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*Published in:*  
Journal of Mass Spectrometry

*DOI:*  
[10.1002/\(SICI\)1096-9888\(199606\)31:6<609::AID-JMS334>3.3.CO;2-S](https://doi.org/10.1002/(SICI)1096-9888(199606)31:6<609::AID-JMS334>3.3.CO;2-S)

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*Citation for published version (APA):*

Matimba, H. E. K., Ingemann Jorgensen, S., & Nibbering, N. M. M. (1996). Competing reactions leading to propene loss from the molecular ions of aryl n-propyl ethers. *Journal of Mass Spectrometry*, 31, 609-622. [3.3.CO;2-S](https://doi.org/10.1002/(SICI)1096-9888(199606)31:63.3.CO;2-S)

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# Competing Reactions Leading to Propene Loss from the Molecular Ions of Aryl *n*-Propyl Ethers

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The mechanisms of the elimination of a propene molecule from the molecular ions of a series of 3- and 4-substituted aryl *n*-propyl ethers ( $YC_6H_4OC_3H_7$ , Y = H, CH<sub>3</sub>, CF<sub>3</sub>, NO<sub>2</sub>, CH<sub>3</sub>S and CH<sub>3</sub>O) were examined with the use of deuterium labelling and tandem mass spectrometry. Propene loss dominates in the ion-source reactions and is the exclusive process observed for the metastable molecular ions of most of the aryl *n*-propyl ethers. This process is concluded to proceed by two distinct pathways on the basis of the relative importances of the losses of C<sub>3</sub>H<sub>4</sub>D<sub>2</sub> and C<sub>3</sub>H<sub>3</sub>D from the ionized ethers labelled with two deuterium atoms at the β-position of the *n*-propyl group in combination with the results of an analysis of the product ion structures. One pathway involves intermediate formation of an ion-neutral complex composed of a YC<sub>6</sub>H<sub>4</sub>O<sup>•</sup> radical and a <sup>+</sup>CH(CH<sub>3</sub>)<sub>2</sub> carbenium ion. This complex reacts further by proton transfer prior to dissociation with the formation of product ions, which have the same structure as the corresponding ionized and substituted phenols, YC<sub>6</sub>H<sub>4</sub>OH<sup>+</sup>. The second pathway involves a reversible 1,5-H shift from the β-position of the propyl group to the 2- or 6-position of the aromatic ring with the formation of a distonic ion, which expels propene to afford the molecular ion of a substituted cyclohexa-2,4-dienone species. The first pathway prevails for most of the ionized ethers with the exception of the molecular ions of the 3-methoxy- and 3-methylthio-substituted ethers, which expel propene largely by the second pathway. In addition, the 1,5-H shift-initiated propene loss is particularly pronounced for the metastable molecular ions of these latter two ethers, suggesting that this reaction is associated with a lower critical energy than the reaction involving formation of an ion-neutral complex.

KEYWORDS: aryl *n*-propyl ethers; propene loss; ion-neutral complexes; hydrogen shifts; metastable ions

## INTRODUCTION

The unimolecular dissociations of (radical) cations of relatively simple organic molecules are often discussed as involving the intermediate formation of ion-neutral complexes<sup>1-6</sup> and/or distonic ions.<sup>7-9</sup> In particular, the loss of the positional identity of atoms or functional groups within an ionic species prior to the dissociation step is frequently described as involving the conversion of a covalent bond into an electrostatic interaction between a neutral species and an ion.<sup>1</sup> The thus formed ion-neutral complexes are short-lived species, which normally escape direct experimental observation. Nevertheless, their involvement in various reactions of organic (radical) cations is commonly suggested on the basis of the results of labelling experiments in combination with energetic considerations. The various reactions which are considered to proceed with formation of ion-neutral complexes include CO loss from simple acylium ions such as the CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sup>+</sup> ion,<sup>10,11</sup> the elimination of an alkene from oxonium<sup>4,11</sup> or immonium<sup>12</sup> ions and the loss of a neutral species consisting of atoms or functional groups originating from remote sites in the molecular ions of bifunctional steroids.<sup>3,13</sup>

Even though an extensive series of reports indicates that ion-neutral complexes may be formed in the disso-

ciations of, in particular, metastable organic ions in the gas phase,<sup>1-5</sup> the involvement of such intermediates is seldom directly predictable. It appears particularly significant, therefore, to obtain experimental insight into the structural features which may promote the involvement of ion-neutral complexes and/or induce the occurrence of other pathways in the same overall process of a given ionic species. In this respect, the loss of an alkene from the molecular ions of alkyl phenyl ethers represents a process which has been proposed repeatedly to involve the formation of ion-neutral complexes.<sup>14-19</sup> For the molecular ion of phenyl *n*-propyl ether, propene loss is viewed mostly as cleavage of the bond between the oxygen atom and the alkyl group with formation of a complex of a phenoxy radical and a secondary propyl carbenium ion. Subsequently, this complex reacts by proton transfer prior to the occurrence of dissociation with the formation of C<sub>6</sub>H<sub>6</sub>O<sup>+</sup> ions, which are known to have only the structure of ionized phenol.<sup>14,17,18</sup> A more complex picture emerges, however, for the propene loss from the molecular ion of the corresponding phenyl *n*-propyl thioether, as indicated in a recent report.<sup>20</sup> For this system, propene loss is indicated to involve three competing reactions: (i) a 1,2-hydride shift-assisted cleavage of the bond between the propyl group and the sulphur atom, yielding an ion-neutral complex of a phenylthio radical and a secondary propyl carbenium ion; (ii) a partially reversible 1,5-H shift from the β-position of the *n*-propyl group to the 2- or 6-position of the ring; and (iii) a 1,3-H shift from the β-position to the sulphur atom. The

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occurrence of a relatively complex chemistry is reported also for the dissociations of the molecular ions of 2-fluoro-, 2-chloro- and 2-bromoethyl phenyl ether.<sup>21-25</sup> These species are known to expel a halogen-substituted ethene by a number of pathways, including a process involving a 1,5-H shift to the aromatic ring and dissociation with formation of stable cyclohexa-2,4-dienone radical cations. Such findings suggest that the mechanism of the loss of an alkene from ionized alkyl phenyl ethers may be influenced by the introduction of additional functional groups or atoms. However, a systematic study of the effect of the presence of different types of substituents on the mechanism of alkene loss from the molecular ions of various aromatic ethers has not been performed.

To obtain this insight into the effects of substituents, we decided to examine this process for the molecular ions of various alkyl phenyl ethers containing a functional group at the aromatic ring. In this paper, we report the results for the elimination of propene from the molecular ions of a series of aryl *n*-propyl ethers (YC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>; Y = H, CH<sub>3</sub>, CF<sub>3</sub>, NO<sub>2</sub>, CH<sub>3</sub>S and CH<sub>3</sub>O) and a number of deuterium-labelled analogues. These substituents were chosen primarily in order to explore whether the mechanism of propene loss depends on the electron-withdrawing or electron-donating properties of the substituent. Only the 3- and 4-substituted ethers were included in this study in order to exclude possible *ortho* effects leading to the dominance of reactions other than propene loss.<sup>26,27</sup>

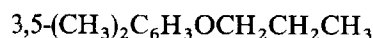
## EXPERIMENTAL

Electron impact (EI) ionization, mass-analysed ion kinetic energy (MIKES)<sup>28</sup> and collision-induced dissociation (CID)<sup>29</sup> spectra were recorded with a Fisons VG ZAB-HFqQ reverse geometry double-focusing quadrupole hybrid mass spectrometer.<sup>30,31</sup> Volatile samples were introduced into the ion source through a heated septum inlet (temperature 180°C). Solid compounds and high-boiling ethers were introduced with a heated direct insertion probe. The pressure in the ion source was mostly  $\sim 10^{-5}$  Pa as measured by an ionization gauge placed in a side-arm to the entrance of the diffusion pump situated beneath the ion-source housing. The ion-source parameters were: ionization energy 10, 15 or 70 eV, temperature 150–200°C, ion repeller potential 2–5 V and acceleration voltage 8 kV. The CID spectra were recorded with helium as the collision gas and with a reduction in the main beam intensity of 50%.

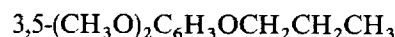
### Materials

The 3- and 4-YC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (Y = H, CH<sub>3</sub>, CH<sub>3</sub>O, CH<sub>3</sub>S and CF<sub>3</sub>) ethers and the analogues labelled with two deuterium atoms at the  $\beta$ -position of the *n*-propyl group ( $\geq 97\%$  *d*<sub>2</sub>) were prepared by reacting the YC<sub>6</sub>H<sub>4</sub>O<sup>-</sup> ion with the appropriate 1-bromopropane in a mixture of water and *N,N*-dimethylformamide for one or several days.<sup>32</sup> The same

procedure was applied for the syntheses of the



and



ethers and for the preparation of their analogues labelled with two deuterium atoms at the  $\beta$ -position of the *n*-propyl group. The 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> ether and the deuterium-labelled species ( $\geq 97\%$  *d*<sub>2</sub>) were prepared by reacting 4-FC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> with the sodium salt of the appropriate alcohol in tetrahydrofuran for 24 h.<sup>33</sup> The C<sub>6</sub>D<sub>5</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> ether (94% *d*<sub>5</sub> and 6% *d*<sub>4</sub>) was prepared by reacting C<sub>6</sub>D<sub>5</sub>O<sup>-</sup> with CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br in a mixture of D<sub>2</sub>O and dry *N,N*-dimethylformamide. The 3-CH<sub>3</sub>O-2,4,6-D<sub>3</sub>C<sub>6</sub>HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> ether (97% *d*<sub>3</sub>) was synthesized by first preparing 3-CH<sub>3</sub>O-2,4,6-D<sub>3</sub>C<sub>6</sub>HOH by an acid-catalysed hydrogen-deuterium exchange between the 3-methoxyphenol and D<sub>2</sub>O.<sup>34</sup> Subsequently, the sodium salt of the labelled 3-methoxyphenol was reacted with CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br in a mixture of D<sub>2</sub>O and dry *N,N*-dimethylformamide.

