</td>
<td>-7.1</td>
<td>795</td>
<td>788</td>
<td>981</td>
<td>666</td>
<td>984</td>
<td>869</td>
<td></td>
</tr>
<tr>
<td>2-Methyl-3,5-cycloheptadieneon</td>
<td>-29.7</td>
<td>794</td>
<td>632</td>
<td>956</td>
<td>653</td>
<td>1063</td>
<td>870</td>
<td></td>
</tr>
<tr>
<td>4-Nitrotoluene</td>
<td>-41.4</td>
<td>805</td>
<td>761</td>
<td>997</td>
<td>803</td>
<td>1037</td>
<td>854</td>
<td></td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>-94.0</td>
<td>808</td>
<td>714</td>
<td>968</td>
<td>640</td>
<td>1030</td>
<td>828</td>
<td></td>
</tr>
<tr>
<td>3-Chlorobenzyl alcohol</td>
<td>-124</td>
<td>821</td>
<td>698</td>
<td>900</td>
<td>646</td>
<td>965</td>
<td>830</td>
<td></td>
</tr>
<tr>
<td>4-Chlorobenzyl alcohol</td>
<td>-130</td>
<td>828</td>
<td>689</td>
<td>882</td>
<td>648</td>
<td>973</td>
<td>832</td>
<td></td>
</tr>
<tr>
<td>4-Chloroanisole</td>
<td>-111</td>
<td>752</td>
<td>641</td>
<td>1005</td>
<td>773</td>
<td>967</td>
<td>846</td>
<td></td>
</tr>
<tr>
<td>2-Chloroanisole</td>
<td>-105</td>
<td>812</td>
<td>707</td>
<td>1001</td>
<td>774</td>
<td>963</td>
<td>836</td>
<td></td>
</tr>
<tr>
<td>2,3-Xylenol</td>
<td>-157</td>
<td>797</td>
<td>640</td>
<td>1026</td>
<td>726</td>
<td>1062</td>
<td>873</td>
<td></td>
</tr>
<tr>
<td>3,4-Xylenol</td>
<td>-163</td>
<td>781</td>
<td>618</td>
<td>1049</td>
<td>744</td>
<td>1056</td>
<td>860</td>
<td></td>
</tr>
</tbody>
</table>

The heats of formation values for [C,H,O] and [C,H,O] are not corrected for the experimentally observed kinetic energy release values given in Tables 1 and 2. These kinetic energy release values are not considered to be of any real significance in terms of other experimental errors. Data reported in kJ mol⁻¹.

Thermochemical data

Thermochemical data for selected ions are contained in Table 3. Based on these data the heats of formation for hydroxybenzyl ions are estimated to be 735 ± 8 kJ mol⁻¹, 728 ± 12 kJ mol⁻¹ and 731 ± 12 kJ mol⁻¹ for 2-, 3- and 4-hydroxybenzyl ions, respectively. There have been relatively few thermochemical measurements reported for [C,H,O] ions formed by dissociation of methylphenols. Harrison et al. have reported thermochemical data for several [C,H,O] ion precursors that yield heats of formation of 840 ± 1 kJ mol⁻¹, 850 ± 1 kJ mol⁻¹ and 777 ± 1 kJ mol⁻¹ for 3- and 4-methylphenol and 4-ethylphenol, respectively. Our values have been checked using two different instruments and various reference compounds (see Experimental section) for calibration of the electron energy, therefore we feel confident that these values are correct within experimental limits (0.1-0.2 eV).

The heats of formation for the hydroxytropylium ion, the [C,H,O] ion from benzyl alcohol, substituted benzyl alcohols and substituted anisoles are estimated as 653 ± 12 kJ mol⁻¹, 640 ± 12 kJ mol⁻¹, 645 ± 8 kJ mol⁻¹ and 773 ± 10 kJ mol⁻¹, respectively. In addition, the heat of formation for the [C,H,O] ion is estimated at 856 ± 8 kJ mol⁻¹. This estimate for the heat of formation for the [C,H,O] ion agrees well with values obtained by other experimental and theoretical methods.

