Ion–Molecule Complexes in Unimolecular Fragmentations of Gaseous Cations. Alkyl Phenyl Ether Molecular Ions

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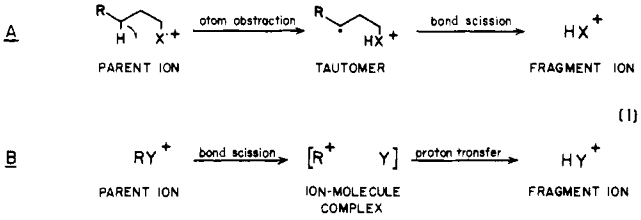
Abstract: A decomposition pathway that bears a formal resemblance to first-order elimination in solution is demonstrated for parent ion fragmentations of alkyl phenyl ethers under electron impact (EI) and chemical ionization (CI). The sequence of steps in the gas phase, parent ion → ion–molecule complex → fragments, is analogous to first-order elimination in solution (which goes through ion pairs). Such a mechanism for expulsion of $PhOH^{+\cdot}$ from molecular ions has been tested by examining neutral products from 70-eV electron bombardment of neopentyl phenyl ether in a specially constructed electron bombardment flow (EBFlow) reactor. The C_5H_{10} isomers 2-methyl-1-butene (**2**) and 2-methyl-2-butene (**3**) are recovered in the same ratio (**2**/**3** = 1.14) as is produced by gas-phase deprotonation of *tert*-amyl cation. This result is validated by a mass spectrometric study of deuterated analogues, for which the ratio of γ-transfer (corresponding to product **2**) to α-transfer (corresponding to product **3**) is calculated to be 1.46. Intermediacy of an ion–molecule complex, $PhOCH_2C(CH_3)_3{}^{+\cdot} \rightarrow [PhO\cdot\ CH_3CH_2(CH_3)_2C^+] \rightarrow PhOH^{+\cdot} +$ **2** or **3**, predicts this outcome, where the species in brackets represents an electrostatically bound complex of the neutral phenoxyl radical and an alkyl cation. This mechanism explains the published mass spectrometric (EI and CI) and EBFlow results for *n*-propyl and *n*-butyl phenyl ethers. Several confirmatory experiments support the intermediacy of an ion–molecule complex and rule out other interpretations of the experimental data.

Any unimolecular reaction that is not a fragmentation passes through a cyclic transition state. The ring size of this transition state imposes constraints that affect the rate or lead to selectivity. Pioneering studies have compared intramolecular reactions with their intermolecular analogues[1] or have focused on hydrogen abstraction to discover why heteroatoms with unpaired electrons attack some sites in preference to others.[2] Winnik[3a] and Green[3b] have proposed that intramolecular hydrogen transfer in the mass spectrometer provides an empirical approach to conformational analysis of flexible chains in the gas phase.

This paper will contrast the two pathways depicted in reaction 1 for internal hydrogen transfer in gaseous ions.



(1)

Mechanism A represents a conventional picture based on analogy to unimolecular reactions of neutral molecules. The first step is tautomerization of the parent ion via a cyclic transition state. Because the hydrogen atom affinities of ionized functional groups (e.g., aliphatic ethers)[4] are often greater than carbon–hydrogen bond dissociation energies, thermodynamic arguments support the inference that such functionalities can abstract hydrogen from any site on a hydrocarbon chain. Overall, the reaction depicted for mechanism A corresponds to a 1,3 elimination, a reaction rarely encountered in solution.

The prevalence of remote eliminations in the mass spectrometric literature is a subject of great interest, and several fragmentations corresponding to 1,3 eliminations have been studied in this laboratory.[5-7] Evidence will be presented here to show that, for alkyl phenyl ethers, these fragmentations proceed by mechanism B, which bears a formal resemblance to E1 elimination in solution. The first step is scission of a covalent bond to form an electrostatic bond. In a subsequent step, a proton is transferred from the resulting cation (R^+) to the leaving group (Y). The species in brackets represents an ion–molecule complex bound by ion–dipole attraction.

Background

Some intramolecular hydrogen transfers show high regioselectivity, while others show none. The McLafferty rearrangement of gaseous cations, where X is a carbonyl function, proceeds exclusively via γ-hydrogen abstraction (the first step shown in reaction 1A). Many related ion decompositions do not share this degree of site specificity. Instead, hydrogen transfer from several sites of a saturated chain takes place.[8]

Previous investigators have discussed nonspecific hydrogen transfer in terms of mechanism A, with close competition among transition states of different sizes.[8-11] Alkyl phenyl ethers (X = -OPh) have been widely studied as an example where the major decomposition pathway involves hydrogen transfer from every position of the alkyl chain. Under 12–70-eV electron impact, the phenol molecular ion constitutes the base peak.[9-12] Borchers, Levsen, and Beckey[11] and Nibbering[12] have demonstrated that the hydrogen transferred from the chain remains distinct, consistent with the formula $C_6H_5OH^{+\cdot}$. Benoit and Harrison[10] report a small translational kinetic energy release (0.02 eV) that is independent of the position from which hydrogen was transferred. Mass spectra of specifically deuterated compounds show that, while transfer from the γ position is preferred, selectivity is remarkably low. For *n*-propyl (R = H) and *n*-butyl ($R = CH_3$) phenyl ethers, transfer from the most favored site is only two to three times more prevalent than transfer from the least favored site. The magnitude of the reported kinetic energy release suggests that every hydrogen-transfer pathway is stepwise. Several studies demonstrate that complete alkyl hydrogen scrambling does not, in general, precede fragmentation. All previous workers have concluded that reaction 1A, which proceeds via a five-member cyclic transition state, occurs slightly faster than abstraction via larger or smaller transition states.[9-11] This picture raises two questions:

(1) Since the first step of mechanism A is endothermic for $X = -OC_6H_5$ (based on a bimolecular analogue), why is abstraction nonselective? The hydrogen atom affinity of an ionized phenyl ether is ≤3.5 eV (80 kcal/mol), based on the proton affinity[13] and ionization potential[14] of anisole. This is much lower than for aliphatic ethers and also lower than most C–H bond dissociation energies.[15]

(2) Why do chemical ionization (CI) results so closely resemble electron impact (EI) ionization? Gas-phase protonation (CI) of *n*-propyl phenyl ether produces $C_6H_7O^+$.[10] One of the

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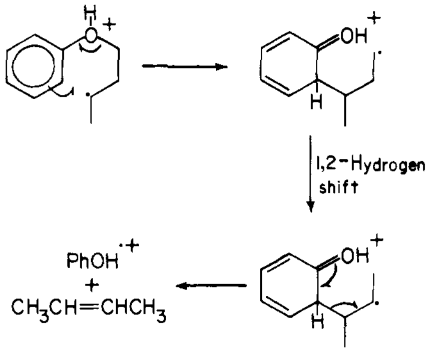
hydrogens in this fragment ion comes from the alkyl chain, and specific deuterium labeling studies show that it is transferred from all three chain positions. The proportions from each position are similar to those seen from EI, with γ-transfer favored.