With the exception of the 3-CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>OH and 3-CH<sub>3</sub>O-5-NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH ethers, the substituted phenols used for the synthesis of the aryl *n*-propyl ethers were commercially available and used without further purification. 3-CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>OH was synthesized by diazotization of 3-CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> followed by decomposition of the hydrogensulphate salt of the diazonium species in a heated aqueous solution of sulphuric acid.<sup>35</sup> 3-CH<sub>3</sub>O-5-NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH was prepared from 3,5-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NO<sub>2</sub> by first forming 3,5-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OCH<sub>3</sub> by a nucleophilic substitution<sup>36</sup> prior to reduction of one of the nitro groups.<sup>32</sup> The resulting aniline, 3-CH<sub>3</sub>O-5-NO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub>, was subsequently converted into the desired phenol by diazotization and decomposition by the same procedure as applied in the preparation of 3-CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>.<sup>35</sup>

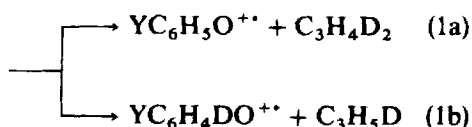
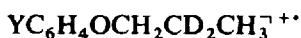
All the aryl *n*-propyl ethers were purified by preparative gas chromatography (Reoplex 400 column, temperature 140–170°C). The isomeric identity of the compounds was confirmed by NMR spectrometry and the label content was determined by EI mass spectrometry.

## RESULTS

### Ion-source reactions of the molecular ions of the aryl *n*-propyl ethers

The base peak in the 70 eV EI mass spectra of the unlabelled aryl *n*-propyl ethers, YC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (Y = H, CH<sub>3</sub>, CF<sub>3</sub>, NO<sub>2</sub>, CH<sub>3</sub>O and CH<sub>3</sub>S), corresponds to a YC<sub>6</sub>H<sub>5</sub>O<sup>+</sup> ion formed by loss of propene from the molecular ions. For the molecular ions of the ethers labelled with two deuterium atoms at the  $\beta$ -position of the *n*-propyl group, this process is observed to involve the competing losses of C<sub>3</sub>H<sub>5</sub>D and

$C_3H_4D_2$ , as indicated in Eqn (1). The relative abundances of the product ions generated by these competing reactions are given in Table 1 for molecular ions formed with an ionization energy of 70 and 15 eV, respectively.

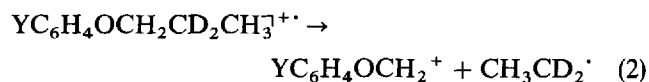


With an ionization energy of 70 eV, the ions formed by the competing losses of  $C_3H_5D$  and  $C_3H_4D_2$  fragment to some extent further in the ion source. Most of these secondary processes are observed also for the metastable fragment ions generated by propene loss from the molecular ions as described in the section.

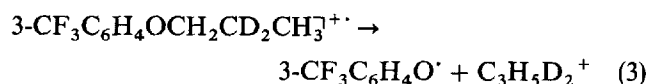
### Reactions of the product ions of propene loss.

As expected, the molecular ions and the product ions of propene loss are observed as the dominant species if the energy of the ionizing electrons is 15 eV. Irrespective of the occurrence of the secondary processes following 70 eV ionization, only minor changes in the relative importances of the losses of  $C_3H_5D$  and  $C_3H_4D_2$  are observed for most of the ethers upon lowering the electron energy from 70 to 15 eV. For the molecular ions of 3-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CD<sub>2</sub>CH<sub>3</sub>, however, the loss of  $C_3H_5D$  is significantly less pronounced if the ionization energy is 15 instead of 70 eV, as shown in Table 1. The reverse is observed for the molecular ions of 3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CD<sub>2</sub>CH<sub>3</sub>, that is, the decrease in the energy of the ionizing electrons results in a pronounced preference for the expulsion of a  $C_3H_5D$  molecule (see also Discussion).

In addition to propene elimination,  $\alpha$ -cleavage with the formation of minor amounts of  $YC_6H_4OCH_2^+$  ions is observed for the molecular ions of the ethers substituted with a methyl, methoxy or methylthio group. According to the results for the deuterium-labelled species, this process occurs without the loss of positional identity of the hydrogen and deuterium atoms of the propyl group:



The molecular ions formed by 70 eV EI and substituted with an electron-withdrawing group (CF<sub>3</sub> and NO<sub>2</sub>) at the 3-position also undergo heterolytic cleavage of the bond between the oxygen atom and the alkyl group to afford propyl carbenium ions, as illustrated in Eqn (3). This cleavage reaction is not observed for the molecular ions of the corresponding ethers with a CF<sub>3</sub> or NO<sub>2</sub> group at the 4-position.



Heterolytic cleavage of the oxygen-carbon bond is also observed for the molecular ions of the ethers containing a methylthio group. For these species, however,

**Table 1.** Normalized abundances (%) of the product ions formed in the ion source and the second field-free region (2nd FFR) by the competing losses of  $C_3H_4D_2$  and  $C_3H_5D$  from the molecular ions of the aryl *n*-propyl ethers (M) labelled with two deuterium atoms at the  $\beta$ -position of the alkyl group<sup>a</sup>

Substituent(s)	[M - C <sub>3</sub> H <sub>4</sub> D <sub>2</sub> ] <sup>+</sup> : [M - C <sub>3</sub> H <sub>5</sub> D] <sup>+</sup>		
	Ion source		
	70 eV	15 eV	2nd FFR
H	80:20	82:18	84:16
4-NO <sub>2</sub>	85:15 <sup>b</sup>	85:15 <sup>b</sup>	84:16 <sup>c</sup>
4-CF <sub>3</sub>	85:15	86:14	88:12
4-CH <sub>3</sub>	80:20	83:17	81:19
4-CH <sub>3</sub> O	76:24	76:24	74:26
4-CH <sub>3</sub> S	75:25	76:24	72:28
3-NO <sub>2</sub>	86:14	84:16	85:15
3-CF <sub>3</sub>	74:26	84:16	88:12
3-CH <sub>3</sub>	79:21	81:19	72:28
3-CH <sub>3</sub> O <sup>d</sup>	70:30	38:62	10:90
3-CH <sub>3</sub> S	76:24	—	36:64
3,5-(CH <sub>3</sub> ) <sub>2</sub>	75:25	—	45:55
3,5-(CH <sub>3</sub> O) <sub>2</sub>	33:67	29:71	5:95
3-CH <sub>3</sub> O-5-NO <sub>2</sub>	77:23	—	40:60

<sup>a</sup> The abundances of the  $YC_6H_4DO^{+ \cdot}$  ions formed in the ion source have been corrected for contributions from the <sup>13</sup>C isotope of the  $YC_6H_5O^{+ \cdot}$  ions.

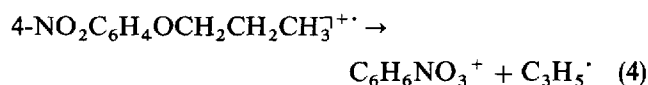
<sup>b</sup> Values obtained after correction for the occurrence of  $C_3H_4D_2^{\cdot}$  loss. This correction is based on the relative extent of the losses of  $C_3H_6$  and  $C_3H_6^{\cdot}$  in the ion-source reactions of the ionized unlabelled 4-nitrophenyl *n*-propyl ether and with a neglect of isotope effects (see text).

<sup>c</sup> Values obtained after correction for the loss of  $C_3H_4D_2^{\cdot}$ . This correction is based on the relative extent of the occurrence of the losses of  $C_3H_6$  and  $C_3H_6^{\cdot}$  from the metastable molecular ions of the unlabelled 4-nitrophenyl *n*-propyl ether and with a neglect of isotope effects (see text).

<sup>d</sup> Minor amounts of  $YC_6H_3D_2O^{+ \cdot}$  ions are also formed from the metastable molecular ions of this ether (see text and Fig. 1).

free propyl carbenium ions are formed irrespective of the position of the substituent with respect to the ether function.

A distinct reaction is observed for the 4-nitrophenyl *n*-propyl ether ions, that is, loss of a  $C_3H_5^{\cdot}$  radical (Eqn (4)) occurs to a minor extent in addition to the expulsion of a propene molecule.



For the molecular ions of 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CD<sub>2</sub>CH<sub>3</sub>, a minor loss of a  $C_3H_4D^{\cdot}$  radical is observed in addition to the losses of  $C_3H_4D_2^{\cdot}$  and  $C_3H_5D^{\cdot}$ .<sup>37</sup> The loss of a  $C_3H_3D_2^{\cdot}$  radical is expected to occur also, but gives rise to a product ion which is isobaric with the species generated by the elimination of  $C_3H_5D$ . Notwithstanding that the relative extent of the occurrence of these latter two processes in the ion source has not been ascertained, we have corrected the results in Table 1 for the anticipated contribution from the expulsion of  $C_3H_3D_2^{\cdot}$  on the

basis of the relative importances of the expulsions of  $C_3H_6$  and  $C_3H_5^+$  from the molecular ions of the unlabelled ether.