The heat of formation for the hydroxytropylium ion reported in Table 3 (652 kJ mol⁻¹) is derived from appearance energy measurements using a heat of formation of -7.1 kJ mol⁻¹ for the 3,5-cycloheptadiene neutral. This heat of formation of the neutral was obtained by the group activity method of Benson et al. For comparison, proton affinity measurements for protonated 2,4,6-cycloheptatrienone yields a heat of formation of 652 kJ mol⁻¹. Using MINDO/3 a value of 654 kJ mol⁻¹ and 560 kJ mol⁻¹ is obtained for the hydroxytropylium [C,H,O] ion. The absolute accuracy of MINDO/3 calculated heats of formation is questionable and has been shown to overestimate resonance stabilization; however, the relative heats of formation calculated for isomeric structures are usually much better. The difference in the measured heat of formation for 4-hydroxybenzyl ions and hydroxytropylium ions (80 kJ mol⁻¹) agrees reasonably well with differences obtained by MINDO/3 (~60 kJ mol⁻¹).

DISCUSSION

Hydroxybenzyl versus hydroxytropylium [C,H,O] ion structures

In Ref. 1 the experimental results for 'stable' [C,H,O] ions are interpreted as dissociating methylphenols and substituted methylphenols producing both hydroxybenzyl (a) and hydroxytropylium (b) [C,H,O] ions. However, the results of studies on 'activated' [C,H,O] ions (metastable branching ratios, kinetic energy release measurements and thermochemical data) are consistent with hydroxybenzyl...
precursors producing \([C_6H_5O]^+\) ions which are structurally distinct from hydroxytropylium ions. This observation appears to be inconsistent with what is known about rearrangement reactions of gas phase ions. That is, from a potential energy surface concept, if low energy ions isomerize to a common structure (or mixture of structures) it is expected that ions with higher energies would also exist as a mixture of structures. For a system where two (or more) structures are energetically accessible, the relative population of a given structural form may change as the system’s energy is increased, but the structural population should not shift to favor the higher energy form as the internal energy is increased, i.e. in the present case the population distribution shifts to favor formation of hydroxybenzyl ions.

It may be argued that the larger kinetic energy release values and different branching ratios for hydroxybenzyl ions as opposed to hydroxytropylium ions arise from different internal energies of the ion. That is, the \([C_6H_5O]^+\) ion from the methylphenols, which decompose in the metastable time window, could have higher averaged internal energies than the hydroxytropylium ions and some fraction of the measured kinetic energy release could arise from excess of non-fixed energy\(^\text{23}\) (see Note at end of paper). To probe this question the kinetic energy release and metastable ion branching ratios for selected \([C_6H_5O]^+\) ions were measured in the first and third field free regions (FFR) of a triple analyzer mass analyzed ion kinetic energy (MIKE) spectrometer.\(^\text{23}\) In all cases the values obtained for first FFR reactions agree (±5%) with the values obtained using the Kratos MS-50. The kinetic energy release for loss of CO and \(CH_2O\) (reactions (10) and (11)) in the third FFR are slightly lower (<10%) than for first FFR reactions; however, these differences are not considered significant because of differences in the energy discrimination of the two scan modes on this particular instrument.\(^\text{23}\) On the other hand, the third FFR metastable ion branching ratios differ significantly from the first FFR values (see Table 1). Similar changes in branching ratios have been observed for comparison between first and second FFR reactions, and these differences attributed to different critical energies for reaction, i.e. the reaction with the lowest critical energy is favored as longer lived (lower averaged internal energy) ions are sampled.\(^\text{24}\) Although accurate appearance energies for \([C_6H_5]^+\) were not determined in this study, due to \([C_6H_5]^+\) arising from several precursors, measurement of metastable ion intensities (reactions (10) and (11)) at various ionizing energies (0.5 eV above threshold to c. 30 eV, see Experimental section) indicate that the appearance energy for \([C_6H_5]^+\) (via reaction (11)) is 0.2–0.3 eV higher than the appearance energy of \([C_6H_5]^+\) (via reaction (10)). Thus, the observed decrease in the relative \([C_6H_5]^+\) metastable ion signal as longer-lived ions are sampled is consistent with the system’s thermochemistry. In addition, the different branching ratios for the hydroxybenzyl ions can be understood in terms of different averaged internal energies of \([C_6H_5O]^+\), e.g. \(-CO/-CH_2O = 60/40\) for 4-methylphenol, \(-CO/-CH_2O = 35/65\) for 4-ethylphenol; thus, metastable decomposing \([C_6H_5O]^+\) ions from 4-ethylphenol are formed with higher averaged internal energies than \([C_6H_5O]^+\) ions from 4-methylphenol (see Note at end of paper).