The above conclusions are drawn from analyses of the charged products from ion decompositions. The neutral products provide complementary data about the reaction pathway, but most mass spectrometric instrumentation is not equipped to identify them. Important information comes from characterization of isomer distributions, which requires that these products be collected. A specially constructed electron bombardment flow (EBFlow) reactor, which permits collection and analysis of neutrals, provides a unique capability for investigating gas-phase ion chemistry in this laboratory. Our examination[6] of neutral products from molecular ion decompositions showed that $\geq$30-eV electron impact on *n*-butyl phenyl ether produces 1-butene and *cis*- and *trans*-2-butenes in roughly a 2:1:1 ratio. The production of 2-butenes (and the absence of isobutene and methylcyclopropane) rules out many possibilities for the second step of mechanism A, but does not exclude simple C-O bond cleavage to expel an excited 1,3 diradical. Field ionization studies[11] subsequently showed that the corresponding mass spectrometric elimination in *n*-propyl phenyl ether is seen on the 10^{-11} s time scale. This makes the diradical hypothesis preferable to the more complicated mechanism shown in reaction 2, which requires three sequential rearrangements of the molecular ion for the elimination of 2-butene.



(2)

Ion-Molecule Complexes

What is the alternative to mechanism A? Bowen and Williams[16] have recently presented mechanism B, which can be generalized as follows: parent ion → ion-molecule complex → fragments. An energy profile corresponding to this sequence of steps is drawn in Figure 1 for the fragmentation of *n*-butyl phenyl ether molecular ion. As can be seen, simple cleavage of the C-O bond is endothermic by at least 1.5 eV (35 kcal/mol),[17] even given the assumption that the alkyl moiety rearranges from a primary to a more stable secondary cation. Neither this nor any other single bond cleavage contributes a peak greater than one-tenth the intensity of the base peak, even under 70-eV electron impact. Certainly, a fraction of the molecular ions do not have sufficient internal energy to overcome the thermodynamic barrier to simple bond cleavage, the first two excited states (0.82 and 0.94 eV above the ground state),[6] for example. Even those ions that do have enough energy may be slow to break the bond. For comparison, RRKM calculations on the cleavage that dissociates $H_5O_2^+$ to H_2O plus H_3O^+ give a unimolecular rate constant on the order of 1×10^8 s^{-1} when the bond strength is taken to be about the same as shown in Figure 1.[18] While bond cleavage (i.e., separation of the fragments by distances > 10 Å) may take place on the nanosecond time scale, partial separation (i.e., by a few ångströms) may occur orders of magnitude faster. At these distances, proton transfer from the alkyl cation to the neutral phenoxyl radical can occur very rapidly, creating the exit channel represented by the lower dashed line in Figure 1.

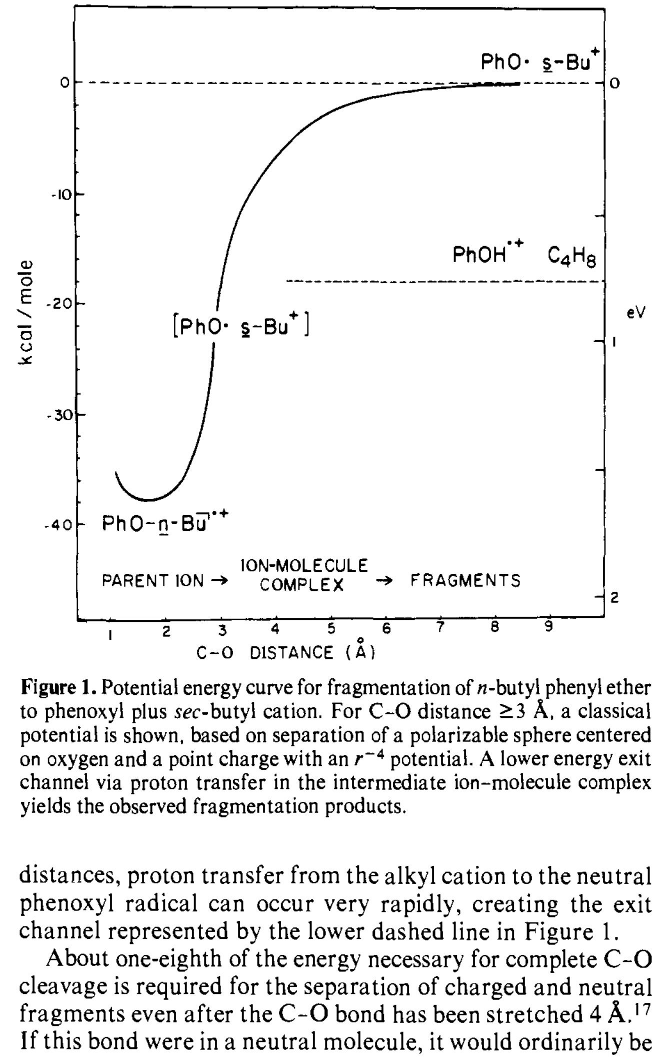


Figure 1. Potential energy curve for fragmentation of *n*-butyl phenyl ether to phenoxyl plus *sec*-butyl cation. For C-O distance $\geq$3 Å, a classical potential is shown, based on separation of a polarizable sphere centered on oxygen and a point charge with an r^{-4} potential. A lower energy exit channel via proton transfer in the intermediate ion-molecule complex yields the observed fragmentation products.

