J. Am. Chem. Soc. **1991**, *113*, 9729–9734

Ion–Radical Complexes in the Gas Phase: Structure and Mechanism in the Fragmentation of Ionized Alkyl Phenyl Ethers

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Received April 1, 1991

Abstract: The threshold fragmentation behavior of ionized alkyl (C_2–C_5) phenyl ethers has been investigated in detail. Their lowest energy dissociation produces ionized phenol and an alkene. For some C_5 homologues formation of an ionized alkene and neutral phenol becomes a competitive reaction. These low-energy, (metastable ion) decompositions all involve the formation of a complex consisting of a phenoxy radical and an alkyl ion. For secondary and tertiary alkyl phenyl ethers, an irreversible β-H^+ transfer in the complex yields the $[C_6H_5OH]^{\bullet+}$ ion; the activation energy for these transfers is 145 ± 6 kJ mol^{-1} for secondary ions and 83 ± 1 kJ mol^{-1} for tertiary ions. The transition state for this process is discussed with reference to the theoretically calculated charge distributions in alkyl cations, in which the positive charge is mostly located in the groups attached to the formal charge-bearing carbon atom. With the exception of the ethyl analogue, primary alkyl ions undergo a rate-determining, single 1,2 H-shift producing a secondary or tertiary ion which then undergoes its characteristic β-H^+ transfer and rapidly dissociates. The activation energy for this rearrangement is 189 ± 9 kJ mol^{-1}. For a primary alkyl group having no β-H atom (e.g., $CH_2C(CH_3)_3$), a 1,2 methyl shift takes place in the complex (activation energy ca. 129 kJ mol^{-1}), producing a tertiary ion which undergoes rapid β-H^+ transfer and then fragments. For ethyl phenyl ether, it is proposed that the transition state is best represented as a symmetrical H^+ bridged species involving the nonclassical ethyl ion. For C_5H_{11} isomers, new dissociation channels become competitive. The 1-pentyl and the 2-methyl-2-butyl phenyl ethers also showed loss of an ethyl radical in the metastable time frame producing the daughter ion $C_6H_5OC^+(CH_3)_2$, the first ether after a rearrangement, and the second by a simple bond cleavage. The 3-methyl-1-butyl and 2,2-dimethylpropyl analogues displayed *m/z* 70, $C_5H_{10}^{\bullet+}$ ions, in their metastable ion mass spectra. These arose from specific β-H *atom* transfer, competing with β-H^+ transfer, from the tertiary ion in the complex. The conclusions outlined above were reached with the aid of isotopic labeling, appearance energy measurements, and charge stripping mass spectrometry. For the C_4 and C_5 ions, more complex reactions come into play at higher internal energies, e.g., for ions which fragment in the ion source.

Introduction

Gas-phase ion–molecule and ion–radical complexes are species in which an ion and a neutral are bound chiefly by electrostatic forces. The formation of such complexes could be described as the gas-phase analogue of solvolysis,[1] because both involve the transformation of a covalent bond into an electrostatic bond. Morton[2] has recently redefined these ion-neutral complexes as "a noncovalently bonded aggregate of an ion with one or more neutral species in which at least one of the partners rotates freely (or nearly so) in all directions".

Recent advances in gas-phase ion chemistry have clearly indicated the importance of such species and the central role that they can play in reaction mechanisms.[3] It is, however, no simple matter generally to identify these species (and other newly discovered types of ion, such as hydrogen bridged ion–radical pairs[4]) by experimental procedures alone. The combination of high-level ab initio molecular orbital theory calculations with experimental data frequently leads to a detailed description of ion fragmentation behavior and a clear understanding of the relationships between conventional (covalently bound) ions and their elusive, complex counterparts. However, for ions containing many atoms (say, more than 10), high-level calculations are still expensive and very time consuming. As can be ascertained from recent reviews,[3] there is a temptation to introduce complex ions liberally and with little experimental (or computational) justification. It is therefore particularly challenging to devise experimental tests for the identification of complex ionic intermediates, and recent work in this laboratory has been directed particularly toward that end.[5]

One of the most thoroughly studied systems, in which the involvement of complex ions is clearly indicated, is that of the metastable alkyl phenyl ether molecular ions in which an alkyl ion–phenoxy radical complex is formed prior to the transfer of a β-proton from the alkyl cation to the phenoxy radical. The products are thus ionized phenol and an alkene. The results of isotopic labeling studies[6–13] and examination of the neutral olefins produced[10,11] could only satisfactorily be explained by invoking ion–radical complexes in which, for example, a primary alkyl ion rearranged to a secondary ion. Exchange of H between the phenyl ring and the alkyl group was never observed. For 1-propyl[8,9,14] and 1-butyl phenyl ethers[6,7] it was found that proton transfer occurred from all positions in the alkyl chain. However, complete loss of positional identity of H and D atoms in the labeled analogues did not apparently take place, and H^+/D^+ transfer became more specific (with the γ- (or 3-) position preferred) as observations were made on ions of increasing lifetime (e.g., from source generated to metastable ions). It was concluded that for these ions an ion–radical pair is produced by elongation of the $[C_6H_5O^\bullet$–alkyl$^+]$ bond, i.e., the reaction coordinate for their formal separation. Beyond a certain extension, coupling between this mode and the internal degrees of freedom of the radical and ion effectively cease. Such an extension has been identified[14] as greater than ca. 3 Å. Under these conditions isomerization of the alkyl ion, via H-atom shifts, becomes possible, but *not* skeletal rearrangements.[11,15] Thus a primary, straight-chain alkyl ion becomes

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a secondary ion but a tertiary ion is not accessed. For secondary and tertiary alkyl ethers, transfer of a β-proton is strongly preferred[12,13] among metastable ions, and without prior rearrangement of the alkyl cation.