The metastable peak profile and estimated kinetic energy release for decomposing hydroxybenzyl \([C_6H_5O]^+\) ions, in particular the 4-hydroxybenzyl ion, can be utilized to estimate an upper limit for the fraction of hydroxytropylium \([C_6H_5O]^+\) ions formed by dissociation of 4-methylphenol and related precursor ions. Holmes has characterized the peak profile for metastable reactions associated with large kinetic energy releases in terms of percent ‘dish-top’ and the mass of the parent \((m_1)\) and daughter \((m_2)\) ions.\(^\text{25}\) Metastable peak profiles for reaction (10) employing the Kratos MS-50, the triple analyzer MIKES spectrometer and a Kratos (AEI) MS-902 mass spectrometer have less than a 20% dish; however, the results of Holmes suggest that this metastable signal should have a substantial dished component (~50%).\(^\text{25}\) We feel that this observation is significant, since other metastable reactions with comparable kinetic energy release values and \(m_1/m_2\) ratios have dish-topped profiles comparable to those reported by Holmes.\(^\text{25}\) For example, the metastable peak profile for decarbonylation of phenol \([C_6H_5O]'\rightarrow[C_6H_5O]+CO; m_1=94, m_2=66, m_1/m_2=1.42\) (see Fig. 1) and 4-methylphenol \([C_6H_5O]'\rightarrow[C_6H_5O]+CO; m_1=108, m_2=80, m_1/m_2=1.35\) are dish-topped with a dish depth of 55% and 60%, respectively. These values for percent dish-top agree reasonably well with the predicted value using the method described by Holmes, 65–70% for each case.

Owing to the disparity between the observed and predicted metastable peak profiles for reaction (10) specifically for 4-hydroxybenzyl ions, we propose that there are two structurally different decomposing \([C_6H_5O]^+\) ions, viz. 4-hydroxybenzyl and hydroxy-

---

**Figure 1.** Metastable peak profile for decarbonylation of phenol \(([C_6H_5O]'\rightarrow[C_6H_5O]+CO)\) obtained by accelerating voltage scan method (first field free region).
tropylium ions. A computer convoluted metastable peak profile corresponding to average kinetic energy releases of 200 meV (15% relative abundance) and 500 meV (85% relative abundance) agrees well with the experimentally observed peak profile. The computer convoluted peak profile and the experimentally observed profile are contained in Fig. 2. The absolute intensity of the metastable signal for reaction (10) from hydroxytropylium ions, i.e. \( m^*/m_1 \), where \( m^* \) is the metastable ion intensity (obtained by integration of the peak envelope) and \( m_1 \) is the intensity (peak height) of the normal ion \( (m/z \ 107) \), generated by dissociation of 3,5-cycloheptatriene, 2-methyl-3,5-cycloheptadiene and protonated 2,4,6-cycloheptatriene (hydrogen CI), is 0.0018, 0.0014 and 0.0016, respectively. Based on these data and the computer convoluted peak profiles, we estimate that not greater than 6-8% of the \([\text{C}_7\text{H}_7\text{O}]^+\) ions formed by dissociation of 4-methylphenol which dissociate via reaction (10) in the metastable time window \( (1-5 \times 10^{-9} \text{ s}) \) are present as hydroxytropylium ions. Similar measurements for 4-ethylphenol, bis(4-hydroxyphenyl)methane and 4-cresyl acetate yield maximum values for the fraction of hydroxytropylium ions formed from these precursors as 8-10%, 4-6% and 3-5%, respectively. Although these values are subject to relatively large errors (±25%, relative), the estimated percentage of hydroxytropylium ions present does not begin to approach the value of 80% obtained for stable ions.

We interpret these results as evidence that hydroxybenzyl and hydrotropylium \([\text{C}_7\text{H}_7\text{O}]^+\) ions with averaged internal energies near the dissociation threshold, i.e. energies corresponding to \( k(E) \sim 10^3 \text{ s}^{-1} \), do not structurally interconvert to any significant extent. Dewar and Landman have suggested, based on MINDO/3 calculations, that these structural forms do interconvert and that the critical energy for isomerization is approximately 190 kJ mol\(^{-1}\). However, our results indicate that \([\text{C}_7\text{H}_7\text{O}]^+\) ions (4-hydroxybenzyl) with roughly 330 kJ mol\(^{-1}\) of internal energy \((\Delta E \approx [\text{C}_6\text{H}_5\text{CH}_3]^+ - \Delta H_0(\text{C}_7\text{H}_7\text{O})])\) do not interconvert on the microsecond time-scale. This does not necessarily invalidate the MINDO/3 results since the calculations do not specify the kinetics of isomerization. If we accept this interpretation of the unimolecular dissociation results, then an explanation for the experimental results for stable ions must be sought which does not require \( a = b \). It may be argued that the different time-scales for the two studies (ICR, \( 10^{-3} \text{ s} \)) and metastable ions, \( 10^{-6} \text{ s} \) give rise to the observed differences. However, it seems unlikely that this is the case. That is, if stabler ions isomerize in the span of a few milliseconds, this would imply that the isomerization reaction is subject to a low energy barrier; consequently, ions with internal energies of approximately 330 kJ mol\(^{-1}\), i.e. energies well in excess of the isomerization threshold, should also structurally equilibrate.