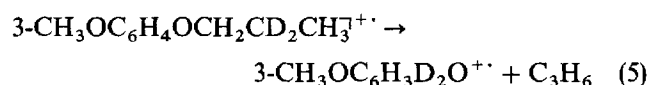
### Reactions of the metastable molecular ions

The molecular ions of the aryl *n*-propyl ethers dissociate on the microsecond time-scale nearly exclusively by loss of a propene molecule. The relative abundances of the ions formed by the competing losses of  $C_3H_4D_2$  and  $C_3H_5D$  from the metastable molecular ions of the ethers labelled with two deuterium atoms at the  $\beta$ -position of the *n*-propyl group are given in Table 1. For the ionized phenyl *n*-propyl ether labelled with deuterium at the  $\beta$ -position, the losses of  $C_3H_4D_2$  and  $C_3H_5D$  occurs in a ratio of 84:16, in agreement with results published previously.<sup>17,19</sup> A similar ratio is obtained for the metastable ions of the ether with a nitro group at the 4-position, whereas the ionized deuterium labelled 4-trifluoromethyl-substituted ether expels  $C_3H_4D_2$  and  $C_3H_5D$  in a ratio of 88:12. In contrast, the metastable molecular ions of the  $\beta$ - $d_2$ -labelled 4-methoxy- and 4-methylthio-substituted ethers show a tendency to eliminate relatively more  $C_3H_5D$  than the molecular ions of the other ethers containing a substituent at the 4-position (Table 1).

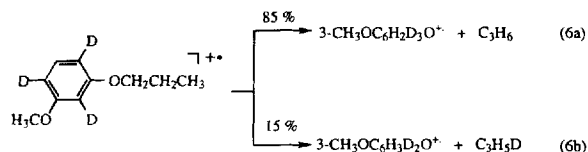
For the metastable molecular ions of the unlabelled 4-nitrophenyl *n*-propyl ether, the loss of a  $C_3H_5^+$  radical (Eqn (4)) is observed as a minor process in addition to  $C_3H_6$  elimination (~5%  $C_3H_5^+$  loss and ~95%  $C_3H_6$  loss). For the metastable molecular ions of the labelled ether, the loss of a  $C_3H_4D^+$  radical is visible, whereas the occurrence of the loss of  $C_3H_3D_2^+$  cannot be ascertained since this process gives rise to an ion which is isobaric with the product ion of  $C_3H_5D$  expulsion, as mentioned also for the ion-source reactions. Nevertheless, we have corrected the results for the metastable ions of the labelled 4-nitro-substituted ether for the expected loss of a  $C_3H_3D_2^+$  radical based on the relative abundances of the product ions of the competing losses of  $C_3H_5^+$  and  $C_3H_6$  from the metastable molecu-

lar ions of the unlabelled ether with a nitro group at the 4-position.

The ratio between the losses of  $C_3H_4D_2$  and  $C_3H_5D$  from the molecular ions of the ethers substituted with a nitro or trifluoromethyl group at the 3-position is similar to the value obtained for the corresponding 4-substituted species. A distinct pattern is observed, however, for the molecular ions of the ethers containing a methyl, methoxy or methylthio group at the 3-position. For these ions a pronounced increase in the relative importance of  $C_3H_5D$  loss is observed with increasing ion lifetime. In particular, the ratio for the losses of  $C_3H_4D_2$  and  $C_3H_5D$  from the molecular ions of 3- $CH_3OC_6H_4OCH_2CD_2CH_3$  changes from 70:30 in the ion source to 10:90 in the second field-free (2nd FFR) region of the instrument (see Table 1). Moreover, the molecular ions of this latter ether expel to a minor extent a  $C_3H_6$  molecule (Eqn (5) and Fig. 1), indicating the occurrence of interchange between the deuterium atoms at the  $\beta$ -position of the alkyl group and the hydrogen atoms at the aromatic ring.



The occurrence of the interchange between the hydrogen atoms of the alkyl and phenyl groups is further corroborated by the occurrence of the additional loss of  $C_3H_5D$  from the metastable ions of the ring-labelled compound shown in Eqn (6).



A few disubstituted aryl *n*-propyl ethers labelled with two deuterium atoms at the  $\beta$ -position of the alkyl group were also included in the present study in order to examine the effects of two similar substituents and the balance between the effects due to the presence of two different substituents at the aromatic ring. The

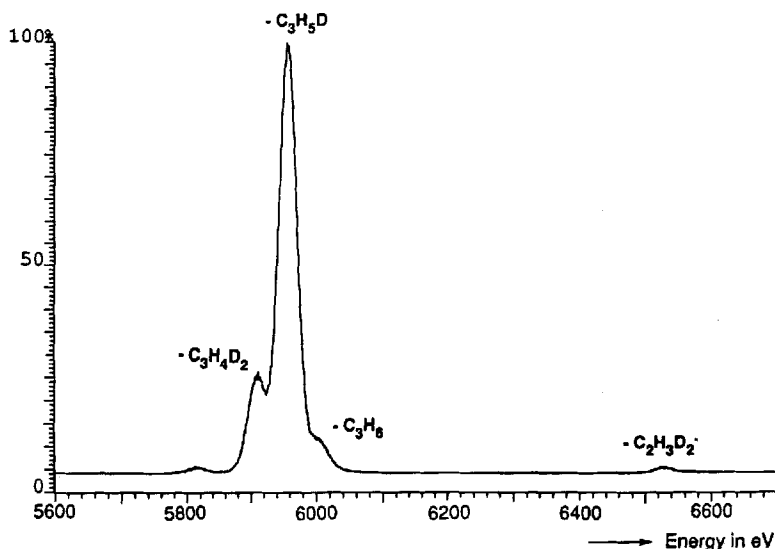
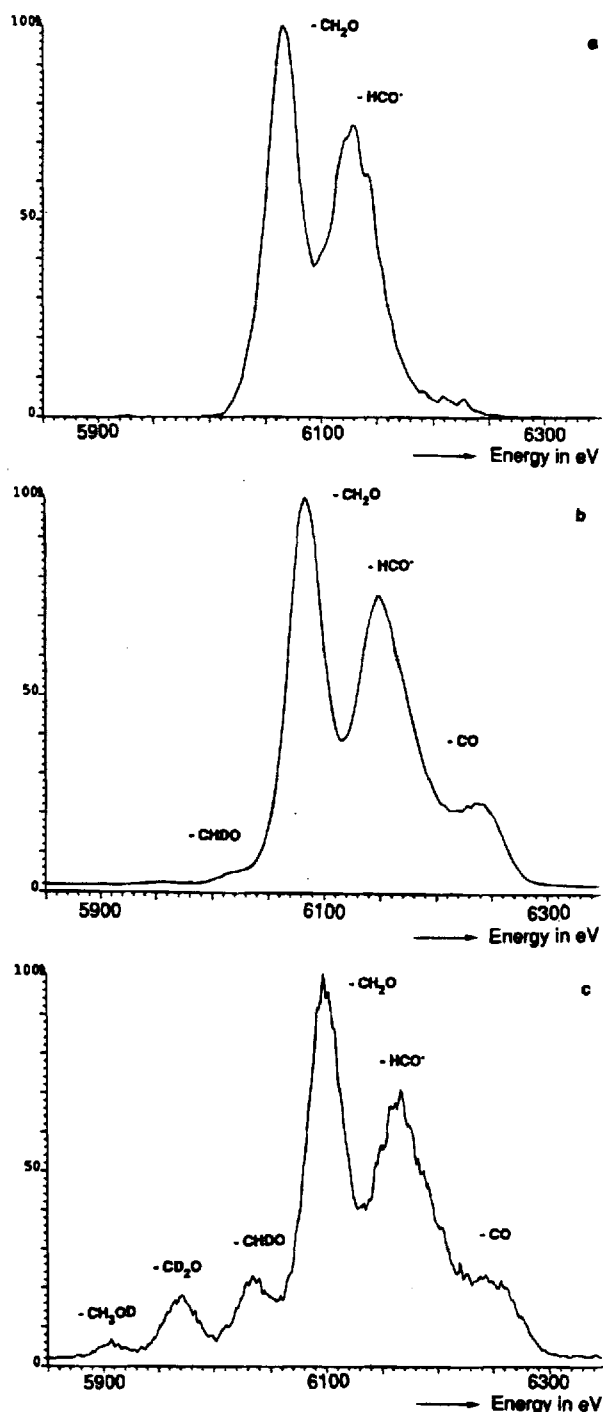


Figure 1. Partial MIKE spectrum of the metastable molecular ions of 3- $CH_3OC_6H_4OCH_2CD_2CH_3$ .



**Figure 2.** Partial MIKE spectra of the metastable ions formed by the losses of  $C_3H_4D_2$ ,  $C_3H_5D$  and  $C_3H_6$  from the molecular ions of 3- $CH_3OC_6H_4OCH_2CD_2CH_3$  generated with an ionization energy of 70 eV. (a) Spectrum of the metastable ions formed by  $C_3H_4D_2$  loss; (b) spectrum of the metastable ions formed by  $C_3H_5D$  loss; (c) spectrum of the metastable ions formed by  $C_3H_6$  loss. The metastable peak ascribed to the loss of  $CD_2O$  can be assigned in part also to the loss of  $CH_3OH$ .

results in Table 1 indicate that the presence of a methyl group at the 3-position as well as the 5-position introduces a preference for transfer of a deuterium atom from the  $\beta$ -position of the *n*-propyl group. In addition, the presence of a methoxy group at both of these sites causes propene elimination from the metastable ions to

involve almost exclusively the transfer of a  $\beta$ -deuterium atom. However, the metastable molecular ions of the deuterium-labelled 3-methoxy-5-nitro-substituted ether expel  $C_3H_4D_2$  and  $C_3H_5D$  in a ratio of 40:60, whereas the sole presence of a methoxy group at the 3-position leads to a ratio of 10:90 between the losses of these neutral species (Table 1). In other words, the preference for transfer of a  $\beta$ -deuterium atom in the propene loss from the metastable methoxy-substituted ions is counterbalanced to some extent by the introduction of a nitro group at the 5-position.