Until quite recently, little was known about the energetics of these reactions, it being generally supposed that they took place at close to the product energies. It is now apparent[16] that the energetics are governed by several major factors: (i) the strength of the $[C_6H_5O{-}R]^{\bullet+}$ bond in the ionized ether (i.e., which leads to the phenoxy radical and alkyl ion, R^+); (ii) whether the β-proton, which is finally transferred to the phenoxy radical, is primary, secondary, or tertiary.

It was also concluded in that study[16] that distonic ion intermediates or hydrogen-bridged species are not necessary to explain the experimental observations, even though their estimated energies lay below the dissociation thresholds.

The purpose of the present study was to investigate the relationships between ion structure, energy, and fragmentation mechanism for the C_2 to C_5 alkyl phenyl ethers. In particular, additional evidence to support the involvement of phenoxy radical-alkyl ion complexes was sought, and rearrangements in the carbocation moiety were to be probed by isotopic labeling studies and, where practicable, by analysis of isomeric products. Finally, it was hoped that the new results and considerations of the charge distribution in alkyl ions could be related to the transition states for these reactions.

Results and Discussion

Ethyl and 2-Propyl Phenyl Ethers. The possible observation of the involvement of the classical and nonclassical $C_2H_5^+$ ions in the loss of ethene from ionized ethyl phenyl ether was examined first, using $C_6H_5OCH_2CD_3$. Note that the classical ethyl cation, $CH_3CH_2^+$, is not a potential minimum on the $C_2H_5^+$ hypersurface, but lies some 27 kJ mol^{-1} above the thermodynamically most stable configuration, symmetrically proton-bridged ethene. They are not separated by an energy barrier. These results come from high-level ab initio molecular orbital theory calculations.[17] Our earlier study[16] showed that for metastable ionized ethyl phenyl ether, fragmentation takes place at an energy ca. 1.4 eV (137 kJ mol^{-1}) above the product energies, a result recently confirmed by Riley and Baer.[18] These authors showed, in a photoelectron–photoion coincidence study, that for such ions the excess energy is made up from a reverse energy barrier and a sizable kinetic shift. However, they were undecided as to the best model for the transition state. Their favored model involved vibrational frequencies for a relatively tight transition state with a small negative entropy of activation, -2.1 cal mol^{-1} K^{-1}. However, a better fit to the observed rate constant versus internal energy curve resulted when a loose transition state (lower vibrational frequencies), $\Delta S^{\neq} = 4.1$ cal mol^{-1} K^{-1}, was employed. This latter seems in keeping both with Morton's description of such ions and with the continuing discussion below.

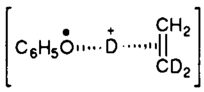
The average kinetic energy release for this process (obtained from the half-height width of the Gaussian-shaped metastable peak[19]) was only 6.3 kJ mol^{-1}, showing that little of the excess energy of the fragmenting ion is partitioned among translational degrees of freedom of the products. Thus the latter must contain the bulk of the above excess energy. That the ethene generated is not in its ground-state energy level is shown by its cross section for collision-induced dissociative ionization and its subsequent fragmentation characteristics.[20]

The degree of H^+ versus D^+ transfer to the phenoxy radical, as a function of ion lifetime (and hence internal energy), is shown in Table I. Clearly, in spite of the high excess internal energy of the longer lived fragmenting ions, very little H/D mixing takes place; formal β-D^+ transfer predominates for all metastable ions, even though their internal energy lies about half-way to the dissociation limit to $C_6H_5O^\bullet + C_2H_5^+$ (256 kJ mol^{-1} above the products). The metastable ions, then essentially do not involve a complex between an ethyl cation and a phenoxy radical in which the classical and nonclassical forms can be in equilibrium. The dissociation species is then best represented as a symmetrical deuterium bridged complex

Table I. Effect of Ion Lifetime on the Production of $C_6H_5OD^{\bullet+}$ (m/z 95) and $C_6H_5OH^{\bullet+}$ (m/z 94) from $C_6H_5OCH_2CD_3$

ion lifetime, μs	m/z 94	m/z 95
<1[a]	23	77
2[b]	9	91
15[c]	6	94
30[d]	4	96
(statistical)	40	60

[a] Ion source, VG Analytical ZAB-2F mass spectrometer. [b] First field-free region, Kratos MS902S mass spectrometer. [c] Second field-free region (ZAB-2F). [d] Third field-free region (ZAB-2F, see Experimental Section).



certainly a more loosely bound state than a five-centered intermediate leading to β-D^+ transfer. Finally, to see if there was a significant isotope effect involved in the dissociation, the m/z 94:m/z 95 ratio was measured for $C_6H_5OCH_2CH_2D^{\bullet+}$ ions. For the metastable ions the above ratio was 76:24 and for ion source generated fragments, 74:26. This corresponds to an unremarkable isotope effect for H^+ versus D^+ transfer of ~1.5.