The results for both 'stable' and activated ions can be explained by the mechanism originally proposed by Dunbar and later extensively investigated by Jackson, Lias and Ausloos. Dunbar proposed that equilibration between tolueone and cycloheptatriene \([\text{C}_7\text{H}_7\text{H}^+]\) structures prior to dissociation gives rise to the corresponding benzyl and tropylium \([\text{C}_7\text{H}_7^+]\) ions (Scheme 1). It was further suggested that the formation of tropylium ions was favored due to a lower critical energy for the dissociation of cycloheptatriene as compared with toluene \([\text{C}_7\text{H}_7^+]\) ions. The observed decrease in the fractional population of tropylium ions at higher energies was interpreted as evidence that the isomerization could not compete effectively with direct fragmentation (loss of \( \text{H}^+ \)) at high internal energies. The results of Jackson, Lias and Ausloos on deuterated tolueone ions \((\text{C}_7\text{H}_7\text{CD}_3\) and \(\text{C}_6\text{D}_5\text{CD}_3\)) at a larger fraction of tropylium ions was detected than for non-deuterated ions, due to dissociating ions having longer lifetimes, is in agreement with the mechanism of Scheme 1.

![Figure 2. Experimental and computed peak profile for decarbonylation of \([\text{C}_7\text{H}_7\text{O}]^+\) (precursor neutral is 4-methylphenol). The deconvoluted peak profiles are for average kinetic energy release values of 200 meV (a) and 500 meV (c) and the convoluted profile (b) is the summation of the two values with weighting values of 0.15 and 0.85, respectively. The solid line is the experimental peak profile for decarbonylation of \([\text{C}_7\text{H}_7\text{O}]^+\) (4-methylphenol).](image-url)

Based on experimental results for 'stable' ions and the characteristically different unimolecular chemistry of hydroxybenzyl and hydroxytropylium ions, we propose that a similar mechanism is operative for this ionic system. That is, stable \([\text{C}_7\text{H}_7\text{O}]^+\) ions (stable implying ion lifetimes greater than a few hundred milliseconds, this would imply that the isomerization reaction is subject to a low energy barrier; consequently, ions with internal energies of approximately 330 kJ mol\(^{-1}\), i.e. energies well in excess of the isomerization threshold, should also structurally equilibrate. The results for both 'stable' and activated ions can be explained by the mechanism originally proposed by Dunbar and later extensively investigated by Jackson, Lias and Ausloos. Dunbar proposed that equilibration between tolueone and cycloheptatriene \([\text{C}_7\text{H}_7^+]\) structures prior to dissociation gives rise to the corresponding benzyl and tropylium \([\text{C}_7\text{H}_7^+]\) ions (Scheme 1). It was further suggested that the formation of tropylium ions was favored due to a lower critical energy for the dissociation of cycloheptatriene as compared with toluene \([\text{C}_7\text{H}_7^+]\) ions. The observed decrease in the fractional population of tropylium ions at higher energies was interpreted as evidence that the isomerization could not compete effectively with direct fragmentation (loss of \( \text{H}^+ \)) at high internal energies. The results of Jackson, Lias and Ausloos on deuterated tolueone ions \((\text{C}_7\text{H}_7\text{CD}_3\) and \(\text{C}_6\text{D}_5\text{CD}_3\)) at a larger fraction of tropylium ions was detected than for non-deuterated ions, due to dissociating ions having longer lifetimes, is in agreement with the mechanism of Scheme 1.

![Scheme 1](image-url)
THE STRUCTURE OF DECOMPOSING [C,H,O]+ IONS

Figure 3. (a) Metastable peak profile for [C,H,O]+ (precursor 2-chloro-4-methylphenol), formed by unimolecular dissociation of the parent ion in the first field free region, undergoing unimolecular dissociation in the third field free region of a triple analyzer MIKE spectrometer. (b) Same metastable transition as contained in (a), except that the [C,H,O]+ ion is formed by unimolecular dissociation within the ion source.