About one-eighth of the energy necessary for complete C-O cleavage is required for the separation of charged and neutral fragments even after the C-O bond has been stretched 4 Å.[17] If this bond were in a neutral molecule, it would ordinarily be considered broken at such a distance. But, in charged species, ion-dipole attractive terms greater than thermal energies extend over longer distances. There are bound states in which the covalent character of a bond may be largely lost. In these vibrational states, the structure will be considered to be an electrostatically bound complex of an alkyl cation and neutral phenoxyl. Such an ion-molecule complex is represented as the species in brackets.

The ion-molecule complex need not represent a potential minimum, but there are advantages to treating it as an intermediate. The reactivity of alkyl cations is known. Their rearrangements and isomerizations in solution have been observed by NMR.[19] If ion-molecule complexes are conjectured to have lifetimes on the order of picoseconds or longer, then a wide range of disparate results can be reconciled and explained on the basis of known reactions of the cation moieties.

An ion-molecule complex cannot be distinguished from its parent ion by mass spectrometry. Its decomposition, though, should yield the same products that would be expected from a second-order ion-molecule reaction of the partners in the complex. In Figure 1, this reaction is proton transfer from the cation to phenoxyl to form $C_6H_5OH^{+\cdot}$ and neutral olefins. Phenoxyl has an estimated proton affinity of 8.6 eV (198 kcal/mol, based on $\Delta H_f°(g)$ of $C_6H_5OH^{+\cdot} = 7.5$ eV),[14,15] which is at least as great as the proton affinity of isobutene[20] (or, presumably, any other acyclic olefin).

How might mechanisms A and B be distinguished? One test is to probe for rearrangements that are characteristic of alkyl cations. The isomerization of neopentyl to *tert*-amyl cation[21] is a well-precedented example. As depicted in reaction 3, mechanism B predicts that the neutral products from the

$$\underset{\text{molecular ion}}{\underset{\mathbf{1}}{(CH_3)_3CCH_2Y^{+\cdot}}} \rightarrow \underset{\text{ion-molecule complex}}{[CH_3CH_2(CH_3)_2C^+ \quad Y\cdot]}$$

$$\xrightarrow{-HY^{+\cdot}} \underset{\mathbf{2}}{CH_2{=}C(CH_3)CH_2CH_3} + \underset{\mathbf{3}}{CH_3CH{=}C(CH_3)_2} \quad (3)$$

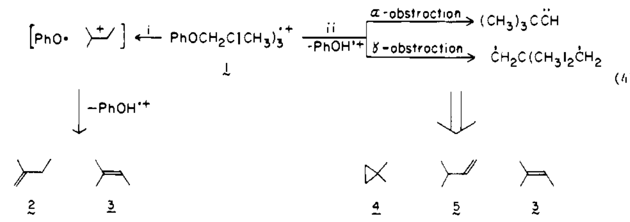
neutral products

molecular ion of neopentyl phenyl ether (**1** where Y = OC_6H_5) will be 2-methyl-1-butene (**2**) and 2-methyl-2-butene (**3**). This reaction is well suited for an EBFlow study, particularly since the C_5H_{10} isomer distribution from deprotonation of *tert*-amyl cation has already been characterized; the less stable isomer, **2**, is the more abundant product, and the **2**/**3** ratio increases with the basicity of the proton acceptor. Values of **2**/**3** of 1.2 and 2.5 are reported,[7] and the lower value would be anticipated from reaction 3, based on the proton affinity of phenoxyl. Also, this **2**/**3** ratio should equal the ratio of γ-hydrogen transfer to α-hydrogen transfer in the mass spectrum of **1**.

This paper will present three new experimental data: first, the C_5H_{10} isomer distribution from 70-eV EBFlow radiolyses of neopentyl phenyl ether; second, a mass spectrometric study of deuterium-labeled ethers that confirms the EBFlow results; third, results pertaining to other phenyl ethers, which provide negative evidence demanded by the acyclic mechanism. The Discussion section will show how these and published data support the intermediacy of an ion-molecule complex.

Results

The purpose of examining the neutral products from decomposition of **1** is to distinguish between the two pathways shown in reaction 4. The assumption that **1** fragments by the same mechanism as does *n*-butyl phenyl ether restricts the products that might come from mechanism A. The likely candidates are shown in path ii: *tert*-butylcarbene from α-hydrogen transfer and 2,2-dimethyltrimethylene diradical from γ-hydrogen transfer. The ultimate products from the carbene are 1,1-dimethylcyclopropane (**4**) as the major product and 2-methyl-2-butene (**3**) as a minor product.[22] (This result was confirmed by decomposing *tert*-butyldiazomethane at 300 °C on a quartz-lined injector block of a gas chromatograph.) The ultimate products from the diradical should be **4** as well as 2-methyl-2-butene (**3**) and 3-methyl-1-butene (**5**), which are formed in roughly equal quantities from isomerization of vibrationally excited **4**.[23] Only trace quantities of 2-methyl-1-butene (**2**) are observed in either case. As mentioned above, mechanism B (path i) should produce **2** and **3** in a ratio on the order of unity.

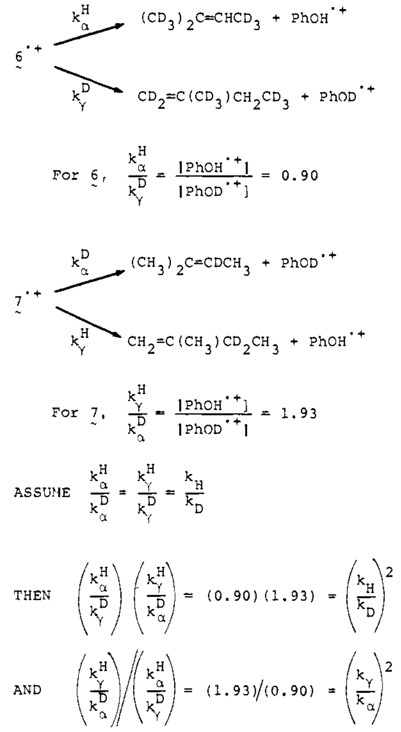


(4)

The 70-eV mass spectrum of neopentyl phenyl ether shows $C_6H_5OH^{+\cdot}$ as base peak. EBFlow radiolyses of the gaseous ether at pressures on the order of 1 × 10^{-4} Torr (under conditions where ~10% of the substrate is ionized) produce a C_5H_{10} isomer ratio of **2**:**3**:(**4** + **5**) = 1.10:1:0.03. The standard deviation of the value of **2**:**3** is 0.08. The product distribution is independent of pressure, since EBFlow radiolysis at 1.2–1.4 × 10^{-3} Torr affords an isomer distribution of 1.05:1:0.03.