A similar, but even more clear-cut result was obtained for deuterium-labeled 2-propyl phenyl ether. Ionized $(CD_3)_2CHOC_6H_5$ showed no $C_6H_5OH^{\bullet+}$, m/z 94 (<0.02, relative to m/z 95 = 100) in the metastable time frame, and species fragmenting in the ion source displayed m/z 94:m/z 95 = 3:100. The excess energy above products of the transition state for metastable ions has been measured to be 45 kJ mol^{-1} (see Table II), an energy well below that believed to be necessary for the $(CH_3)_2CH^+ \rightleftharpoons CH_3CH_2CH_2^+$ interconversion, 86 kJ mol^{-1}. According to the most recent ab initio calculations,[21] hydrogen atom scrambling in the 2-propyl cation involves interconversion via the 1-propyl cation which does not independently exist in a potential well. Thus the above excess energy indeed cannot be expected to lead to loss of positional identity of H and D atoms in labeled $C_6H_5OCH(CH_3)_2$. The observations on this ion are in keeping with those reported by Uggerud et al.[22] on the behavior of ionized 2-propyl trimesitylvinyl ether.

For 1-propyl phenyl ether, the excess energy of the transition state for $C_6H_5OH^{\bullet+}$ generation from metastable ions[16] is 97 kJ mol^{-1} above the products energies, sufficient for isomerization *and* H atom scrambling in isolated 1-propyl cations. This has already been discussed in detail by Chronister and Morton,[14] and the results are compatible with incomplete H/D scrambling in 2-propyl ions produced via a phenoxy radical-1-propyl cation complex in which the primary carbocation rearranges via a single 1,2 H shift.

Isobutyl Phenyl Ether. In our earlier report,[16] results of appearance energy (AE) measurements on isobutyl phenyl ether were presented. It was found that, for metastable ions, the dissociation energy to $C_6H_5OH^{\bullet+}$, 9.60 eV, lay 26 kJ mol^{-1} above that required for the simple bond cleavage to $C_6H_5O^\bullet + (CH_3)_3C^+$, ($\Delta H^\circ_f[C_6H_5OCH_2CH(CH_3)_2] = -158$ kJ mol^{-1},[23] $\Delta H^\circ_f[(CH_3)_3C]^+ = 694$ kJ mol^{-1},[24] $\Delta H^\circ_f[C_6H_5O]^\bullet = 48$ kJ mol^{-1} [25]), and 63 kJ mol^{-1}

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Table II. Metastable Peak Appearance Energies (AE) and Related Thermochemical Data for Alkyl Phenyl Ethers[h]

	alkyl group, R	$\Delta H^\circ_f[C_6H_5OR]$, kJ mol^{-1} [23]	ionization energy, eV, ±0.05	AE (eV), m/z 94		energy of transition state above products[a]	AE eV, m/z 135	AE eV, m/z 70
				obs	calc			
	$CH(CH_3)_2$	−143	8.10	9.64 (15)	9.17	45[b]		
	$CH_3CHCH_2CH_3$	−163	8.15	9.62 (17)	9.05	55[c]		
I	$CH_2(CH_2)_3CH_3$	−168	8.10	10.16 (26)	8.90	122[d]	10.14 (27)	
II	$CH_3CHCH_2CH_2CH_3$	−186	8.15	9.62 (14)	9.08	52[d]		
III	$CH(CH_2CH_3)_2$	−186	8.15	9.70 (15)	9.08	60[d]		
IV	$CH_2CH_2CH(CH_3)_2$	−177	8.15	10.06 (23)	8.88	114[e]		10.02 (22)
V	$CH_2C(CH_3)_3$	−190	8.18	9.52 (19)	9.02	48[e]		9.52 (17)
VI	$C(CH_3)_2CH_2CH_3$	−194	8.15	9.02 (6)	9.06	0[e]	9.34 (13)	
VII	c-C_6H_{11}	−161	*g*	9.54 (17)	9.10	42[f]		

[a] Products: $[C_6H_5OH]^{\bullet+}$, 722 kJ mol^{-1}, and [R–H]. [b] C_3H_6, 20 kJ mol^{-1}. [c] But-2-ene, −12 kJ mol^{-1}. [d] Pent-2-ene, −32 kJ mol^{-1}. [e] 2-Methylbut-2-ene, −42 kJ mol^{-1}. [f] Cyclohexene, −4.6 kJ mol^{-1}. [g] Assumed to be 8.15 eV to calculate $\Delta H^\circ_f[C_6H_{11}OC_6H_5]$. Enthalpies from ref 24.

above the thermochemical minimum for $C_6H_5OH^{\bullet+}$ + $(CH_3)_2CCH_2$. (Note that ionized *tert*-butyl phenyl ether fragments at this energy, i.e., with *no* barrier.) Moreover, m/z 57, $[C_4H_9]^+$, is only a weak peak in the normal mass spectrum of the compound. It was proposed that rearrangement of the isobutyl cation did not occur and that direct transfer to oxygen of the weakly bound tertiary β-H^+ took place instead in the ion–radical complex, this being energetically favored over the 1,2 H-shift in the isobutyl cation. The validity of this proposal can be checked by a deuterium-labeling experiment. Accordingly, two labeled compounds were synthesized, $C_6H_5OCH_2CD(CH_3)_2$ and $C_6H_5OCHDCH(CH_3)_2$. In the metastable time frame, the results for the two isotopomers were *identical*, with m/z 94:m/z 95 = 89:11. This result is only compatible with complete isomerization of the isobutyl cation in an ion–radical complex, to the *tert*-butyl ion prior to fragmentation and with no isotope effect for the H^+ versus D^+ transfer to the phenoxy radical. For the first labeled compound, ion source fragmentation produced the same m/z 94:m/z 95 ratio, whereas for $C_6H_5OCHDCH(CH_3)_2$ the ratio was slightly smaller, 86:14. It must be concluded that, at this internal energy (vide infra), the β-H^+ transfer from the tertiary alkyl ion to the phenoxy radical is very fast, even relative to simple O–C bond fission.