On the other hand, [C,H,O]+ ions which subsequently dissociate in the metastable ion time window \((k(E) \sim 10^6 \text{s}^{-1})\) originate from parent ions with higher averaged internal energies and lifetimes sufficiently short that isomerization prior to dissociation is not competitive with direct dissociation to form hydroxybenzyl ions.

To probe the kinetics for isomerization of the parent ions, we generated the [C,H,O]+ ion by unimolecular dissociation of 2-chloro-4-methylphenol in the first field free region (FFR) (this corresponds to an ion lifetime of c. 1–6 \(\times 10^{-6}\) s) of a triple analyzer MIKE spectrometer and then plotted the metastable peak profile for this ion dissociating unimolecularly in the third FFR. The peak profiles recorded in this way are contained in Fig. 3. As can be seen from these data, the peak profile for metastable generated [C,H,O]+ ion is approximately gaussian (kinetic energy release 240 meV) (Fig. 3(a)) in contrast to the dish-topped profile for ion-source generated [C,H,O]+ which subsequently dissociates in the third FFR (Fig. 3(b)). It is interesting to note that the peak profile for [C,H,O]+ ions formed in the first FFR from 4-methylphenol, 4-ethylphenol and bis(4-hydroxyphenyl)methane are approximately the same as observed for source generated [C,H,O]+ ions which dissociate in the third FFR; however, the percent dish-top does change by a significant amount, e.g. 18% dish-top for [C,H,O]+ ions formed from 4-methylphenol (normal metastable ion) as compared with 0% dish-top for [C,H,O]+ ions formed in the first FFR.

A similar effect of the halogen atom was noted by Jackson et al., however, for the [C,H]+ ion the abundance of the tropylium structure decreased with decreasing energy and fluorine atoms favor tropylium structures ([C,H,F]+) at lower energies. The results of Jackson et al. and the metastable ion data suggest that the structural distribution of benzyl/tropylium ions is subject to substituent effects. We are presently investigating these effects further employing metastable ion methods, ion-molecule reactions and fast-beam photodissociation spectroscopy.

It is rather tenuous to argue whether the metastable ion data for the 2- and 3-hydroxybenzyl ion precursors indicate that the dissociating \((k(E) \sim 10^6 \text{s}^{-1})\) [C,H,O]+ ions have a benzyl or tropylium ion structure. Clearly, the thermochemical measurements are consistent with threshold energy ions having different structures (Table 3). Although the kinetic energy release values for these ions are significantly greater than the corresponding values for hydroxytropylium ions, it is unclear whether these metastable profiles arise from a single valued (unique decomposing structure) kinetic energy release or a multicomponent kinetic energy distribution. It is of interest to note that the third field free region (FFR) peak profile for ion source and metastable reaction (first FFR) generated [C,H,O]+ ions from the 2- and 3-hydroxybenzyl precursors listed in Table 1 are the same with the exception of the chloromethylphenols, e.g. 4-chloro-2-methylphenol, 2-chloro-5-methylphenol and 4-chloro-3-methylphenol.

We feel that the observed constant kinetic energy release for metastable (first FFR) and ion-source gen-
The metastable ion chemistry for \([C_7H_7O]^+\) ions derived from benzyl alcohols (see Table 2) are clearly consistent with this ion not isomerizing to a hydroxybenzyl ion structure. Owing to very similar kinetic energy release values for decarbonylation of benzyl alcohol and hydroxytropylium ions, we cannot rule out a common decomposing structure for these two ions. In addition, the heats of formation for the hydroxytropylium and benzyl alcohol \([C_7H_7O]^+\) (probably protonated benzaldehyde) (see Table 3) ions are very nearly the same, suggesting the possibility of common structures. For a discussion of the chemistry of stable ions, see Ref. 1.

In Scheme 2 it is suggested that hydrogen rearrangement gives rise to structural equilibration between 2-hydroxybenzyl and methylarylxyloxy \([C_7H_7O]^+\) ions. The close proximity of the methyl (or methylene) and keto oxygen (hydroxyl) groups in the 2-methylaylxyloxy ion make this rearrangement very facile (‘ortho’ effect). This is supported by the lack of structural equilibration for the 3- and 4-methyarylxyloxy and 3- and 4-hydroxybenzyloxy cations; note the markedly different kinetic energy values for the two ion structures. In fact, the kinetic energy release measurements for 3- and 4-methyarylxyloxy ions are very similar to that for hydroxytropylium ions. However, the heat of formation for 4-methyarylxyloxy ions (from 4-nitrotoluene) is significantly greater than that for hydroxytropylium ions (802 kJ mol\(^{-1}\) compared with 652 kJ mol\(^{-1}\)). This suggests that the methyarylxyloxy ions (or some fraction of the ion population) are formed with sufficient internal energy to undergo isomerization to the hydroxytropylium ion structures. The data for stable ions (from Ref. 1) also suggests that competing rearrangement reactions are operative for the methyarylxyloxy ions, e.g. approximately 60% of the stable ions have the hydroxytropylium ion structure, whereas 40% are presumably present as the methyarylxyloxy ion. However, one cannot rule out the possibility that the structural form is determined by that of the decomposing parent ions. For example, if decomposing parent ions exist in two structural forms,