The usual type of control was performed. An EBFlow run with the electron energy at ionization threshold (and a negligible current entering the reaction vessel) produced **3** as the most abundant C_5H_{10} isomer, with an absolute yield (per unit time) 0.08 the yield at 70 eV. This proves that the 70-eV products come neither from impurities in the starting material nor from decomposition in the electron source. When correction of the 70-eV yield is made by subtracting the control yields, a value for **2**/**3** = 1.14 is determined.

Scheme I



A mass spectrometric experiment provides independent verification of the EBFlow results. In mechanism B, **2** comes from nominal γ-hydrogen transfer and **3** from α-hydrogen transfer. A separate determination of the ratio of γ- to α-transfer was made by analyzing $C_6H_5OH^{+\cdot}$:$C_6H_5OD^{+\cdot}$ ratios in the 70-eV mass spectra of labeled compounds **6** and **7**. The measured ion ratios are 0.90 and 1.93, respectively

$(CD_3)_3CCH_2OPh$ **6** $(CH_3)_3CCD_2OPh$ **7**

(standard deviation in each case is 3%). If the deuterium kinetic isotope effects for **6** and **7** are assumed to be the same, a value of k_H/k_D = 1.32 is obtained by using the algebra in Scheme I. This value is to be compared with the value k_H/k_D = 1.34 reported for *n*-propyl phenyl ether.[10]

The ratio of γ- to α-hydrogen transfer is 1.46. Ideally, this ratio should have been 1.14, the value of **2**/**3** from the EBFlow experiment. No large systematic errors are apparent in the mass spectrometric result. Neither incomplete deuteration nor deviations from the assumption that isotope effects are the same for **6** and **7** substantially affect the ratio calculated from the experimental data. The difference, then, between the mass spectrometric and EBFlow values measures the extent of systematic error in the latter. The cause is probably contamination of the product mixture by **3** from sources other than decomposition of **1**. A likely source would be neutralization of $C_5H_{10}^{+\cdot}$ and $C_5H_{11}^+$ on the walls or in the trap of the EBFlow reactor. These ions, together, constitute one-quarter of the base peak intensity in the mass spectrum of neopentyl phenyl ether. If they yield **3** predominantly, then the contamination would be sufficient to account for the discrepancy. Except for **1** itself, no other fragment ions are present that might produce C_5H_{10} through neutralization.

This check on the accuracy of the EBFlow experiment shows

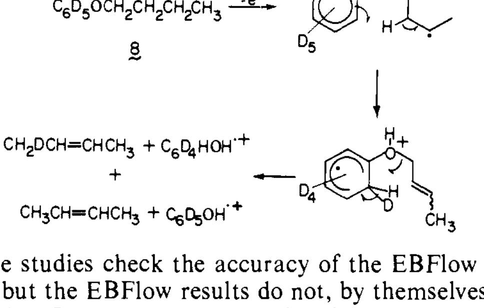
Table I. Fractions of Hydrogen Transfer from Various Chain Positions in Alkyl Phenyl Ether 70 eV Electron Impact (EI) and Chemical Ionization (CI) Mass Spectra[a]

alkyl group		α	β	γ	δ
	statistical (complete scrambling)	$^2/_7$	$^2/_7$	$^3/_7$	
n-propyl	reported (EI)[b]	0.27	0.26	0.47	
	statistical (no scrambling)	$^1/_3$	$^1/_6$	$^1/_2$	
	reported (CI)[b]	0.34	0.17	0.49	
n-butyl	statistical[c]	$^1/_6$	$^1/_4$	$^1/_3$	$^1/_4$
	reported (EI)[d]	0.18	0.29	0.34	0.19
neopentyl	statistical[e]	$^7/_{15}$		$^8/_{15}$	
	observed (EI)	0.41		0.59	

[a] Based on [*m/e* 95]/([*m/e* 94 + *m/e* 95]) from deuterated analogues. [b] Reference 10; CI refers to chemical ionization using isobutane reagent gas. [c] Based on a 1:1 ratio of 1-butene:2-butenes. [d] Reference 9. [e] Based on **2**/**3** = $^8/_7$.

reasonable agreement (1.14 vs. 1.46) with the mass spectrometric result. The supposition that *n*-butyl phenyl ether molecular ion decomposes by the same mechanism as **1** will be emphasized, and great weight will be given to the production of 2-butenes from the EBFlow study of this reaction.[6] It is important to gauge the accuracy of this latter result and assess the effects of free alkyl cations. Free butyl cations are generated by electron impact on *n*-butyl halides.[24] A 70-eV EBFlow radiolysis of gaseous 1-bromobutane at 4 × 10^{-4} Torr yields a C_4H_8 isomer distribution of 1-butene:isobutene:methylcyclopropane:*trans*-2-butene:*cis*-2-butene = 10:4:2:3:2. When a mixture of diethyl ether (1 × 10^{-4} Torr) and 1-bromobutane (3 × 10^{-4} Torr) was radiolyzed under the same conditions,[25] the C_4H_8 isomer distribution was 10:8:4:14:4. Regardless of how C_4H_8 is formed in the radiolysis of neat 1-bromobutane, it is clear that addition of a good proton acceptor causes major changes. These changes must be attributed to the presence of diethyl ether, and the isomers that increase when it is added are taken to be the products of deprotonation of $C_4H_9^+$. Isobutene is a major product, which implies that free $C_4H_9^+$ produced by electron impact undergoes substantial rearrangement to the *tert*-butyl structure.[26] But isobutene constitutes less than 1% of C_4H_8 recovered from EBFlow radiolysis of *n*-butyl phenyl ether;[6] hence, free butyl cations contribute negligibly to the observed products in that experiment.