It is worth remarking again upon the lack of any isotope effect for the H^+ transfer at this modestly elevated internal energy, 63 kJ mol^{-1} above the threshold for fragmentation of *tert*-butyl phenyl ether. For the ethyl analogue, where the β-H^+ transfer, rather than an isomerization, is the rate-determining step, an H^+/D^+ isotope effect of ~1.5 was observed.

A conventional picture of a *tert*-butyl cation, with the formal charge located at the central carbon atom, is an incorrect representation. The charge density calculations by Bader[26] show that the positive charge resides in the methyl groups, that the tertiary carbon atom is weakly *negatively* charged (−0.098 e), and that the ground state of the ion is planar. The nearby presence of the electronegative phenoxy oxygen atom should distort the ion, attracting the positively charged methyl groups into closer proximity to oxygen while repelling the central carbon atom, thus facilitating proton transfer. It is worth remarking that a similar picture obtains with the 2-propyl cation,[26] and so the ion–radical complex involving a point positive charge at carbon-2, as depicted in the calculations of Chronister and Morton (see Figure 3 and ref 14) may well be inappropriate. Very recently Perrin[27] has criticized Bader's calculations[26] and has shown that they tend to exaggerate electron densities at electronegative atoms. However, this does not invalidate our qualitative description of the ion–radical complexes.

Pentyl Phenyl Ethers. Energetics. Six of the eight pentyl phenyl ethers were examined: 1-pentyl (I), 2-pentyl (II), 3-pentyl (III), 3-methyl-1-butyl (IV), 2,2-dimethylpropyl, (V), and 2-methyl-2-butyl (VI); the 2-methyl-1-butyl and 3-methyl-2-butyl analogues were not studied.

Table II gives the thermochemical data and energy measurements for the ions observed in the metastable ion (MI) mass spectra of compounds I–VI.

Before discussing the fragmentation energetics, it is worth briefly noting that the ionization energies of the homologous alkyl phenyl ethers, from anisole to *n*-pentyl phenyl ether, change very little with increase in molecular size (anisole IE = 8.21 ± 0.02 eV, $C_6H_5OC_2H_5$ IE = 8.12 ± 0.05 eV to the *n*-pentyl ether, IE = 8.15 ± 0.05 eV). Chain branching in the alkyl group also has no effect. This lack of a significant decrease in IE with increase in substituent size is typical of monoalkyl-substituted aromatic compounds (see data in ref 24) but markedly different for aliphatic molecules where IE falls with homologation approximately in inverse proportion to molecular size.[28]

Apart from the ubiquitous m/z 94 ion, the 1-pentyl (I) and the tertiary ether (VI) showed a significant peak at m/z 135 (3% and 16% relative to m/z 94, respectively) loss of $C_2H_5^\bullet$, and for IV and V m/z 70, $[C_5H_{10}]^{\bullet+}$ was present in the MI mass spectrum. These four compounds are the first alkyl phenyl ether homologues to show other than the phenol molecular ion in their MI mass spectra. As with the earlier results[16] on the energetics of this olefin loss process from metastable ions, the energy of the transition state above the reactant ion depends largely on the nature of the carbocation in the initially formed ion–phenoxy radical complex. These energies are in kJ mol^{-1}: C_2H_5 (232), 1-C_3H_7 (181), 2-C_3H_7 (149), 1-C_4H_9 (180), 2-C_4H_9 (142), *i*-C_4H_9 (140), *t*-C_4H_9 (82), 1-C_5H_{11} (198), 2-C_5H_{11} (142), 3-C_5H_{11} (150), 3-methyl-1-butyl (184), 2,2-dimethylpropyl (129), and 2-methyl-2-butyl (84). Thus for primary ions the dissociation energy is greatest, 189 ± 9 kJ mol^{-1} (excluding ethyl, as discussed below); for secondary ions the energy is 145 ± 6 kJ mol^{-1} and for tertiary ions 83 ± 1 kJ mol^{-1}. For the latter, reaction proceeds at the thermochemical threshold. Two exceptions are the branched primary ethers, isobutyl and 2,2-dimethyl propyl (V), discussed separately below. Finally the cyclohexyl ether (VII) behaves as a typical secondary

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alkyl species, transition-state energy 139 kJ mol^{-1}. Note that the ethyl ether's energy barrier to dissociation arose partly from a significant kinetic shift as well as an activation energy term.[18] The constancy of the above threshold energies for each ion type leads us to propose that the kinetic shift is a less important factor in their overall energy requirement.

We propose the following general picture for the ionized alkyl phenyl ethers. For tertiary ethers, proton transfer from the carbocation moiety to phenoxy oxygen is easiest because the charge density is greatest in the three ($-CH_2$ or $-CH_3$) groups attached to the tertiary C atom. The latter is weakly *negatively* charged according to Bader's calculations,[26] and so the planar ion can readily be distorted by the polar phenoxy radical. Secondary ions also fragment in the metastable time frame but without isomerization, even though the charge density at the two groups α to the formal secondary ion site is slightly greater than for the tertiary species. However, the planarity of the ion is less readily distorted, there being minimal negative charge (−0.010 e) at the secondary C atom.[26]