Scheme 2

There are two additional interesting observations on this ion. (i) All the phenylmethylether \([C_7H_7O]^+\) ions which undergo decarbonylation appear to have the same structure(s). That is, ions generated directly as phenylmethylether \([C_7H_7O]^+\), e.g. 2-phenoxyethanol, 1-phenoxy-2-propanone and phenoxycetic acid, and those formed initially as the methylphenylium ether \([C_7H_7O]^+\) ion, e.g. the ring-substituted chloroanisoles, are associated with similar kinetic energy releases for decarbonylation and this reaction channel is the dominant dissociation pathway. (ii) With the exception of 4-chloroanisole the relative branching ratios for loss of CO and CH\(_2\)O are the same for phenylmethylether and methylphenylium ether ions. We interpret these observations as evidence that rearrangement of the ring and methyl hydrogen atoms is rapid and subject to a low energy barrier. Owing to this interpretation, we find it most interesting that the relative branching ratios for CO and CH\(_2\)O loss are so markedly different in the case of the 4-chloroanisole system. There is insufficient data available to identify the origin of this difference. The fact that all other observables, kinetic energy release for loss of CO and CH\(_2\)O and the composite nature of the metastable peak profile for decarbonylation, remain unchanged for this ion suggest the structure of the \([C_7H_7O]^+\) is unchanged and the characteristicall different branching ratios arise from internal energy differences.
then the product ion structure ([C7H7O]+) is dependent on the fractional population of the two precursors. In fact, the kinetic energy release observed for NO⁺ loss from 4-nitrotoluene molecular ions is consistent with two decomposing ion structures and/or two product ion structures.121 Thus, it is not necessary to rationalize the experimental results in terms of isomerization of [C7H7O]+ since independent evidence is consistent with competing isomerization reactions of the parent ion. Clearly, further studies on this question are warranted, and are presently underway.

**EXPERIMENTAL**

The metastable ion measurements were performed on a Kratos MS-50 instrument equipped with a standard metastable ion scan accessory. Samples were introduced via a volatile sample direct insertion probe at a temperature ranging between ambient and 150 °C. Typical operating conditions were: ion source normal accelerating voltage 8 kV, trap current 500 μA (100–20 μA at low ionizing energy (10–20 eV), ionizing energy 70 eV and source pressure ~5×10⁻⁸ Torr. Metastable peaks were recorded by the accelerating voltage scan technique using narrow source and energy resolving β-slits (0.1–0.2 mm). Energy release values were calculated in the usual way from the metastable peak width (FWHM) using the difference of squares method for correcting the main beam width. The metastable peaks recorded on the Kratos (AEI) MS-902 instrument were obtained in a similar manner using similar experimental conditions. The measurements using the ORNL triple analyzer mass analyzer ion kinetic energy (MIKE) spectrometer were obtained in the usual manner.

The ionization/appearance energy measurements were reported on the Kratos MS-50 operating at a trap current of 20 μA and a source pressure of 5×10⁻⁷ Torr. The threshold values were estimated by the semi-log method with the energy axis calibrated using the AE ([C6H5]+) (literature value 13.94 eV) and IE ([C6H6]+) (literature value 9.25 eV) from benzene and the AE ([C6H7]+) (literature value 10.1 eV) and IE ([C6H8]+) (literature value 8.82 eV) from toluene. For the low ionizing energy metastable studies the ionization voltage was lowered while monitoring the metastable signal. The reaction threshold is defined as the electron energy corresponding to a diminution of the metastable signal to a value of 0.01 relative to the 50 eV metastable signal. Thus, the 0.5 eV above threshold measurements correspond to increasing the ionizing electron voltage to a value of 0.5 V above threshold.