A more remote possibility for systematic error is that *n*-butyl ethers rearrange to *sec*-butyl ethers under electron impact conditions. The 70-eV EBFlow radiolysis of *n*-butyl phenyl ether was reinvestigated, and neutral products were examined for *sec*-butyl phenyl ether. This product is barely detectable and corresponds to a normalized yield ≤ 0.1 μmol A^{-1} s^{-1}, based on a throughput of substrate = 24 μmol Torr^{-1} s^{-1} (and not mmol, as erroneously printed in ref 6). By contrast, the normalized yield of C_4H_8 is at least an order of magnitude greater.



(5)

These studies check the accuracy of the EBFlow experiments, but the EBFlow results do not, by themselves, prove mechanism B. Rearrangements of molecular ion tautomers could fortuitously give the same product distributions. Reaction 5 provides a pathway by which 2-butenes might be produced following γ-hydrogen transfer in the *n*-butyl phenyl ether molecular ion (reaction 1A where R = CH_3 and X = OC_6H_5). Like many other rearrangements that can be conceived to form these products, scrambling of ring hydrogens with alkyl hydrogens is necessary. Because such scrambling had not previously been probed directly, the mass spectrum of compound **8** was examined. The $C_6D_5OH^{+\cdot}$ ion constitutes the base peak, and no $C_6D_4HOH^{+\cdot}$ is seen above the level corresponding to incomplete deuteration of the starting material. Thus, a whole class of mechanisms can be ruled out, since ring-alkyl scrambling does not take place.

$$\underset{\mathbf{9}}{PhCH_2CH_2OPh} \xrightarrow{-e^-} \underset{\mathbf{10}}{[PhC_2H_4^+ \quad PhO\cdot]}$$

$$\not\rightarrow PhCH{=}CH_2 + PhOH^{+\cdot} \qquad (6)$$

Mechanism B makes a negative prediction, shown in reaction 6, as a necessary (but not a sufficient) condition. Styrene has a proton affinity of 8.8 eV (20 kcal/mol, based on a proton affinity for ammonia of 9.0 eV),[4] which is greater than the proton affinity of phenoxyl. Therefore, protonated styrene ought not to transfer a proton to phenoxyl in dissociation of an ion-molecule complex such as species **10** (from the molecular ion of β-phenethyl phenyl ether, **9**). The mass spectrum of **9** shows a prominent peak for protonated styrene ($C_6H_5C_2H_4^+$, *m/e* 105), a minor peak for styrene itself ($C_6H_5C_2H_3^{+\cdot}$ one-eighth the intensity of *m/e* 105), and a negligible peak for $C_6H_5OH^{+\cdot}$ (less than $^1/_{20}$ the intensity of *m/e* 105). This bears out the prediction that **9** does not fragment by the same route as *n*-alkyl phenyl ethers.

Discussion

The EBFlow results are necessary to demonstrate mechanism B. With the neutral product distributions, mass spectrometric results can be predicted, and comparisons between prediction and experiment are summarized in Table I. The results for neopentyl phenyl ether are shown in the last entries, and prediction from the EBFlow data agrees with the mass spectrometric observation.

Mechanism B for gaseous ion decomposition resembles first-order elimination in solution, in that a covalent bond is converted to an ionic bond. In the gas phase, the intermediate is an ion-molecule complex bound by charge-dipole electrostatic attraction. The solution analogue is an ion pair.[27] Both reactions are first order, but the second step in each case is, strictly speaking, bimolecular.

***n*-Propyl Phenyl Ether.** The justification for an ion-molecule complex comes from isomerization and scrambling seen in phenyl ether ion decompositions. Consider *n*-propyl phenyl ether. Suppose that a propyl cation-phenoxyl complex is intermediate in the fragmentation of the molecular ion. If all seven of the propyl hydrogens randomize completely, the statistical proportions of hydrogen transferred from the various positions of the side chain are listed in the first line of Table I. The results from 70-eV electron impact match closely.[10] The propyl ion formed under these conditions scrambles all of its hydrogens in the ion-molecule complex, a process that, for the free cation in solution,[19] has Arrhenius parameters $E_a = 0.7$ eV (16 kcal/mol) and $\log A = 13.2 \pm 0.3$. As expected on the basis of mechanism B, ortho disubstitution of the benzene ring is reported to have no effect on the observed fractions.[10]

$$CH_3CH_2CH_2OPh \xrightarrow{AH^+} [(CH_3)_2CH^+ \quad C_6H_6O] \rightarrow CH_2{=}CHCH_3 + C_6H_7O^+ \quad (7)$$

For less energetic ions, the rate of scrambling should become slower. If only the initial isomerization of *n*-propyl to isopropyl occurs, then the statistical fractions have the values given in line 3 of Table I. The least energetic method of ionization is CI by *tert*-butyl cation, which is endothermic, as estimated using group equivalents[15] and the proton affinities of isobutene[4,20] and phenol.[14] Mechanism B for the CI of *n*-propyl phenyl ether is depicted in reaction 7, and the reported fractions of hydrogen transfer from each chain position agree perfectly with the statistical prediction, as shown in Table I. For more energetic ionizations (both CI and EI),[10,11] reported fractions lie between the probabilities in lines 1 and 3 of Table I, as expected on the basis of incomplete scrambling. In a few experiments, fractions of γ-hydrogen transfer are reported that appear too high to accommodate an acyclic mechanism (the highest is 0.58),[11] for which a value of one-half is the upper limit. These tend to be seen in low-energy regions, generally from metastable peaks. Possibly this aberration is a consequence of large isotope effects (and large differences between them) that would make the algebra of Scheme I inaccurate for computing fractions of hydrogen transfer from the various chain positions.

The most energetic ion-molecule complexes must have lifetimes on the order of picoseconds. Field ionization kinetics of *n*-propyl phenyl ether[11] show that alkyl hydrogen randomization is complete in ions that decompose within 10^{-11} s of formation. The intermediate complex must live long enough for scrambling to occur on this time scale. Unless the propyl cations in the complex are very highly excited, the activation energy must be much lower than the value from solution studies. For the purposes of predicting relative rates of scrambling, it may be appropriate to ignore the E_a values from solution and to compare only the Arrhenius preexponential factors.