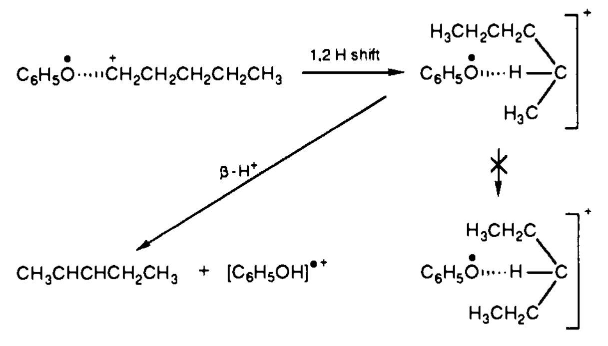
For unbranched primary ions, the rate-determining step is the 1,2 H shift which produces an energy-rich secondary ion which rapidly fragments, so rapidly that a *second* 1,2 H shift (e.g., from 2-pentyl to 3-pentyl (see Discussion below) cannot take place. Clear exceptions to this are the isobutyl and 2,2-dimethylpropyl ethers. For the former, a 1,2 (*tertiary*) H shift produces the *tert*-butyl cation with a lower energy requirement than for the other primary ions. Similarly, the neopentyl cation in V undergoes a 1,2 *methyl* shift to produce the *tert*-pentyl ion, after which the molecular ion rapidly fragments. The ethyl cation, which cannot isomerize to a species of lower enthalpy, provides the highest activation energy for β-H$^+$ transfer. The experiments on deuterium-labeled ions of ***higher*** internal energy (those which fragment in the ion source) have shown that H$^+$ transfer from other than β-C atoms can occur, as well as H/D scrambling, prior to olefin loss[6–9,14] (see also the detailed discussion on individual pentyl phenyl ethers below).

2- and 3-Pentyl Phenyl Ethers. These molecules showed only *m/z* 94 in their metastable ion mass spectra. The excess energy of the products, 52 and 64 kJ mol^{-1}, respectively, is similar to that observed for the other metastable secondary ions; see Table II. The labeling experiments of Sozzi et al.[12] are compatible with the formation of pent-2-ene.

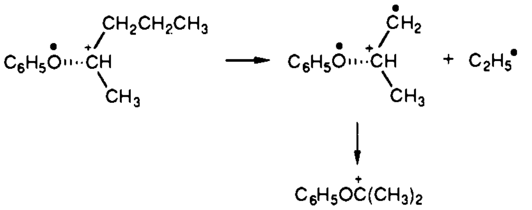
1-Pentyl and 2-Methyl-2-butyl Phenyl Ethers. These compounds lose $C_2H_5^•$ as well as C_5H_{10} in the metastable time frame. For the 1-pentyl compound, the energy for loss of $C_2H_5^•$ is the same as that for the generation of *m/z* 94, $C_6H_5OH^{•+}$; in the case of the *tert*-pentyl analogue, $C_2H_5^•$ loss takes place at a higher energy than for C_5H_{10} loss (see Table II). The fragment ion, $[C_6H_5OC_3H_6]^+$, from the above two pentyl ethers has the same structure as the ion generated by loss of $CH_3^•$ from *tert*-butyl phenyl ether, namely, $C_6H_5OC^+(CH_3)_2$, *m/z* 135. This was shown by comparing the collisional activation mass spectra of the three fragment ions which were found to be identical. The AE of the *m/z* 135 ion, measured using energy-selected electrons (see Experimental Section) was 8.85 ± 0.05 eV. This, together with $\Delta H°_f[CH_3^•]$ = 146 kJ mol^{-1} [24] and $\Delta H°_f[C_6H_5OC(CH_3)_3]$ = −174 kJ mol^{-1} [23] gives $\Delta H°_f[C_6H_5OC^+(CH_3)_2]$ = 534 kJ mol^{-1}. (Note the *destabilizing* effect of phenoxy relative to methoxy, $\Delta H°_f[CH_3OC^+(CH_3)_2]$ = 477 kJ mol^{-1} [24]). Thus the calculated threshold energies for the $C_2H_5^•$ ($\Delta H°_f$ = 118 kJ mol^{-1} [24]) loss from 1-pentyl phenyl ether, 8.50 eV, and from 2-methyl-2-butyl phenyl ether, 8.77 eV, both lie well below the observed values (Table II). For the former compound, the rate-determining step for both fragmentations is the isomerization of the 1-alkyl ion.

For metastable [1,1-$^2H_2$]-1-pentyl phenyl ether ions, *m/z* 94 exceeded *m/z* 95 in the ratio 90:10 (second field-free region, ZAB-2F mass spectrometer, ion lifetime ca. 15 μs), and *m/z* 135 was wholly shifted to *m/z* 137 showing that *only* $CH_3CH_2^•$ was lost. At shorter ion lifetimes (ca 1 μs), the *m/z* 137 peak remained alone, but the *m/z* 94:*m/z* 95 ratio fell to 78:22. We propose, by analogy with the behavior of the metastable 1-propyl and 1-butyl homologues, that the metastable 1-pentyl ether ion rearranges to the energy-rich 2-pentyl isomer prior to loss of but-2-ene.

Scheme I



Scheme II

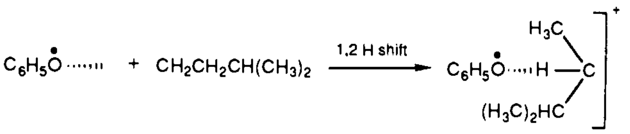


The increase in $C_6H_6OD^{•+}$ production at higher internal energies, relative to that from metastable ions, reflects the greater primary D$^+$ transfer relative to the thermochemically favored secondary H$^+$ transfer.