Propene loss from the metastable ions of all the aryl *n*-propyl ethers is associated with a Gaussian-shaped peak and a moderate kinetic energy release.<sup>28</sup> The kinetic energy release for loss of  $C_3H_4D_2$  and  $C_3H_5D$  from the metastable ions of  $C_6H_5OCH_2CD_2CH_3$  is the same (20 meV, as determined from the full width at half-height,  $T_{0.5}$ ) and a similar result is obtained for nearly all the ethers examined. In contrast, the metastable ions of 3- $CH_3OC_6H_4OCH_2CD_2CH_3$  expel  $C_3H_4D_2$  with a kinetic energy release of 35 meV, whereas the value for the loss of  $C_3H_5D$  is 10 meV lower,  $T_{0.5} = 25$  meV.

### Reactions of the product ions of propene loss

A number of studies have established that the loss of propene from the molecular ions of *n*-propyl phenyl ether yields  $C_6H_6O^{+}$  ions which have the structure of ionized phenol.<sup>14,25,38-40</sup> For the present substituted aryl *n*-propyl ethers no previous results are available concerning the possible structures of the ions generated by propene loss. In order to probe the structure(s) of the present  $YC_6H_5O^{+}$  product ions, the spontaneous reactions and collision-induced dissociations (CID) of these species were studied and compared with the results for the molecular ions of the corresponding  $YC_6H_4OH$  phenols.

The reactions of the metastable ions formed by propene loss in the ion-source reactions of the substituted aryl *n*-propyl ethers are summarized in Table 2. For the methyl-substituted ethers, the metastable ions formed by propene loss dissociate further by the losses of a CO and a water molecule. These processes are observed for the ions derived from both methyl-substituted ethers with the only difference being that the CO loss is more pronounced for the ions originating from the 3-methyl- than from the 4-methyl-substituted ether.

The metastable product ions generated by propene loss from the ionized trifluoromethyl-, methoxy-, methylthio- and nitro-substituted ethers undergo a number of reactions, which involve primarily the substituent. These reactions are observed to depend strongly on the position of the substituent in the parent species, as indicated by the results in Table 2. For example, the metastable ions generated from the 3-trifluoromethyl-substituted ether expel CO and HF in addition to  $HO^+$ ,  $F^+$  and  $CF_2^+$ , whereas only the last three losses are observed for the ions derived from the 4-trifluoromethyl-substituted ether. A distinct reactivity is found also for the ions derived from the 4-methoxy-substituted ether, which expel only a methyl radical. In

Table 2. Main reactions of the metastable product ions generated by the competing losses of  $C_3H_3D$  and  $C_3H_4D_2$  from the molecular ions of the deuterium-labelled aryl *n*-propyl ethers<sup>a</sup>

Ether	Metastable product ion	Loss of <sup>b</sup>	%		
3- $CH_3C_6H_4OCH_2CD_2CH_3$	$CH_3C_6H_4DO^{+\cdot}$	$H_2O$	25		
		$HDO$	45		
		$CO$	30		
4- $CH_3C_6H_4OCH_2CD_2CH_3$	$CH_3C_6H_4DO^{+\cdot}$	$H_2O$	60		
		$CO$	40		
		$H_2O$	30		
3- $CF_3C_6H_4OCH_2CD_2CH_3$	$CF_3C_6H_4DO^{+\cdot}$	$H_2O$	30		
		$HDO$	50		
		$CO$	20		
3- $CF_3C_6H_4OCH_2CD_2CH_3$	$CF_3C_6H_4DO^{+\cdot}$	$H_2O$	75		
		$CO$	25		
		$DO^{\cdot}$	20		
		$F^{\cdot}$	30		
		$HF$	5		
		$DF$	10		
		$CO$	5		
		$CDFO^c$	5		
		$CF_2$	25		
		$HO^{\cdot}$	20		
		$F^{\cdot}$	35		
		$HF$	10		
4- $CF_3C_6H_4OCH_2CD_2CH_3$	$CF_3C_6H_4DO^{+\cdot}$	$CO$	5		
		$CHFO^d$	5		
		$CF_2$	25		
		$DO^{\cdot}$	5		
		$F^{\cdot}$	75		
		$CF_2$	20		
		$HO^{\cdot}$	5		
		$F^{\cdot}$	75		
		$CF_2$	20		
		3- $CH_3OC_6H_4OCH_2CD_2CH_3$	$CH_3OC_6H_4DO^{+\cdot}$	$CO$	10
				$HCO^{\cdot}$	40
				$CH_2O$	50
4- $CH_3OC_6H_4OCH_2CD_2CH_3$	$CH_3OC_6H_4DO^{+\cdot}$	$HCO^{\cdot}$	40		
		$CH_2O$	60		
		$CH_3^{\cdot}$	95		
3- $CH_3SC_6H_4OCH_2CD_2CH_3$	$CH_3SC_6H_4DO^{+\cdot}$	$CH_2D^{\cdot}$	5		
		$CH_3^{\cdot}$	100		
		$CH_3^{\cdot}$	5		
4- $CH_3SC_6H_4OCH_2CD_2CH_3$	$CH_3SC_6H_4DO^{+\cdot}$	$HS^{\cdot}$	90		
		$CH_2S$	5		
		$HS^{\cdot}$	95		
3- $NO_2C_6H_4OCH_2CD_2CH_3$	$NO_2C_6H_4DO^{+\cdot}$	$CH_2S$	5		
		$CH_3^{\cdot}$	95		
		$CH_2D^{\cdot}$	5		
3- $NO_2C_6H_4OCH_2CD_2CH_3$	$NO_2C_6H_4DO^{+\cdot}$	$CH_3^{\cdot}$	100		
		$NO^{\cdot}$	35		
		$NO_2^{\cdot}$	25		
		$HNO_2$	5		
		$DNO_2$	10		
		$NO^{\cdot} + CO$	25		
		$NO^{\cdot}$	35		
		$NO_2^{\cdot}$	20		
		$HNO_2$	20		
		$NO^{\cdot} + CO$	25		
		4- $NO_2C_6H_4OCH_2CD_2CH_3$	$NO_2C_6H_4DO^{+\cdot}/NO_2C_6H_6O^{+\cdot}$ <sup>a</sup>	$HO^{\cdot e}$	15
				$NO^{\cdot}$	85
$NO^{\cdot}$	100				

<sup>a</sup> See also text.

<sup>b</sup> Assumed composition of the neutral species eliminated in the dissociation of the metastable ions.

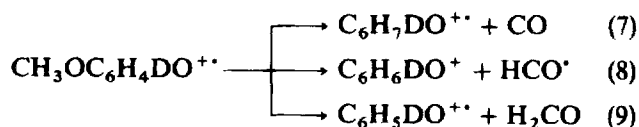
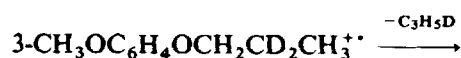
<sup>c</sup> May also represent the combined loss of  $DF$  and  $CO$ .

<sup>d</sup> Can also be ascribed to the combined loss of  $HF$  and  $CO$ .

<sup>e</sup> The  $HO^{\cdot}$  radical is expelled from the  $NO_2C_6H_6O^{+\cdot}$  ion generated by the loss of a  $C_3H_3D_2^{\cdot}$  radical from the molecular ion (see also text).

contrast, the  $\text{CH}_3\text{OC}_6\text{H}_5\text{O}^{+\cdot}$  ions generated from the 3-methoxy-substituted ether dissociate by the competing losses of a  $\text{CH}_2\text{O}$  molecule and a  $\text{HCO}^\cdot$  radical (see below). Similarly, the ions formed by propene loss from the ionized 4-methylthio-substituted ether expel only a methyl radical, whereas the corresponding ions derived from the 3-methylthio ether expel mainly an  $\text{HS}^\cdot$  radical and to a minor extent a  $\text{CH}_2\text{S}$  molecule. For the ethers containing a nitro group, the product ions of propene loss from the molecular ions of the 4-substituted ether expel only an  $\text{NO}^\cdot$  radical, whereas the corresponding ions from the ether with the nitro group situated at the 3-position dissociate by the competing losses of  $\text{NO}^\cdot$ ,  $\text{NO}_2^\cdot$  and  $\text{HNO}_2$  and the combined loss of  $\text{NO}^\cdot$  and  $\text{CO}$  (Table 2).