***n*-Butyl Phenyl Ether.** What do the experimental results for EI of *n*-butyl phenyl ether require of mechanism B? Assume that *n*-butyl isomerizes to *sec*-butyl in the ion-molecule complex. Three rearrangements are reported for *sec*-butyl cation in solution:[19] very fast ($E_a < 0.25$ eV) hydride shifts between the 2 and 3 positions, complete randomization of all the hydrogens ($E_a = 0.34$ eV, $\log A = 12.3 \pm 0.1$), and the exothermic rearrangement to *tert*-butyl. In the ion-molecule complex, the 2,3-hydride shift is to be expected, but the other reactions may be slower than proton transfer. In particular, the preexponential factor for complete hydrogen randomization is an order of magnitude smaller than for the corresponding process in isopropyl. It is reasonable to anticipate that complete randomization in *sec*-butyl will not take place before the ion-molecule complex decomposes.

A prediction based upon mechanism B is given in Table I. Isomerization from *n*-butyl to *sec*-butyl is essentially irreversible, and scrambling of the hydrogens in the 2 and 3 positions is complete. Since gaseous *sec*-butyl cation is stable on the microsecond time scale,[26] isobutene is neither expected nor observed in significant quantities.[6] The statistical fractions are computed on the basis of the assumption that equal amounts of 1- and 2-butenes are formed in the proton-transfer step and that the methyl hydrogens do not scramble with the 2 and 3 positions.

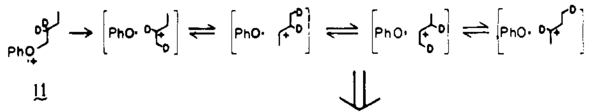
Statistical fractions were computed for likelihoods of proton transfer to phenoxyl. The only product from α-transfer is 1-butene, and only two of six possible protons in *sec*-butyl originate from the α-methylene. If 1-butene is taken to represent one-half of the C_4H_8 product, the expected fraction is $(1/3)(1/2) = 1/6$. Three of six possible protons originate from the δ position, and the expected fraction is $(1/2)(1/2) = 1/4$. Only the transfer of protons from the original β and γ positions yields 2-butenes. Because of rapid hydride shifts, one β hydrogen becomes scrambled with two γ hydrogens. With 2-butene as one-half the C_4H_8 yield, the fraction of transfer from the γ position is $(2/3)(1/2) = 1/3$. Since one of the protons in the original β position migrates to form a methyl, one-sixth of the 1-butene and one-third of the 2-butene come from transfer of an initially β proton, giving an expected fraction $(1/6)(1/2) + (1/3)(1/2) = 1/4$. As shown in Table I, there is a small discrepancy in that the β contribution is too high and the δ contribution is low.

The experimental values can be matched exactly if two minor adjustments are made. If (1) some hydrogen transfer takes place from *n*-butyl before isomerizing to *sec*-butyl and (2) if some hydrogen transfer takes place from *sec*-butyl before any interchange of the 2 and 3 positions, then the β contribution can be raised at the expense of the δ contribution. For instance, allowing 8 and 12% of the cations to operate by the first and second of these alternatives, respectively, would generate proportions of α-, β-, γ-, and δ-transfer of 0.17, 0.30, 0.33, and 0.20.

A more serious correction must be applied to the EBFlow results. The ratio of 1-butene to 2-butene, which has an experimental value of unity, should be lowered to account for 1-butene that is produced by nonionic decomposition of starting material. The yield of 1-butene at 8 eV (ionization threshold) is approximately 0.2 the 70-eV yield, while the 8-eV yield of 2-butenes is <0.04 the 70-eV yield.[6] It seems reasonable to surmise that perhaps one-fifth of the 1-butene recovered at 70 eV came from nonionic sources.

The reported and statistical fractions for *n*-butyl phenyl ether agree with one another. The variation seen when ionizing energy is decreased (γ contribution increases at the expense of the other three positions)[9] is consistent with a decrease in the rate of 2,3-hydride shift relative to proton transfer.

A final test is based upon observed levels of deuteration in neutral products from the molecular ion of *n*-butyl-*2,2-d*$_2$ phenyl ether (**11**). Mechanism B (with scrambling of the 2 and 3 positions of the *sec*-butyl cation) predicts levels of deuteration of recovered 1- and 2-butenes shown in reaction 8. For the 2-butenes, there are two hydrogens and one deuterium that interchange. The odds of transferring a proton rather than a deuteron from these positions are 2:1, giving a statistical prediction of two-thirds 2-butene-d_2 and one-third 2-butene-d_1. One can also determine these fractions by enumerating individual isomers of the *sec*-butyl cation, but it is necessary to bear in mind that some of them are chiral and must be weighted accordingly.



11

(8)

	1-butene	2-butenes
Statistical	5/6-d_2, 1/6-d_1	2/3-d_2, 1/3-d_1
Observed[25]	60 ± 15% d_2	65 ± 15% d_2

If an isotope effect is taken into account, the prediction does not change greatly. For $k_H/k_D = 1.3$, the prediction for 2-butenes becomes 0.72 d_2 and 0.28 d_1. For 1-butene, the statistical fractions are five-sixths d_2 and one-sixth d_1 and become, for the above isotope effect, 0.87 d_2 and 0.13 d_1.