For the ethyl loss to remain so isotope specific, it follows that further rearrangement to the symmetrical 3-pentyl species cannot take place (Scheme I). In addition, to generate the observed *m/z* 135 ion, $[C_6H_5OC^+(CH_3)_2]$, a further 1,2 H shift must accompany (or follow) the loss of $C_2H_5^•$. In spite of the low enthalpy requirement for the overall reaction leading to $C_6H_5OC^+(CH_3)_2$, it should be noted that the bond $[CH_3^+CHCH_2-CH_2CH_3]$ in the isolated secondary ion is very strong, 345 kJ mol^{-1} ($\Delta H°_f[CH_3^+CHCH_2CH_2CH_3]$ = 732 kJ mol^{-1}, $\Delta H°_f[CH_3CHCH_2]^{•+}$ = 959 kJ mol^{-1}).[24]

For the tertiary pentyl ether it appears that the β-proton transfer is *less* energy demanding than the enthalpy favored simple C–C bond cleavage. This must relate to the structure and charge distribution in the ion–radical complex (Scheme II).

3-Methyl-1-butyl and 2,2-Dimethylpropyl Phenyl Ethers (IV and V). These isomers also generate $[C_5H_{10}]^{•+}$ and $[C_6H_5OH]$ in the metastable time frame; now H$^+$ transfer competes (at the same internal energy for each isomer; see Table II) with H-atom transfer from the carbocation to phenoxy. Metastable IV ions can be predicted to rearrange to the 3-methyl-2-butyl isomer prior to β-H$^•$ or β-H$^+$ transfers:



β-H$^•$ transfer can yield two products, ionized 2-methylbut-2-ene from tertiary H$^•$ transfer and ionized 3-methylbut-1-ene from primary H$^•$ transfer. The measured threshold energy, 10.02 eV, leads to $\Delta H°_f[C_5H_{10}]^{•+}$ = 886 kJ mol^{-1}, slightly below that for the latter ion (891 kJ mol^{-1} [24]), but appreciably above that for the ion $CH_3CHC(CH_3)_2^{•+}$, $\Delta H°_f$ = 795 kJ mol^{-1}. Note, however, that the threshold dissociation energy is governed by the rearrangement energy barrier, which at 184 kJ mol^{-1} is typical of a primary to secondary cation isomerization (vide infra) in such systems. The β-proton transfer should preferentially take place from the tertiary carbon atom at position 3 to yield 2-methylbut-2-ene as the neutral product.

The identity of isomeric $[C_5H_{10}]^{•+}$ ions can be determined by charge stripping (CS) mass spectrometry,[28] and so the CS mass

Table III. Charge Stripping Mass Spectra of Ion Source Generated $[C_5H_{10}]^{\bullet+}$ Ions

precursor	31	31.5	32	32.5	33	33.5	34	34.5	35
$C_6H_5OCH_2CH_2CH(CH_3)_2$	19	4	9	9	15	10	32	<0.6	2.5
$C_6H_5OCH_2C(CH_3)_3$	19	5	9	8	15	11	33	0	0
$C_6H_5OC(CH_3)_2CH_2CH_3$	19	5	10	8	15	9	25	1.6	7
$H_2CC(CH_3)CH_2CH_3$	20	5	9	10	19	12	18	7	0
$H_2CCHCH(CH_3)_2$	19	5	10	9	15	10	32	0	0
$(CH_3)_2CCH_2CH_2$	20	5	9	11	14	9	31	0	0
$CH_3CHC(CH_3)_2$	15	4	7	7	16	10	23	2	17
$CH(CH_3)CH(CH_3)CH_2$	15	4	9	9	16	10	27	4	5

Scheme III

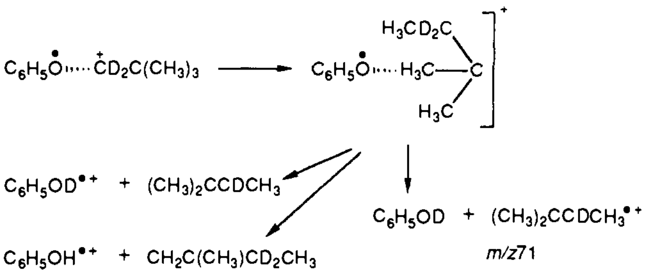


Table IV. Effect of Ionizing Electron Energy and Observational Time Frame on the Generation of $[C_5H_9D]^{\bullet+}$, *m/z* 71, and $[C_5H_8D_2]^{\bullet+}$, *m/z* 72, from $C_6H_5OCD_2C(CH_3)_3$

ionizing electron energy, eV	observation timescale	*m/z* 71	*m/z* 72
70	0–1 μs[a]	71	29
20	0–1 μs[a]	53	47
13.8	0–1 ms[b]	38	62
12.9	0–1 ms[b]	35	65
12.3	0–1 ms[b]	33	67
11.6	0–1 ms[b]	30	70
11.4	0–1 ms[b]	20	80
11.1	0–1 ms[b]	17	83
70	1–2 μs[c]	70	30
12	1–2 μsc	91	9
70	11–14 μs[d]	100	0

[a] Ion source, Kratos AEI MS902S mass spectrometer. [b] Quadrupole mass spectrometer with electron energy selector (see Experimental Section). [c] Metastable ions, MS902S mass spectrometer, first field-free region. [d] VG-Analytical ZAB-2F mass spectrometer, second field-free region.

spectrum of the ion source generated *m/z* 70 ions was recorded. The result (Table III) shows that the predominant ion is 3-methylbut-1-ene, but the 2-methylbut-2-ene ion must also be present, the latter being the only $[C_5H_{10}]^{\bullet+}$ isomer to produce a significant, doubly charged *m/z* 70^{2+} ion. Note that the CS mass spectrum of ionized 1,1-dimethylcyclopropane (ΔH°_f = 858 kJ mol^{-1} from its IE, 8.98 eV,[29] and $\Delta H^\circ_f[(CH_3)_2CCH_2CH_2] = -8$ kJ mol^{-1} [24]) is indistinguishable from that of its closest ring-opened isomer, 3-methylbut-1-ene. Efforts were made to record the CS mass spectrum of the *metastably* generated *m/z* 70 ions, but the CS peaks therefrom were too weak to even be measured by accumulated signal averaging.