The reactions of the metastable ions formed by propene loss are, for most of the ethers studied, indistinguishable from the dissociations observed for the metastable molecular ions of the corresponding substituted phenols. Consequently, we have not included a listing of the reactions observed for the metastable molecular ions of the substituted phenols in Table 2. Significantly, some of the product ions of propene loss from the ionized ethers containing a substituent at the 3-position react differently from the metastable molecular ions of the corresponding phenolic ions. This is particularly evident for the ions derived by loss of a  $\text{C}_3\text{H}_5\text{D}$  molecule from the molecular ions of the deuterium-labelled 3-methylthio- and 3-methoxy-substituted ethers. The former product ions expel on the microsecond time-scale to a minor extent a methyl radical, whereas this reaction is not observed for the metastable ions formed by the loss of  $\text{C}_3\text{H}_4\text{D}_2$  from the ionized 3- $\text{CH}_3\text{SC}_6\text{H}_4\text{OCH}_2\text{CD}_2\text{CH}_3$  ether (Table 2). A more striking difference is observed for the product ions formed by the competing losses of  $\text{C}_3\text{H}_4\text{D}_2$ ,  $\text{C}_3\text{H}_5\text{D}$  and  $\text{C}_3\text{H}_6$  (Eqn (5)) from the molecular ions of the deuterium-labelled 3-methoxy ether (see Fig. 2). The metastable product ions of the former reaction expel only a  $\text{CH}_2\text{O}$  molecule and an  $\text{HCO}^\cdot$  radical (Fig. 2(a)), whereas the ions derived by  $\text{C}_3\text{H}_5\text{D}$  loss undergo the additional expulsion of a  $\text{CO}$  molecule (see Eqns (7)–(9) and Fig. 2(b)). The expulsion of a  $\text{CO}$  molecule is observed also for the metastable ions generated by the loss of  $\text{C}_3\text{H}_6$  from the parent species, as shown in Fig. 2(c). In addition, these metastable product ions react further by the competing losses of  $\text{CH}_2\text{O}$ ,  $\text{CDHO}$  and  $\text{CD}_2\text{O}$ , indicating the occurrence of hydrogen-deuterium atom interchange prior to this dissociation.



The loss of a  $\text{CO}$  molecule from the metastable ions generated by elimination of  $\text{C}_3\text{H}_5\text{D}$  is the minor process if the molecular ions of the labelled 3-methoxy-substituted ether are formed by ionization with 70 eV electrons (Fig. 2(b)). The relative importance of  $\text{CO}$  loss increases significantly, however, upon lowering the electron energy to about 20 eV, as can be seen from Fig.

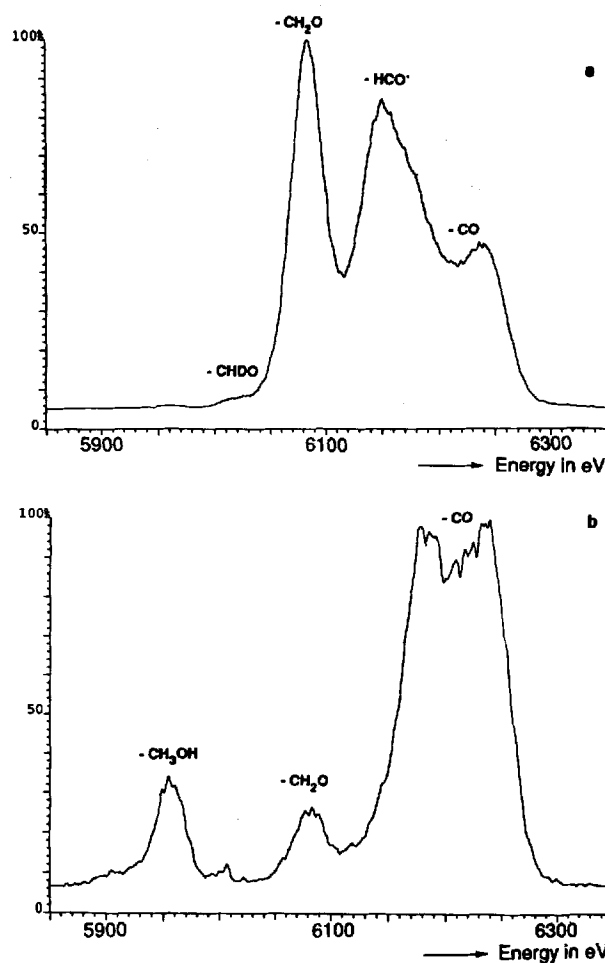


Figure 3. Partial MIKE spectra of the metastable ions formed by  $\text{C}_3\text{H}_5\text{D}$  loss from the molecular ions of 3- $\text{CH}_3\text{OC}_6\text{H}_4\text{OCH}_2\text{CD}_2\text{CH}_3$  generated with an ionization energy of (a) 20 and (b) 10 eV.

3(a). A further decrease in the electron energy to about 10 eV causes  $\text{CO}$  loss to dominate and, in addition, loss of methanol becomes observable (see Fig. 3(b)).

The CID spectra of the product ions of propene loss from the molecular ions of the various deuterium-labelled aryl *n*-propyl ethers were also recorded. For most of the ionized ethers, the CID spectra of the ions generated by  $\text{C}_3\text{H}_4\text{D}_2$  loss are virtually identical with the CID spectra of the molecular ions of the corresponding substituted phenols. Moreover, the ions formed by  $\text{C}_3\text{H}_5\text{D}$  loss give rise to CID spectra which are similar to the spectra of the corresponding unlabelled and substituted phenol ions, with the exception of the shifts in the  $m/z$  ratios owing to the presence of a single deuterium atom. For the ethers with a methoxy or nitro group at the 3- or 4-position, the CID spectra of the product ions generated by the losses of  $\text{C}_3\text{H}_4\text{D}_2$  and  $\text{C}_3\text{H}_5\text{D}$  are given in Tables 3 and 4 together with CID spectra of the corresponding unlabelled ionized phenols.

With respect to the ions derived by the loss of  $\text{C}_3\text{H}_4\text{D}_2$  from the ionized 4-methoxy-substituted ether, no significant difference is observed between the CID spectrum of these ions and the spectrum of the molecular ion of 4-methoxyphenol. A similar situation applies to the ions generated by  $\text{C}_3\text{H}_5\text{D}$  loss with the exception



**Table 3.** Collision-induced dissociation spectra of the product ions formed by propene loss from the molecular ions of 3- and 4- $\text{CH}_3\text{OC}_6\text{H}_4\text{OCH}_2\text{CD}_2\text{CH}_3$  together with the spectra of ionized 3- and 4-methoxyphenol (see also text)

<i>m/z</i>	3- $\text{CH}_3\text{OC}_6\text{H}_4\text{OCH}_2\text{CD}_2\text{CH}_3$			4- $\text{CH}_3\text{OC}_6\text{H}_4\text{OCH}_2\text{CD}_2\text{CH}_3$		4- $\text{CH}_3\text{OC}_6\text{H}_4\text{OH}^{+\bullet}$
	$\text{C}_7\text{H}_8\text{O}_2^{+\bullet}$ <sup>a</sup>	$\text{C}_7\text{H}_7\text{DO}_2^{+\bullet}$ <sup>b</sup>	3- $\text{CH}_3\text{OC}_6\text{H}_4\text{OH}^{+\bullet}$	$\text{C}_7\text{H}_8\text{O}_2^{+\bullet}$ <sup>a</sup>	$\text{C}_7\text{H}_7\text{DO}_2^{+\bullet}$ <sup>b</sup>	
110		1			77	
109	1	1	2	74	4	80
108	1	1	1	2		2
107	1	1	2			
106	1	1	1			
105	2	1	1			
97		8				
96		21			1	
95	24	39	21	1		1
94	43		35		2	
93	3		5	2		1
82		3			6	
81	3		4	6		6
79	1		1			
77	1	1	1			
69	2	3	3			
66		4	2		2	
65	4		5	3		3
64	2	2	2		1	
63	2	2	2	2		1
56		1				
55	1		1			
54		3				
53	2		3	4	4	3
51	2	1	2	3	1	1
50			1			
41	1	1	1			
40		2				
39	2	2	3	2	1	1
37	1	1	1	1	1	1

<sup>a</sup> Formed by loss of  $\text{C}_3\text{H}_4\text{D}_2$  from the ionized ether.

<sup>b</sup> Formed by loss of  $\text{C}_3\text{H}_5\text{D}$  from the ionized ether.

of the expected shifts in the *m/z* ratios caused by the presence of one deuterium atom in the product ion. The CID spectrum of the product ion of  $\text{C}_3\text{H}_4\text{D}_2$  loss from the ionized 3-methoxy-substituted ether is also indistinguishable from the spectrum of the molecular ion of 3-methoxyphenol. For the product ion of  $\text{C}_3\text{H}_5\text{D}$  loss, the presence of a peak at *m/z* 97 corresponding to CO loss is the only significant difference with respect to the CID spectrum of the ionized phenol (Table 3).

For the ether substituted with a nitro group at the 3-position, similar CID spectra are obtained for the product ions of propene loss and the molecular ion of 3-nitrophenol. Likewise, the CID spectrum of the product ion of  $\text{C}_3\text{H}_4\text{D}_2$  loss from the molecular ion of the 4-nitro-substituted ether is essentially identical with the spectrum of ionized 4-nitrophenol. Unfortunately, a CID spectrum of the ions derived by  $\text{C}_3\text{H}_5\text{D}$  loss unperturbed by the presence of the isobaric product ion of the loss of a  $\text{C}_3\text{H}_3\text{D}_2^{\bullet}$  radical (see above) could not be recorded. The CID spectrum given in Table 4 probably corresponds to a mixture of the ions formed by the competing losses of  $\text{C}_3\text{H}_5\text{D}$  and  $\text{C}_3\text{H}_3\text{D}_2^{\bullet}$  (see Eqn (4)), as indicated, for example, by the pronounced abundance of an ion with *m/z* 123 and the formation of an

ion with *m/z* 109 (Table 4). The probable structure of the product ions of  $\text{C}_3\text{H}_3\text{D}_2^{\bullet}$  loss and a possible mechanism of this process will be discussed elsewhere.<sup>37</sup>