The experimental results from **11** are based on GLC-mass spectrometric analyses of the neutral products collected from three 70-eV radiolyses of a substrate that was 95 atom % D.[6] The 50-eV mass spectra of the butenes showed, as the most prominent ions above m/e 40, peaks at m/e 58, 57, 56, 43, 42, and 41. For the 1-butene, the ratio of peak intensities was 27:27:13:47:100:52. Both 2-butenes showed essentially the same spectra, with an intensity ratio of 43:34:18:53:100:54. Determination of the extent of deuteration is subject to large uncertainties because authentic samples of appropriately labeled dideuterated butenes were not available for reference. A computation can be based on $[M - 1]^+/[M]^{+\cdot} = 0.4$ found for all three undeuterated butenes and for 1-butene-*2-d*$_1$.[25] When correction is made for incomplete deuteration of **11**, the 1-butene is calculated to be 60% d_2 and the 2-butenes 65% d_2. Uncertainty in these values is estimated to be ±15%. The 1-butene value is lower than expectation. This may be a consequence of an impurity from nonionic decomposition of starting material. If 20% of the 1-butene came from such sources, the discrepancy would be accounted for.

$$\mathrm{RCH_2CH_2OPh^{+\cdot}} \rightleftarrows [\mathrm{RCH{=}CH_2\quad PhOH^{+\cdot}}] \rightleftarrows \mathrm{RCH(CH_3)OPh^{+\cdot}} \quad (9)$$

All of the experimental tests support mechanism B for alkyl phenyl ether ion decompositions. Several alternatives can be discarded. One is shown in reaction 9. Nibbering[12] has suggested that molecular ions might transpose the ionized functionality. Reversible expulsion of $C_6H_5OH^{+\cdot}$ is a possible explanation for the scrambling results. This requires that $C_6H_5OH^{+\cdot}$ add rapidly to olefins. If this be true, then phenol ions ought to add easily to double bonds in ion-molecule reactions as well. If the addition product is not stabilized by collisions, then it will revert to the reactants. The addition could still be detected, since hydroxylic and olefinic hydrogens would become scrambled. An example would be production of $C_6H_5OH^{+\cdot}$ from reaction of $C_6H_5OD^{+\cdot}$ with propene. This reaction was investigated by ICR, with $CD_3CD_2OC_6H_5$ as a precursor for $C_6H_5OD^{+\cdot}$. No formation of $C_6H_5OH^{+\cdot}$ was seen at pressures as high as 1×10^{-3} Torr, and addition product was only barely detectable at the highest pressures studied.[28] Reaction 9 seems implausible, since the evidence argues against facile addition of phenol ions to olefins.

Conclusion

The viability of an ion-molecule complex as an intermediate in gaseous cation fragmentation has been demonstrated. Similar types of intermediates have been suggested for nonconcerted fragmentations of oxonium ions[16] and for negative ion-molecule reactions.[29] Mechanism B, exemplified in Figure 1, accounts for the observed decompositions of alkyl phenyl ether parent ions. It makes the following quantitative predictions that have been tested by EBFlow radiolysis and mass spectrometry:

(1) The major products from neopentyl phenyl ether molecular ion, **1**, are **2** and **3** in a ratio slightly greater than unity.

(2) The fractions of α-, β-, and γ-transfer from high-energy ionizations of *n*-propyl phenyl ether are $2/7$, $2/7$, and $3/7$, respectively. The fractions from low-energy ionizations are $1/3$, $1/6$, and $1/2$, respectively.

(3) Ionization of *n*-butyl phenyl ether gives fractions of α-, β-, γ-, and δ-transfer that are close to the fractions $1/6$, $1/4$, $1/3$, and $1/4$, expected on the basis of the EBFlow result that 1- and 2-butenes are produced in equal quantities.

(4) The fraction of $C_4H_6D_2$ in the 2-butene collected from decomposition of **11** is within experimental uncertainty of the statistical value of $2/3$.

Mechanism B unifies electron impact and chemical ionization results. It not only explains a large body of data on the basis of known cation rearrangements, but also strengthens the connection between solution and gas-phase ion chemistry. Ion-molecule complexes from alkyl phenyl ethers contain alkyl cations that are rapidly deprotonated. The analogy to the E1 reaction suggests that gas-phase ion decompositions can be probed for cation rearrangements just as solvolyses are in solution. Experiments that exploit this analogy are currently in progress in this laboratory.

Experimental Section

Materials. All compounds were purified by preparative GLC before EBFlow radiolysis or mass spectrometric studies. For radiolysis experiments, commercial 1-bromobutane (Aldrich) was used, while neopentyl phenyl ether[30] and *n*-butyl phenyl ether[9] were prepared by previously published procedures for phenoxide substitution of the corresponding tosylates. Neopentyl tosylate, prepared from solid commercial neopentyl alcohol (Aldrich), was recrystallized three times from petroleum ether before conversion to the phenyl ether. ^{1}H NMR spectra of both the tosylate and the ether showed them to be free from impurities within the limits of detection. Samples of *sec*-butyl phenyl ether, β-phenethyl phenyl ether, and *n*-butyl phenyl-d_5 ether were prepared from the corresponding tosylates by refluxing in a tetrahydrofuran solution of sodium phenoxide. Commercial phenol-d_6 (Merck, 99 atom % D) was used to prepare *n*-butyl phenyl-d_5 ether. Purified materials gave satisfactory ^{1}H NMR spectra.