The chemicals employed in this study were obtained from standard commercial sources. The isotopically labeled materials were obtained from Merck Isotopes, Inc. 3,5-Cycloheptadienone31 and 4,4-dimethylcyclohexadione32 were synthesized by standard literature methods. The synthesized materials were characterized by ¹H NMR and infrared spectroscopic methods, and the sample purity was confirmed by gas chromatography.

**CONCLUSIONS**

The characteristically different kinetic energy release values and metastable ion branching ratios for hydroxybenzyl and hydroxytropylium [C7H7O]+ ions are interpreted as evidence that these two ions do not interconvert on the microsecond time-scale. The fact that methylphenols, substituted methylphenols and protonated 2,4,6-cycloheptatrienone produce a common structure(s) on the ICR time-scale (~10⁻³ s⁻¹) is not a result of the different observation times of the experimental apparatus, but is attributed to the internal energy of the [C7H7O]+ precursor ions. That is, molecular ions of methylphenols which dissociate to give [C7H5O]+ ions dissociating with rate constants of 10⁶ s⁻¹ (metastable ion time window) have higher averaged internal energies than the corresponding ions giving rise to stable [C7H7O]+ ions. Based on the mechanism originally proposed by Dunbar, i.e. isomerization of toluene and cycloheptatriene molecular ions is competitive with direct dissociation of the unarranged molecular ions to produce benzyl and tropyl ions, the different structural populations of molecular ions to produce benzyl and tropyl ions, the different structural populations of molecular ions undergo ring expansion and subsequently dissociate to hydroxytropylium ions. The marked change in the observed kinetic energy release for 2-chloro-4-methylphenol suggests that the chlorine substituent facilitates isomerization of the molecular ions.

The results from metastable ion studies are not conclusive as to the structure and rearrangement reactions of protonated benzaldehyde and methylarylxy [C7H7O]+ ions. It is evident that these ions do not isomerize to the hydroxybenzyl ion struc-
ture. On the other hand, the metastable kinetic energy release values (decarbonylation) do not rule out the possibility that a substantial fraction of the phenylmethylene ether \([C_6H_4O]^+\) isomerizes to a 2-hydroxybenzyl or 2-methylarylxy ion structure.

Acknowledgements

This research was supported by a grant from the Robert A. Welch Foundation, the Research Corporation and the U.S. Department of Energy, Office of Basic Energy Sciences. We also acknowledge Texas A&M University Center for Energy and Mineral Resources (CEMR) for funds to purchase equipment utilized in these studies.

Note

A referee has suggested that the constant kinetic energy release values for hydroxybenzyl \([C_6H_5O]^+\) ions and the changing branching ratio \((-CO/-CH_2O)\) could be interpreted as evidence for the isomerization \(a \rightleftharpoons b\). He argues that bis(4-hydroxyphene)ethane produces initially a hydroxybenzyl ion which isomerizes (prior to dissociation) to a hydroxytropylium ion. Thus, the large kinetic energy release for the \([C_6H_5O]^+\) ion is attributable to both reverse critical energy and excess or non-fixed energy. The change in the branching ratio \((-CO/-CH_2O)\) for bis(4-hydroxyphenyl)ethane can then be interpreted as evidence that low energy \([C_6H_5O]^+\) ions, those decomposing in the third field free region, have a hydroxytropylium structure. We discount this interpretation because one should also observe a significant change in the kinetic energy release as ions with lower internal energies are sampled, i.e. the non-fixed energy component of the kinetic energy release should also be sensitive to \(E_{\text{int}}\). As noted previously, the differences \((540\ \text{meV versus} \ 495\ \text{meV})\) in the measured kinetic energy releases contained in Table 1 are not significant due to differences in the energy discrimination for high voltage and MIKE scans on the ORNL triple analyzer instrument. We have reinvestigated this point using our Kratos MS-50TA (triple analyzer) instrument and have found that this is the case. For example, the first field free region kinetic energy release (for CO loss) is 550 meV as compared with 545 meV for the third field free region value (MIKE scan). Also, the first field free region kinetic energy release value is unchanged as different reaction times are sampled, e.g. kinetic energy release measurements made at main beam voltages of 6 kV, 4 kV, 2 kV and 1 kV all give the same kinetic energy release value, viz. \(550 \pm 10 \ \text{meV}\).

It could be argued that the constant kinetic energy release value (CO loss) arises from a rate determining isomerization. That is, the critical energy for the isomerization \(a \rightleftharpoons b\) is in excess of the dissociation energy for hydroxytropylium \([C_6H_5O]^+\). In this case the non-fixed energy component of the kinetic energy release would remain constant; however, such a potential energy surface would also require that the branching ratios also remain constant as ions with different energies are sampled (see Ref. 10, pp. 32–36).