## DISCUSSION

With respect to the loss of an alkene from the molecular ions of alkyl phenyl ethers, this process has been put forward repeatedly as a typical reaction which can be described adequately only in terms of the involvement of ion-neutral complexes.<sup>1,5,14-19</sup> This interest in ionized alkyl phenyl ethers as suitable model species for the study of the role of ion-neutral complexes in dissociation processes is related in part to the fact that alkene loss predominates in the ion source and also on the microsecond time-scale and in part to the finding that the  $\text{C}_6\text{H}_6\text{O}^{+\bullet}$  product ions are reported to have only the structure of ionized phenol. In addition, a number of earlier EI studies employing deuterium labelling revealed that ionized *n*-propyl and *n*-butyl phenyl ether eliminate propene<sup>38</sup> and butene,<sup>41</sup> respectively, by a process involving the transfer of a hydrogen atom,

**Table 4.** Collision-induced dissociation spectra of the product ions formed by propene loss from the molecular ions of 3- and 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CD<sub>2</sub>CH<sub>3</sub> together with the spectra of ionized 3- and 4-nitrophenol (see also text)

<i>m/z</i>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> CD <sub>2</sub> CH <sub>3</sub> <sup>+</sup>			4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> CD <sub>2</sub> CH <sub>3</sub> <sup>+</sup>		
	C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> <sup>+</sup> <sup>a</sup>	C <sub>6</sub> H <sub>4</sub> DNO <sub>2</sub> <sup>+</sup> <sup>b</sup>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OH <sup>+</sup>	C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> <sup>+</sup> <sup>■</sup>	C <sub>6</sub> H <sub>4</sub> DNO <sub>2</sub> <sup>+</sup> /C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> <sup>+</sup> <sup>c</sup>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OH <sup>+</sup>
124					2	
123			1	3	18	4
111		4				
110	4	6	2	24	16	23
109	8		4		21	
94		36			8	
93	35	7	33	14	3	14
92	9	5	9	5	2	6
91	3		3	2		2
83					2	
82		12		2	3	4
81	8		8	5	2	5
80				4		2
76					1	
75	2		2	1	1	2
74				2		3
66		9			7	
65	13		16	14		15
64		5			3	
63	4		7	6	2	6
54		3				
53	3	4	4	5	2	4
50	3	2	3	3	2	3
40		2			1	
39	5	3	6	7	2	5
37	3	2	2	3	2	2

<sup>a</sup> Formed by loss of C<sub>3</sub>H<sub>4</sub>D<sub>2</sub> from the ionized ether.<sup>b</sup> Formed by loss of C<sub>3</sub>H<sub>6</sub>D from the ionized ether.<sup>c</sup> Formed by the competing losses of C<sub>3</sub>H<sub>6</sub>D and C<sub>3</sub>H<sub>3</sub>D<sub>2</sub><sup>+</sup>, respectively, from the ionized ether (see also text).

which may originate from any of the positions of the alkyl chain. The participation of a hydrogen atom from the different positions of the alkyl group is not statistical, however, as indicated by these previous studies. In particular, a slight but significant preference for the transfer of a hydrogen atom from the  $\gamma$ -position of the alkyl group was observed in the dissociations of the *n*-propyl phenyl ether molecular ions with a relatively low internal energy.

Similar results were obtained in a field ionization kinetic (FIK) study of propene loss,<sup>39</sup> that is, transfer of a hydrogen atom from any of the positions of the *n*-propyl group was noted even for dissociations of the molecular ions with a lifetime of about 10<sup>-11</sup> s. In addition, a preference for transfer of a hydrogen atom from the  $\gamma$ -position was noticeable and this preference was more marked for molecular ions with a longer lifetime. The unspecific, but non-random, incorporation of a hydrogen atom originating from the different positions of the *n*-propyl or *n*-butyl group was interpreted in the early literature as a result of competing processes involving cyclic transition states with a different ring size.<sup>38,41</sup> In the context of the discussions of ion-neutral complexes, propene loss from *n*-propyl phenyl ether ions is described as an elongation of the bond between the oxygen atom and the  $\alpha$ -carbon atom associated with a 1,2-hydride shift in the incipient primary carbenium to

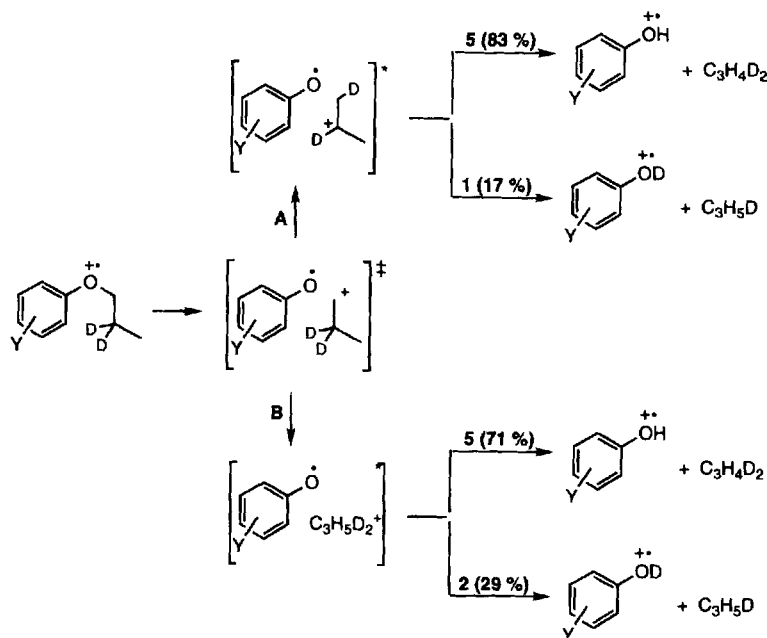
a secondary propyl carbenium ion.<sup>42</sup> The ion-neutral complex subsequently undergoes an irreversible proton transfer from one of the two methyl groups of the carbenium ion to the oxygen atom of the phenoxy radical, thus forming ionized phenol. For ions with a relatively low internal energy the initial 1,2-hydride shift leading to the secondary carbenium ion is considered to be irreversible, whereas the 1,2-hydride shifts can be reversible if the reactant species are formed with a relatively high internal energy.<sup>19</sup> Even though this model accommodates most of the experimental findings, the reported tendency to transfer preferably a hydrogen atom from the  $\gamma$ -position may still be seen as the existence of other pathways for the loss of propene from ionized *n*-propyl phenyl ether.

The ion-neutral complex model has been suggested to describe the loss of an alkene not only from ionized phenyl *n*-propyl ether but also from the molecular ions of alkyl phenyl ethers with a longer primary alkyl group, e.g. *n*-pentyl groups, as well as from ionized aromatic ethers containing a secondary and tertiary alkyl group.<sup>15,18</sup> For the other primary ethers the mechanistic scheme with formation of ion-neutral complexes is essentially the same as described for the *n*-propyl phenyl ether. For phenyl ethers with a secondary or tertiary alkyl group, the elongation of the oxygen-carbon bond is considered to lead directly to an ion-neutral complex

composed of a phenoxy radical and a secondary or tertiary carbenium ion, which reacts further by a rate-determining transfer of a proton from the  $\beta$ -position of the carbenium ion to the phenoxy radical prior to dissociation.<sup>18</sup> A distinct behaviour has been noted, however, for molecular ions of the 2-methyl-2-butyl phenyl ether with a relatively high internal energy.<sup>15</sup> For these ether ions, the loss of  $C_3H_{10}$  is observed to be associated with a preference for transfer of a hydrogen atom from the methylene group at the 3-position of the 2-methylbutyl group. This preference has been concluded to be in contrast with the occurrence of a process involving intermediate formation of an ion-neutral complex containing a tertiary  $CH_3CH_2(CH_3)_2C^+$  carbenium ion and a phenoxy radical.<sup>15</sup> This conclusion was based mainly on an anticipated statistical preference of proton transfer from one of the two methyl groups bonded directly to the positively charged carbon atom to the phenoxy radical in the hypothetical ion-neutral complex. The observed preference for transfer of a hydrogen atom from the 3-position of the 2-methylbutyl group was proposed, therefore, to be a result of a process involving a 1,5-H shift from the methylene group at this site to the 2- or 6-position of the phenyl ring. Subsequently, a 1,3-H shift to the oxygen atom was suggested to take place prior to the expulsion of  $C_3H_{10}$  with formation of ionized phenol.<sup>15</sup> This mechanism was formulated in analogy with the pathway described previously for the process leading to the formation of  $C_6H_6O^{++}$  ions with the phenolic structure by the loss of a halogen-substituted ethene from the molecular ions of phenoxyethyl halides with a relatively high internal energy.<sup>21-25</sup> For these latter species, however, the initial 1,5-H-shift to the aromatic ring is reported to be followed in part by the loss of halogen/substituted ethene to afford ionized cyclohexa-2,4-dienone.

With respect to the present ionized aryl *n*-propyl ethers, propene loss may be assumed, as a first approximation, to proceed as described for ionized *n*-propyl phenyl ether. For the ionized aryl *n*-propyl ethers containing two deuterium atoms at the  $\beta$ -position, the ratios for the losses of  $C_3H_4D_2$  and  $C_3H_5D$  can be predicted relatively easily if isotope effects are neglected. For example, this ratio is estimated to be 83:17 if the elongation of the oxygen-carbon bond is accompanied by an irreversible 1,2-deuteride shift leading to the complex of an aroxy radical and a secondary carbenium ion prior to deuterium or proton transfer and dissociation (see Scheme 1). Provided all hydrogen and deuterium atoms become equivalent by reversible 1,2-deuteride and 1,2-hydride shifts within the carbenium ion part of the complex, the ratio of the losses of  $C_3H_4D_2$  and  $C_3H_5D$  is predicted to be 71:29 (see Scheme 1).