The deuterium-labeled neopentyl phenyl ethers **6** and **7** were prepared from the corresponding alcohols via the tosylates. Neopentyl-d_2 alcohol was prepared by a previously published procedure.[31] Neopentyl-d_9 alcohol was synthesized from acetone-d_6 (Aldrich, 99.7 atom % D) via pinacol-d_{12} and the corresponding pinacolone.[32] Oxidation of the pinacolone to pivalic acid-d_9 with a solution of potassium dichromate in aqueous sulfuric acid,[33] followed by reduction of the pivalic acid-d_9 with lithium aluminum hydride, gave neopentyl-d_9 alcohol. The following mass spectra (corrected for ^{13}C natural abundance) were recorded on an Hitachi Perkin-Elmer RMU 6-D with chamber set at 70 V and target at 110 V (with a few exceptions, peaks below *m/e* 40 or ≤3% the base peak intensity are not reported). Neopentyl phenyl ether: *m/e* (rel intensity) 164 (24), 149 (6.0), 110 (5.0), 108 (3.0), 107 (8.0), 94 (100), 77 (12), 72 (4.5), 71 (7.5), 70 (16), 66 (6.0), 65 (6.0), 57 (6.0), 55 (20), 51 (8.5), 43 (37), 42 (5.0), 41 (19), 39 (14). Neopentyl-d_9 phenyl ether (**6**): *m/e* (rel intensity) 173 (23), 172 (2), 155 (5.5), 110 (1.5), 109 (5.0), 108 (3.5), 107 (1.5), 95 (100), 94 (90), 80 (10), 79 (22), 78 (3.0), 77 (16), 67 (8.0), 66 (9.0), 65 (9.0), 61 (16), 60 (10), 51 (13), 50 (10), 49 (25), 48 (24), 47 (8), 46 (19), 45 (11), 44 (8), 43 (5), 42 (9), 41 (9), 40 (5), 39 (16). Neopentyl-d_2 phenyl ether (**7**): *m/e* (rel intensity) 166 (18), 165 (0.3), 151 (4.5), 110 (2.0) 109 (3.0), 108 (3.0), 107 (1.5), 95 (52), 94 (100), 78 (2.0), 77 (19), 73 (9.0), 71 (18), 67 (2.5), 66 (8.0), 65 (9.0), 57 (20), 56 (13), 55 (5.5), 51 (18), 45 (19), 44 (27), 43 (20), 42 (11), 41 (16), 40 (7.5), 39 (19). *n*-Butyl phenyl-d_5 ether (**8**): *m/e* (rel intensity) 155 (19), 154 (1.0), 112 (2.5), 99 (100), 98 (8.0), 82 (10), 71 (7.0), 70 (7.5), 57 (6.0), 54 (7.0), 42 (8.5), 41 (13). β-Phenethyl phenyl ether (**9**): *m/e* (rel intensity) 198 (13), 154 (9.0), 111 (3.5), 106 (6.0), 105 (59), 104 (7.5), 103 (6.5), 97 (8.0), 95 (8.0), 94 (3.0), 91 (6.0), 85 (45), 84 (31), 83 (33), 82 (12), 79 (12), 77 (17), 71 (14), 70 (33), 69 (49), 68 (15), 67 (6.0), 57 (35), 56 (71), 55 (91), 43 (51), 42 (31), 41 (100).

For a study of the rearrangement products of *tert*-butylcarbene, *tert*-butyldiazomethane was prepared by the method of Friedman and Shechter.[22] The neat liquid was decomposed on a heated GLC injector block and the volatile products were analyzed on a 37 ft × $1/8$ in. 20% dimethylsulfolane column[7] at room temperature. The observed C_5H_{10} isomer ratio **2**:**3**:(**4** + **5**) was 1:15:125.

Apparatus. EBFlow radiolyses of 1-bromobutane and *n*-butyl phenyl ether were performed in apparatus previously described.[6] The radiolysis product from *n*-butyl phenyl ether was analyzed on an 8 ft × $1/8$ in. 5% diisodecyl phthalate/5% Bentone 34 column at 135°C, on which the retention times of *sec*-butyl phenyl ether and *n*-butyl phenyl ether are 6.3 and 9.6 min, respectively. A 6-h 70-eV radiolysis of *n*-butyl phenyl ether was run with average ionizing electron currents of 50 μA measured on the cage and 20 μA at the collector. The level of *sec*-butyl phenyl ether present as an impurity in the starting material was ~6 parts in 10^5; the level in the radiolysis product (identified only by GLC retention time) was ~8 parts in 10^4.

The EBFlow reactor was substantially modified prior to the radiolyses of neopentyl phenyl ether. A stainless steel reaction vessel, 130 × 6 cm diameter, is mounted horizontally, replacing the vertically mounted glass vessel previously used. The thoria-coated iridium filament and first 8 cm of the reaction vessel are immersed in a bank of toroidal permanent magnets (500 G axial field) and enclosed in a 2-L Pyrex envelope that is continuously evacuated by a Varian VHS-2 diffusion pump charged with Convalex 10 polyphenyl ether. The remaining length (120 cm) of the reaction vessel is wrapped with ten layers of no. 14 magnet wire. A constant current of 2.6 A is maintained in this solenoid to give an axial field ≥200 G throughout the entire reaction vessel. The temperature of the reaction vessel during a run is between 320 and 330 K as a consequence of heat generated by the solenoid.

The same procedures as previously described were used. Electron energy was determined by biasing the filament negative to the reaction vessel, which is grounded. At 70 eV the electron current varied from 10 to 80 μA, with roughly half the current measured from the reaction vessel walls and half from a set of collector baffles between the reaction vessel and the liquid nitrogen cold trap. Three runs were performed at pressures between 0.8 and 2×10^{-4} Torr, and a control run at 8 V was performed in the same pressure range. GLC analyses were performed on the dimethylsulfolane column. From addition of a known quantity of *cis*-4-methyl-2-pentene as a standard to the control and to one of the 70-eV runs, absolute yields were determined. Normalized C_5H_{10} yield for the 70-eV run was 4.5 μmol A^{-1} s^{-1}. In the control run a current ≤ 1 μA was measured in the reaction vessel; the C_5H_{10} yield per unit time (not normalized for electron current) was 15 pmol s^{-1} and showed a value of **2**/**3** = 0.7 (no other isomers were detected). A final run was performed in the pressure range 1.2–1.4×10^{-3} Torr with currents on the order of 10 μA measured on the walls of the reaction vessel and ≤ 1 μA at the collector.

Acknowledgment. The author is grateful to Professor Richard William Johnson for helpful comments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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γ-Alkylation of α,β-Unsaturated Ketones. γ-Arylsulfonyl Groups as Regioselective Control Elements

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Abstract: A reaction sequence for γ-alkylation of α,β-unsaturated ketones has been proposed and tested with some success. γ-(Phenylsulfonyl) groups are (1) introduced into the substrate; (2) present during alkylation of the resulting highly delocalized carbanions; (3) finally removed to leave the otherwise inaccessible γ-alkylation product.

Introduction

α,β-Unsaturated ketones are popular and versatile intermediates in organic synthesis.[1-3] Moreover, they are easily preparable by a plethora of methods from various starting materials. These structures can be utilized for both thermal [4 + 2] and photochemical [2 + 2] cycloadditions. New individual carbon–carbon bonds can be formed by highly selective 1,2- or 1,4-nucleophilic additions onto the normally electrophilic enone framework. On the other hand, regioselective

0002-7863/80/1502-1602$01.00/0