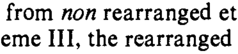
The remaining isomer, 2,2-dimethylpropyl phenyl ether (V), also produces ionized phenol and *m/z* 70 at the same threshold energy, but the excess energy of the transition state (129 kJ mol^{-1}) lies well below that for a primary to secondary carbocation rearrangement by a 1,2-H shift, ca 190 kJ mol^{-1}. In this case, however, the 1,2 H-shift is not possible and so a 1,2 *methyl* shift is proposed to be the governing process, yielding the tertiary 2-methyl-2 butyl cation. This was concluded from the following results.

First, the structure of the C_5H_{10} hydrocarbon accompanying $C_6H_5OH^{\bullet+}$ cannot be identified via the thermochemistry of the fragmentation, all isomers lying below the transition-state energy. However (see Table IV) the deuterium-labeled ion shows almost equal transfer of H^+ and D^+ to phenoxy at the longest times at which metastable ions were observed. More strikingly, *only* $D^\bullet$ is transferred to phenoxy in the same time frame. This latter result is easily rationalized on energetic grounds, $D^\bullet$ transfer from the tertiary pentyl ion produced by the 1,2 methyl shift (see Scheme III) yields the $[C_5H_{10}]^{\bullet+}$ ion of lowest enthalpy, $CH_3CHC(CH_3)_2^{\bullet+}$, ΔH°_f = 795 kJ mol^{-1}.[24] The branched ion, $CH_3CH_2C(CH_3)CH_2^{\bullet+}$, is next highest in energy, by 50 kJ mol^{-1} at 845 kJ mol^{-1}.[24]

In marked contrast, only 6 kJ lies between the olefin products (shown in Scheme III) from H^+ and D^+ transfer. Unfortunately, the CS mass spectrum of the metastably generated $[C_5H_{10}]^{\bullet+}$ ions was again too weak to be recorded, and so only the CS mass spectrum for ion source generated species of higher internal energy content was obtained. The results for ion V are shown in Table III. The *m/z* 70 ion can be identified as [1,1-dimethylcyclopropane]$^{\bullet+}$ or its higher energy, ring-opened form, ionized 3-methylbut-1-ene. The reaction shown in Scheme III predicts the formation of ionized 2-methylbut-2-ene and is supported, for the long-lived metastable ions, by the specific deuterium transfer result (Table IV). It seems, therefore, that in the ion source other reaction paths predominate; the observed products could result from a γ-H$^\bullet$ transfer from *non* rearranged ether molecular ions. According to the Scheme III, the rearranged 2,2-dimethylpropyl phenyl ether ions should yield *m/z* 70 ions indistinguishable from those generated directly from the *tert*-pentyl analogue.

A priori the *tert*-pentyl phenyl ether ion (VI), would be expected to yield the ion $CH_3CHC(CH_3)_2^{\bullet+}$, the lowest energy isomer, by simple β-H$^\bullet$ transfer. However, as can be seen in Table III, a mixture of $[C_5H_{10}]^{\bullet+}$ ions must be generated with only ca. 40% having the 2-methylbut-2-ene ion structure, based on the doubly charged ion peak for *m/z* 70^{2+}.

The fragmentation behavior of the ionized deuterium-labeled ether $C_6H_5OCD_2C(CH_3)_3$ was studied over a range of internal energies and observation times; the results are shown in Table IV. For metastable ion dissociations at intermediate times (1–2 μs), the transfer of $D^\bullet$ becomes internal energy dependent, being the most specific at the lower energy. We propose that these observations reflect an increase in primary $H^\bullet$ transfer to phenoxy from the rearranged (tertiary) ion. The charge stripping mass spectrum for ion source generated *m/z* 70 ions showed that $H^\bullet$ transfer from a *tertiary* ion must be rejected. The transfer of γ-H$^\bullet$ from a methyl group in the neopentyl ion suffices to explain the above CS result. However, this is not at first glance reconcilable with the deuterium labeling results. One proposal which satisfies the observed $D^\bullet$ transfer would be to invoke an ylidion, e.g.



$$C_6H_5-\underset{+}{\overset{D}{O}}-\dot{C}DC(CH_3)_3$$

in which a 1,3 H-shift followed by dissociation could yield ionized 1,1-dimethylcyclopropane. The CS mass spectrum of the ion source generated products shows *no* evidence for significant production of any other ionized branched olefin or cycloalkane, and so extensive isomerization of the carbon skeleton can be rejected. The change in label atom retention as the ionizing electron energy is reduced (Table IV) would result from γ-H$^\bullet$ transfer becoming kinetically favored over the ylidion route.