For the labelled *n*-propyl phenyl ether, the present experimental results are comparable to those reported previously,<sup>19,38,39</sup> that is, in the ion source following 70 eV EI, the ratio between the losses of  $C_3H_4D_2$  and  $C_3H_5D$  is 80:20, whereas a ratio of 84:16 is obtained for the metastable ions (Table 1). As suggested by others,<sup>14-19</sup> this may indicate that reversible 1,2-deuteride and 1,2-hydride shifts occur in the carbenium ion at relatively high internal energy, whereas the formation of ion-neutral complexes in the reactions of the metastable ions involves a single irreversible 1,2-deuteride shift. For the molecular ions of the ether with a nitro group at the 4-position,  $C_3H_4D_2$  and  $C_3H_5D$  are expelled in a ratio of 85:15 irrespective of whether the reaction occurs in the ion source or on the microsecond time-scale. This ratio is close to that predicted for ion-neutral complex formation involving a single irreversible 1,2-deuteride shift. A similar observation applies to ion-source reac-



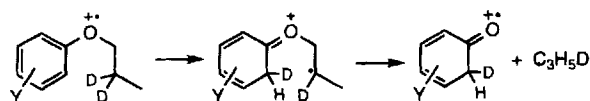
**Scheme 1.** Predicted ratios for the formation of the  $YC_6H_6O^{++}$  and  $YC_6H_4DO^{++}$  ions in the loss of propene from the molecular ions of the aryl *n*-propyl ethers with intermediate formation of ion-neutral complexes. Pathway A represents the formation of ion-neutral complexes by a single irreversible 1,2-deuteride shift followed by statistical transfer of a deuterium or proton assumed to occur without an isotope effect. Pathway B represents the formation of ion-neutral complexes by reversible 1,2-deuteride and hydride shift in the propyl carbenium ion prior to statistical transfer of a deuterium or proton occurring without an isotope effect.

tions of the 4-trifluoromethyl-substituted ether as induced by 70 eV ionization (Table 1), notwithstanding that the tendency to expel  $C_3H_5D$  is lower for molecular ions if the energy of the ionizing electrons is 15 eV. For the 4-methyl-substituted ether ions, the ratio between the losses of  $C_3H_4D_2$  and  $C_3H_5D$  in the ion source changes from 80:20 to 83:17 if the ionization energy is lowered from 70 to 15 eV but becomes 81:19 for the metastable ions. The variations are, of course, minor and not inconsistent with the model that assumes ion-neutral complex formation by a single irreversible 1,2-deuteride shift in the evolving carbenium ion (see Scheme 1). Likewise, the molecular ions of the 4-methoxy- and 4-methylthio-substituted ethers also expel  $C_3H_4D_2$  and  $C_3H_5D$  in a ratio which varies only slightly with internal energy of the dissociating ions. The results for these two ethers (see Table 1), however, are more in line with ion-neutral complex formation and complete loss of the positional identity of the hydrogen and deuterium atoms of the carbenium ion part of the complex. In summary, the results indicate a distinct behaviour of the molecular ions of ethers substituted with an electron-withdrawing group at the 4-position and the species containing a typical electron-donating group at this site of the aromatic ring.

The observation that the ionized ethers with a methoxy or methylthio group at the 4-position expel  $C_3H_4D_2$  and  $C_3H_5D$  in a ratio approaching the value predicted for complete loss of positional identity of the hydrogen and deuterium atoms of the propyl group indicates that the carbenium ion part of the complex is formed with sufficient internal energy to allow reversible hydride-deuteride shifts. A possible reason for this may then be sought in a tendency of the electron-donating groups to stabilize the molecular ions relatively more than the transition state for the step in the overall sequence which leads to the ion-neutral complex. In other words, the critical energy for this step could be relatively large, thus causing a relatively large internal energy to be required for this process to occur within the time-scale of the experiment. Essentially, this implies a larger kinetic shift of the reactions leading to propene loss from the molecular ions of the ethers substituted with a methoxy or methylthio group at the 4-position than of this process of the ionized ethers with a trifluoromethyl or nitro group at this site.

For the molecular ions of the ethers with a  $CF_3$  or  $NO_2$  substituent at the 3-position, the results are comparable to those obtained for the isomers with the substituent at the 4-position. The only exception is that the  $C_3H_4D_2$  loss following 70 eV ionization is more pronounced for the 3- $CF_3$ -substituted ether ions than for the isomer with the  $CF_3$  group at the 4-position (Table 1). A completely different picture emerges for the species with an electron-donating group at the 3-position. This holds in particular for the molecular ions of the ethers with a  $CH_3O$  or  $CH_3S$  group at the 3-position. These tend to eliminate  $C_3H_4D_2$  and  $C_3H_5D$  in the ion source in a ratio close to that predicted for complete loss of positional identity of the hydrogen and deuterium atoms of the propyl group. In contrast, the metastable molecular ions expel preferably a propene molecule with transfer of a hydrogen atom from the  $\beta$ -position of the *n*-propyl group. This behaviour is inconsistent with

the pathways involving ion-neutral complex formation as sketched in Scheme 1 and also in disagreement with the occurrence of a kinetic shift on propene loss from the ionized ethers with an electron-donating group at the 3-position. The experimental findings, however, are readily accommodated by inferring a 1,5-H shift from the  $\beta$ -position of the *n*-propyl group to the 2- or 6-position of the aromatic ring with formation of a distonic ion which then expels a propene molecule (Scheme 2).

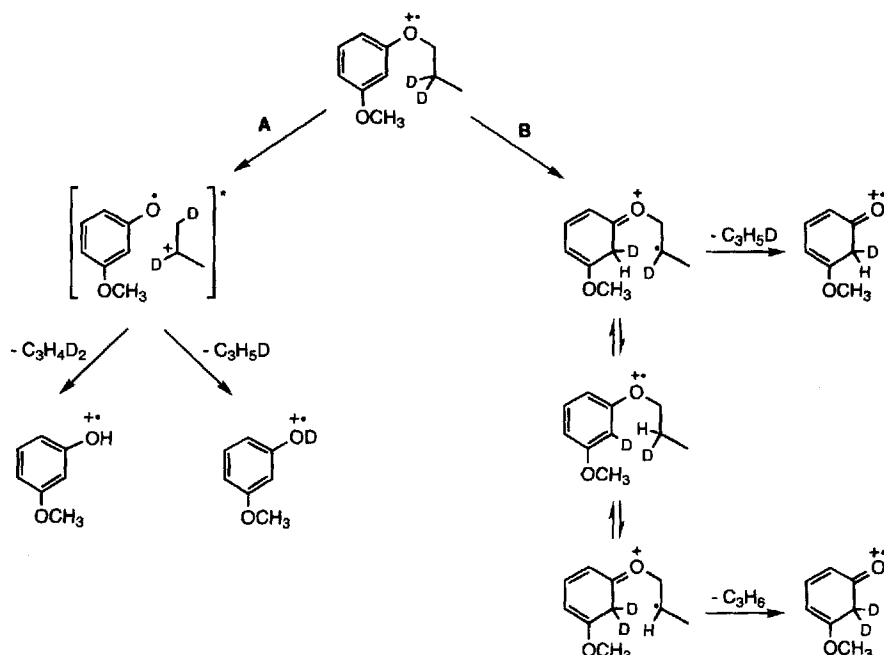


**Scheme 2.** Loss of propene initiated by a 1,5-H shift from the  $\beta$ -position of the *n*-propyl group to the 2- or 6-position of the aromatic ring.

The preference for the loss of  $C_3H_5D$  from the molecular ions formed by ionization with low-energy electrons and from the metastable ions (Table 1) indicate that the implied 1,5-H shift is associated with a lower critical energy than the pathway involving ion-neutral complex formation. In addition, in the ion-neutral complex mediated reaction an ionized substituted phenol is inclined to be formed, whereas an ionized and substituted cyclohexa-2,4-dienone species is predicted to arise by the 1,5-H shift initiated loss of propene, as illustrated for the molecular ion of the deuterium-labelled 3-methoxy-substituted ether in Scheme 3. In path A, ion-neutral complex formation is indicated to lead to the formation of ionized 3-methoxyphenol either unlabelled or with a deuterium atom at the hydroxy function. In path B, a 1,5-D shift is shown to afford a distonic ion, which can expel  $C_3H_5D$  or rearrange to ionized 3-methoxyphenyl *n*-propyl ether with one deuterium atom at the ring and one in the *n*-propyl group. Subsequently, a second 1,5-D shift can occur prior to the loss of  $C_3H_6$  with formation of a cyclohexa-2,4-dienone ion containing two deuterium atoms. The occurrence of  $C_3H_6$  loss implies, of course, that the 1,5-D(H) shifts from the  $\beta$ -position to the ring are reversible (see Eqn (6) and Fig. 1) and that the intermediate distonic ion is a stable species.

The occurrence of a 1,5-H shift from the  $\beta$ -position of the *n*-propyl group to the ring may also play a role in the reactions of the metastable molecular ions of the ethers with an electron-donating group at the 4-position. Such an additional pathway may then be held responsible for the slight increase in the relative importance of the loss of  $C_3H_5D$  from the ionized and deuterium-labelled ethers with a methyl, methoxy or methylthio group at the 4-position. It should be mentioned, however, that for these ethers no evidence is obtained for the generation of product ions by propene loss which have a structure distinct from that of the ionized 4-substituted phenols (see Results).