REFERENCES

4. For example, dissociation of \([CF_X]^+\) (\(X = I, Br, CI\)) ions has been observed and attributed to the absorption of a single \(10 \mu\) IR photon. This has been attributed to the presence of a highly vibrationally excited ion in the ion beam, initially formed with a total energy within \(900-1000\ \text{cm}^{-1}\) of the dissociation limit. See: M. J. Coggiola, P. C. Cosby and J. R. Peterson, J. Chem. Phys. 72, 6507 (1980).
14. A referee has pointed out that the dominant loss of CO for the phenylmethylene ether \([C_6H_5O]^+\) ion is somewhat surprising, i.e. one would predict loss of CH\(_3\)O. The preferred loss of CO is consistent with the thermochemistry. For example, the reaction enthalpy for \([C_6H_5O]^+ -> [C_6H_4O]^+ + CO\) is significantly greater than that for \([C_6H_5O]^+ -> [C_6H_4^+]^+ + CO\). \(\Delta H = (\Delta H_2 - \Delta H_1) = 1003\ \text{kJ}\); \(\Delta H_1 = (\Delta H_2 + \Delta H_3) = 857\ \text{kJ}\). It is not unusual for rearrangement reactions, in the present case of CO, to have lower critical energies than simple cleavage processes—loss of CH\(_3\)O from phenylmethylene ether \([C_6H_5O]^+\).
16. The ionization potential for benzyl alcohol reported in this study is significantly lower than the value previously reported. See S. Pignatavo, A. Foffani, G. Innotra and G. Distefano, Z. Physik Chem. 49, 291 (1966); J. R. Gilbert, W. P. Leach and J. R. Miller, J. Organometal Chem. 49, 219 (1973).
18. S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O’Neal, A. S. Rodgers, R. Shaw and R. Walsh,
THE STRUCTURE OF DECOMPOSING [C_H_3O]^+ IONS


19. (a) In Ref. 1 the proton affinity of protonated 2,4,6-
cycloheptatrienone (hydroxytropylium ion) is estimated at
915 ± 8 kJ mol⁻¹. This value is used to estimate the heat of
formation of [C_H_3O]^+ using 43.4 kJ mol⁻¹ as the heat of
formation for the 2,4,6-cycloheptadienone neutral. See A.
(1982). (b) The PA ([C_H_3O]^+) obtained in our studies is
lower than that reported by H. Dits, N. M. M. Nibbering and

20. M. J. S. Dewar and D. Landman, J. Am. Chem. Soc. 99,
7439 (1977).

4907 (1977).

22. McLafferty has attributed the different kinetic energy re-
lease for the [C_H_3]^+ ion reported by Cooks to different
internal energies, i.e. higher kinetic energies originate from
excess or non-fixed energy. See R. G. Cooks, J. H. Beynon,
M. Bertrand and M. K. Hoffman, Org. Mass Spectrom. 7,
1303 (1973) and p. 5187 of Ref. 6b. It may be argued that
the hydroxy substituent of the [C_H_3O]^+ ion serves to
amplify the differences for kinetic energy releases of benzyl
versus tropylium ion structures. In fact, similar observa-
tions for other substituents (e.g. NH₂, OCH₃, F, Cl, etc.) are
consistent with the benzyl ion always giving rise to larger
kinetic energy release values (D. H. Russell, unpublished
results). See also Note at end of paper.


26. The computer program used for this work is similar to
that described in Ref. 24.

27. See Ref. 19 and M. J. S. Dewar and D. Landman, J. Am.


29. Consecutive metastable ion scanning methods have been
described previously, see D. H. Russell, E. H. McBay and T.

30. For a discussion of the 'ortho' effect see: F. W. McLafferty,
Interpretation of Mass Spectra, 3rd Ed., pp. 206-207, Uni-
versity Science Books, Mill Valley, CA (1980). See also M. L.
Gross, F. L. DeRoos and M. K. Hoffman, Org. Mass Spec-
trom. 12, 258 (1977).

31. K. E. Hine and R. F. Childs, J. Am. Chem. Soc. 95, 3288
(1973); E. E. van Tamelen, D. J. Paeto and A. A. Griswold,
J. Am. Chem. Soc. 84, 1213 (1962); D. I. Schuster, B. R.
Schole and F. T. H. Lee, J. Am. Chem. Soc. 90, 1300
(1968).


Received 7 January 1983; accepted 22 April 1983