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Conclusions

The earlier work[16] rested upon the original proposal that the alkyl phenyl ether molecular ions dissociated via a common type of intermediate, an alkyl ion-phenoxy radical complex. The present work has provided further evidence for these complexes and has indicated the limits of isomerization in the alkyl ion moiety in these systems at low internal energies where the ion–radical complex plays a major role. At higher (ion source) energies, complex formation is much less important, as other dissociation processes become apparent. When complex ions are involved, their dissociation energies are governed solely by the alkyl ion portion. For primary ions, the energy required for the (irreversible) isomerization to a secondary or tertiary ion is rate determining, whereas for secondary and tertiary ions the β-H^+ transfer's energy controls the rate of fragmentation. In general, among metastable ions there is little if any loss of positional identity (scrambling) of hydrogen atoms prior to fragmentation.

Experimental Section

Charge stripping mass spectra were obtained with a VG Analytical ZAB-2F mass spectrometer[30] using O_2 as collision gas, at a pressure corresponding to 90% transmission of the mass-selected ion beam.

The collision cell was situated in the second field-free region of the instrument, between the magnet and the electric sector. The CS mass spectrum of m/z 70 ions selected by the magnet was obtained by scanning the electric sector in the energy range close to that corresponding to transmission of ions having half the translational energy of the m/z 70 ions. The doubly charged ion peaks were sufficiently intense to be recorded by a single scan. The ionizing electron energy was 70 eV. The accelerating voltage was 8 kV and the energy resolving slits were wide open. Corrections for ^{13}C overlap were carried out by measuring the signals of interest first, followed by selection of the immediately preceding peak and recording the signals using only the calibrated divisions of the signal amplifier to scale the signals. The required correction could then be made, using the difference in detector gain (if any), the intensities of the respective signals, and the natural abundances of the ^{13}C isotope, multiplied by the number of carbon atoms in the ion.

Metastable peaks were recorded under conditions of good energy resolution, and kinetic energy release values were measured by established methods.[31] Relative metastable peak abundances were recorded with energy resolving slits wide open, and peak heights were used for their comparison. The third field-free region of the ZAB-2F mass spectrometer is followed by a small magnetic sector and an electron multiplier, thus making possible the observation of ion fragmentations in the third field-free region.

Ionization and appearance energies were obtained using energy-selected electrons and an apparatus comprising an electrostatic electron monochromator together with a minicomputer data system.[32] Metastable peak appearance energies were measured on a Kratos-AEI MS902S mass spectrometer as described ealier.[33] Compounds were obtained from Aldrich Co. or were prepared by standard methods. 2,2-Dimethylpropyl phenyl ether was synthesized as described by Dandrée and Seyden-Penne[34] and 2-methyl-2-butyl phenyl ether by the method of Camps et al.[35]

Labeled compounds were prepared as follows. $C_6H_5OCH_2CH_2D$ and $C_6H_5OCH_2CD_3$ were prepared by reacting the appropriate bromide (from MSD isotopes) with C_6H_5ONa in ethanol. $C_6H_5OCHDCH(CH_3)_2$ was synthesized from $(CH_3)_2CHCHO$ which was first reduced with $LiAlD_4$ in ether to the labeled alcohol; the latter was tosylated and the product reacted with C_6H_5ONa in ethanol. This procedure is similar to that described in ref 33. $C_6H_5OCH_2CD(CH_3)_2$ was similarly prepared starting with $(CH_3)_2CDCHO$ (from MSD isotopes) but reducing with $LiAlH_4$. $C_6H_5OCD_2CH_2CH_2CH_2CH_3$ was made by reducing pentanoic acid with $LiAlD_4$ in ether and reacting the tosylate of the resulting alcohol with C_6H_5ONa. $C_6H_5OCD_2C(CH_3)_3$ was synthesized using the alcohol resulting from the $LiAlD_4$ reduction of pivaloyl chloride, $(CH_3)_3CCOCl$.

Acknowledgment. The authors wish to thank Dr. F. P. Lossing for appearance energy measurements, Professor T. H. Morton for a sample of $(CD_3)_2CHOC_6H_5$, Professor T. Baer for results on ethyl phenyl ether prior to their publication, and Ms. C. Rondeau for experimental assistance. J. L. H. acknowledges continuing financial support from the Natural Sciences and Engineering Research Council of Canada.

Registry No. $C_6H_5OCH_2CH_3$, 103-73-1; $C_6H_5OCH(CH_3)_2$, 2741-16-4; $C_6H_5OCH_2CH(CH_3)_2$, 1126-75-6; $C_6H_5OCH_2CH_2CH_2CH_2CH_3$, 2050-04-6; $C_6H_5OCH(CH_3)CH_2CH_2CH_3$, 14789-87-8; $C_6H_5OCH(CH_2CH_3)_2$, 16158-52-4; $C_6H_5OCH_2CH_2CH(CH_3)_2$, 1129-64-2; $C_6H_5OCH_2C(CH_3)_3$, 2189-88-0; $C_6H_5OC(CH_3)_2CH_2CH_3$, 81634-59-5; $C_6H_5OC_6H_{11}$-c, 2206-38-4; $C_6H_5OCH_2CH_2D$, 136954-62-6; $C_6H_5OCH_2CD_3$, 40932-23-8; $C_6H_5CHDCH(CH_3)_2$, 136954-63-7; $C_6H_5OCH_2CD(CH_3)_2$, 136954-64-8; $C_6H_5OCD_2CH_2CH_2CH_2CH_3$, 136954-65-9; $C_6H_5OCD_2C(CH_3)_3$, 7210-88-0; $C_6H_5OCH(CD_3)_2$, 135388-79-3; D_2, 7782-39-0.

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