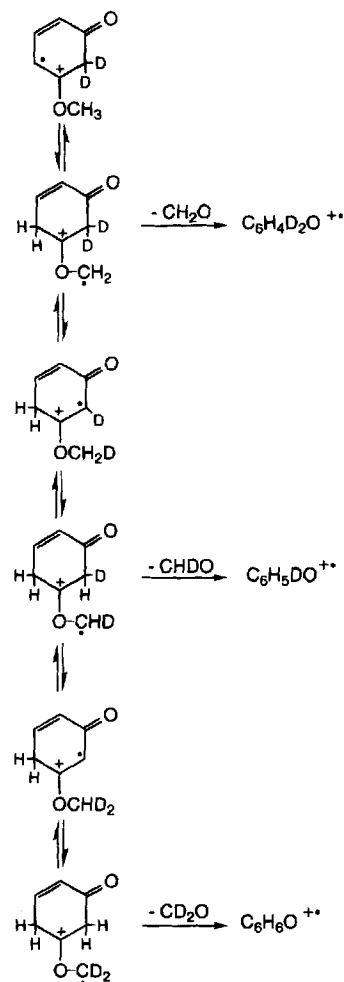
The formation of product ions with the structure of the molecular ions of the substituted phenols can be taken as support for the involvement of ion-neutral complexes in keeping with the fact that the pathway involving a 1,5-H shift is expected to result in the formation of substituted cyclohexa-2,4-dienone ions (Scheme 3). For the molecular ions of the 3-methoxy-substituted ether, the CID results summarized in Table



**Scheme 3.** Proposed mechanisms for the losses of  $C_3H_4D_2$ ,  $C_3H_5D$  and  $C_3H_6$  from the molecular ion of  $3-CH_3OC_6H_4OCH_2CD_2CH_3$  (see also text).

3 and the dissociations of the metastable product ions generated by the loss of  $C_3H_4D_2$  (Table 2) are in agreement with the formation of ions with the structure of ionized 3-methoxyphenol. For the pathway leading to the loss of  $C_3H_5D$ , an ion mixture consisting of ionized 3-methoxyphenol and 5-methoxycyclohexa-2,4-dienone is likely to arise. The formation of the former ion is in line with the occurrence of  $CH_2O$  and  $HCO^+$  expulsion as observed also for metastable molecular ions of 3-methoxyphenol, whereas the expulsion of CO suggests the presence of the other isomer (see Fig. 2(b)). In addition, if the loss of  $C_3H_6$  proceeds as indicated in Scheme 3, this reaction should lead to 5-methoxycyclohexa-2,4-dienone ions containing two deuterium atoms. The occurrence of the loss of CO supports this expectation, whereas the losses of  $HCO^+$  and formaldehyde can be taken to mean that ionized 3-methoxyphenol may arise also in the loss of  $C_3H_6$  and/or that the 5-methoxycyclohexa-2,4-dienone ions undergo the additional losses of the latter two neutral species. With respect to formaldehyde loss, this is preceded by interchange between the hydrogen atoms of the methyl group of the original methoxy group and deuterium atoms originating from the  $\beta$ -position of the *n*-propyl group in the parent species. This interchange leads to the losses of  $CDHO$  and  $CD_2O$  from the metastable product ions of  $C_3H_6$  loss and may occur as depicted in Scheme 4 if it is assumed that the dissociating ions have the initial structure of ionized 5-methoxycyclohexa-2,4-dienone.

The suggested formation of two distinct species in the loss of propene from the molecular ions of the 3-methoxy-substituted ether is further substantiated by the change in reactivity of the metastable ions generated by  $C_3H_5D$  loss as the energy of the ionizing electrons is lowered from 70 to 20 eV and then to 10 eV. As shown in Fig. 3, the loss of CO becomes more prominent if the ions are formed from molecular ions with a lower inter-

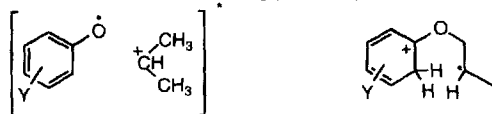


**Scheme 4.** Proposed mechanism for the hydrogen-deuterium interchange prior to the loss of  $CH_2O$ ,  $CDHO$  and  $CD_2O$  from the metastable ions generated by  $C_3H_6$  elimination from the molecular ions of  $3-CH_3OC_6H_4OCH_2CD_2CH_3$  (see also text).

nal energy. Such a finding could indicate that the most facile reaction of the metastable ions is the loss of CO, whereas the losses of CHO $\cdot$  and CH $_2$ O may be associated with relatively large critical energies. This requires, of course, that the metastable product ions of propene loss are formed with a lower internal energy if the electron energy is 10 eV than if the molecules are ionized with 70 eV electrons. However, as the electron energy is decreased, the transfer of a deuterium atom from the  $\beta$ -position becomes more pronounced (see above) and, in line with the suggested 1,5-D shift, the main product is expected to be ionized 5-methoxycyclohexa-2,4-dienone. A consistent picture can then be formulated for propene loss from the molecular ions of the 3-methoxy-substituted ether. That is, at relatively high internal energies this process is likely to proceed with intermediate formation of an ion-neutral complex which then dissociates to afford ionized 3-methoxyphenol. At relatively low internal energies of the molecular ion, ion-neutral complex formation is unable to compete effectively with the reversible 1,5-H shift leading to a distonic ion prior to propene loss with the formation of ionized 5-methoxycyclohexa-2,4-dienone. A similar situation may apply to the 3-methylthio-substituted species even though the metastable product ions of propene loss display a similar chemistry as ionized 3-methylthiophenol (see Table 2 and Results). For the 3-methyl-substituted ether, loss of propene by an initial 1,5-H shift is likely also to play a role for the metastable ions notwithstanding that this process appears to compete effectively with ion-neutral complex formation only if an additional methyl group is present at the 5-position (see Table 1).

## CONCLUSION

The combined results for the loss of propene from the molecular ions of the aryl *n*-propyl ethers indicate that this process proceeds in part by intermediate formation of ion-neutral complexes and in part by a process involving a 1,5-H shift from the  $\beta$ -position of the *n*-propyl group to the ring. The key intermediates in these processes can be formulated as (i) a complex composed of an aroxy radical and a secondary propyl carbenium ion and (ii) a stable distonic ion with a delocalized charge and a radical centre situated in a formal sense at the  $\beta$ -carbon atom of the propyl group.



For the ethers containing a functional group at the 4-position, the results for the ion-source reactions are consistent with propene loss involving the formation of ion-neutral complexes irrespective of the nature of the substituent. For the metastable molecular ions of the ethers with an electron-withdrawing group (NO $_2$  or CF $_3$ ) at the 4-position, no evidence is obtained for the occurrence of a 1,5-H shift. Moreover, propene loss initiated by a 1,5-H shift seems to be of only marginal importance in the reactions of the metastable molecular ions of the ethers with a methyl, methoxy or methylthio

group at the 4-position. In qualitative terms, this may imply that the 1,5-H shift initiated pathway for the latter species is associated with a critical energy which is comparable to the critical energy for the ion-neutral complex mediated reaction. In addition, the increase in the rate constant with increasing internal energy of the reactant molecular ions should be less pronounced for the former reaction than for the predominant channel involving ion-neutral complex formation.

With respect to the ethers with a functional group at the 3-position, the nature of this group exerts a dramatic influence on the relative importance of the two pathways. For the species with an electron-withdrawing group at this position no evidence is obtained for the occurrence of a 1,5-H shift. This may be related to the expected destabilization of the positive charge in the distonic ion (see above), which causes the system to prefer cleavage of the bond between the oxygen atom and the carbon atom at the  $\alpha$ -position of the *n*-propyl group with formation of the ion-neutral complex. In contrast, the introduction of an electron donating group at the 3-position will tend to stabilize the positive charge in the distonic intermediate. This may then be held responsible for the preference for the 1,5-H shift-initiated propene loss observed for the metastable molecular ions of the ether with a methoxy group at the 3-position. Furthermore, this effect is inclined to be more pronounced if a second electron-donating group is present at the 5-position. In agreement with this, the involvement of the 1,5-H shift-initiated propene loss is enhanced by the introduction of, for example, an additional methyl group at the 5-position of the aromatic ring of the 3-methyl-substituted ether (see Table 1). Moreover, the introduction of an electron-withdrawing group at the 5-position in addition to an electron-donating group at the 3-position is expected to destabilize the distonic ion. This may then lead to a decrease in the preference for the transfer of a hydrogen atom from the  $\beta$ -position of the *n*-propyl group, as indicated by the experimental findings for the metastable molecular ions of the deuterium-labelled 3-methoxy-5-nitrophenyl *n*-propyl ether in comparison with the results for the ether carrying only a methoxy group (Table 1). In conclusion, the strong preference for the 1,5-H shift-initiated propene loss for metastable molecular ions of the ethers with a methoxy or methylthio group at the 3-position indicates that this reaction is associated with a significantly lower critical energy than the formation of ion-neutral complexes. A similar conclusion has been reached for the loss of propene from the molecular ions of the phenyl *n*-propyl thioether which at relatively low internal energies proceeds mainly by a 1,5-H shift.<sup>20</sup> For the present ionized aryl *n*-propyl ethers the involvement of ion-neutral complexes in the loss of propene from ionized aryl *n*-propyl ethers is indicated to be dependent on the nature of the group attached to the aromatic ring and also on the position of a given group with respect to the ether function. In retrospect, the present observations in combination with results published previously for ionized phenyl alkyl ethers<sup>14-19</sup> and also the molecular ion of phenyl *n*-propyl thioether seem to indicate that the extent to which ion-neutral complexes are involved as key intermediates is not directly predictable.

### Acknowledgements

The authors thank the Netherlands Organization for Scientific Research (SON/NWO) for financial support. T. A. Molenaar-

Langeveld is acknowledged for assistance during the synthesis of some of deuterium-labelled aryl *n*-propyl ethers.

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