Gas Phase Decomposition of Conjugate Acid Ions of Simple *tert*-Butyl Alkyl Ethers

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Unimolecular decompositions of protonated methyl (MTBE), ethyl (ETBE), *n*-propyl, isopropyl, and isobutyl *tert*-butyl ethers have been examined experimentally and the results compared with the outcome of ab initio calculations. Extensive hydrogen transposition between the hydrogen on oxygen and the nine hydrogens of the *tert*-butyl is revealed by mass-resolved ion kinetic energy spectroscopy (MIKES) experiments on deuterated ions from MTBE and ETBE. Mechanistic possibilities are probed with the help of FT-ICR, and isotope effects are interpreted by comparison with the MIKES of protonated ethyl *tert*-amyl ether and its deuterated analogues. Protonated MTBE displays a single unimolecular decomposition product, *tert*-butyl cation. Of the protonated MTBE ions that decompose, 30% do so without any hydrogen transposition, while 70% completely randomize the non-methoxy hydrogens. This calls for the intervention of at least two noncovalent intermediates. In the case of MTBE, Hartree–Fock-based SCF computations exhibit only one plausible candidate that corresponds to an energy minimum, the hydrogen-bonded complex between protonated methanol and isobutene. The other intermediate is inferred to be the ion–neutral complex [MeOH tBu^+], even though that does not correspond to a well on the SCF potential energy surface. Protonated ETBE yields a pair of unimolecular decomposition products, *tert*-butyl cation and protonated acetaldehyde. Here the ab initio results display two noncovalent potential energy minima, but the observed ion intensities cannot be accounted for without at least three intermediates. Again, the conclusion is that the additional intermediate corresponds to an ion–neutral complex, [EtOH tBu^+], which does not correspond to a potential energy minimum. The transient ion–neutral complexes have non-zero lifetimes because their collapse is prevented by entropic (rather than energetic) barriers.

Methyl *tert*-butyl ether (MTBE) is a widely used fuel additive whose industrial production has increased by nearly a factor of 20 over the past decade.[1] The combustion chemistry[2] of MTBE, heterogeneous acid catalysis of its decomposition,[3] and its reactions with neutral atoms and free radicals[4] have been explored. Its positive ion chemistry in the gas phase has been examined in terms of ionization and thermochemical properties,[5-7] in addition to the reaction of MTBE with methyl cation.[8] Recent proposals have put forth ethyl *tert*-butyl ether (ETBE), as well, for use as a fuel additive.[9] The chemistry of the gaseous conjugate acids of these compounds has not been previously reported. We present here, as a continuation of our systematic investigations of protonated ethers,[10-13] a study of elementary steps by which gaseous MTBE and its higher homologues undergo acid-catalyzed decomposition in the gas phase.

Large scale manufacture of MTBE makes use of heterogeneous catalysts to promote the addition of methanol to isobutene.[14] It turns out that the homogeneous gas phase positive ion chemistry of MTBE brings about the reverse reaction. We find experimentally that the dissociation of protonated MTBE, depicted in eq 1, proceeds cleanly by a single pathway. Since the electrically charged product, *tert*-butyl cation, is acidic enough to protonate MTBE exothermically in a bimolecular step (as eq 2 portrays), our conclusion is that gaseous MTBE is poised to undergo a proton-catalyzed chain reaction which returns it to the materials from which it is

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synthesized. The propagation steps are summarized in eqs 1 and 2.

$$\text{MTBE} \xrightarrow{H^+} \underset{\textbf{1a}}{CH_3OC(CH_3)_3} \xrightarrow{-CH_3OH} (CH_3)_3C^+ \quad (1)$$

$$(CH_3)_3C^+ + \text{MTBE} \xrightarrow{-(CH_3)_2C=CH_2} \textbf{1a} \quad (2)$$

Positive ions are not ordinarily as abundant in combusting mixtures as free radicals, but ion–molecule reactions are typically much faster than reactions between neutral molecules in the gas phase. Bimolecular rate constants are often greater than 10^{10} atm^{-1} s^{-1}. In a gaseous mixture containing 0.1 atm of MTBE (with no base present to scavenge positive ions), one molecule of an electrically charged Brønsted acid catalyst (such as a free *tert*-butyl cation) can turn over a million times per millisecond via eqs 1 and 2 (if eq 2 is rate limiting).

The decomposition drawn in eq 1 is endothermic by approximately 100 kJ/mol (1 eV),[6] but the entropy change is so positive that, around 600 K, the equilibrium shifts to the right. While eq 1 looks like a simple reaction, the deuterium-labeling studies described below reveal an underlying complexity. Moreover, additional pathways open up for the higher homologues **2**–**5**, which provide further insight. In combination with experimental data that we have previously reported for di-*tert*-butyl ether[13] and computational results presented here, our experiments suggest that conjugate acid ions of simple *tert*-butyl ethers react unimolecularly as though they are noncovalent complexes of *tert*-butyl cation with a molecule of neutral alcohol, as eq 3 shows. This may be relevant to the combustion of MTBE and ETBE under high compression.

$$\begin{array}{l} H^+ \\ ROC(CH_3)_3 \\ \textbf{1b}, R = CD_3 \\ \textbf{2a}, R = CH_3CH_2 \\ \textbf{3}, R = (CH_3)_2CH \\ \textbf{4}, R = CH_3CH_2CH_2 \\ \textbf{5}, R = (CH_3)_2CHCH_2 \end{array} \longrightarrow \begin{array}{l} [ROH \quad (CH_3)_3C^+] \\ \text{ion–neutral complex} \end{array} \quad (3)$$

Results

Three sets of data will be presented: studies of the metastable ion decompositions of ions **1**–**5** by mass-resolved ion kinetic energy spectroscopy (MIKES), FT-ICR experiments that provide insights about pertinent ion–molecule reactions, and ab initio calculations. The fragmentation in eq 1 takes place via the mechanism summarized in Scheme 1, in which a portion of the *tert*-butyl cations (corresponding to mole fraction *X*) come from direct cleavage, while the remainder are produced via a pathway that involves interconverting, noncovalently bonded intermediates represented as **6** and **7**. We distinguish between ion–neutral complexes (such as **6**) and hydrogen-bonded complexes (such as **7**) by enclosing the former in brackets.

MIKES Studies. As in our previous studies[10,13] we find that the metastable ion decompositions of a given dialkyl ether conjugate acid are nearly the same, regardless of whether it is created using either of two methods, by protonation of the neutral ether or by ion–molecule reactions of protonated alcohols in the spectrometer source (provided that ions are adequately thermalized by collisions prior to decomposition). The most general bimolecular reaction by which **1**–**5** can be prepared is summarized by eq 4 and has been extensively studied.[15] Under the conditions used here, two alcohols are introduced into the ion source along with a high pressure of water. Electron impact on water leads, by a series of ion–molecule reactions, to H_3O^+, which chemically ionizes the alcohols. In the present experiments, proportions of observed decomposition products differ by ≤12% between the two methods for preparing the ether conjugate acid ion.

Scheme 1

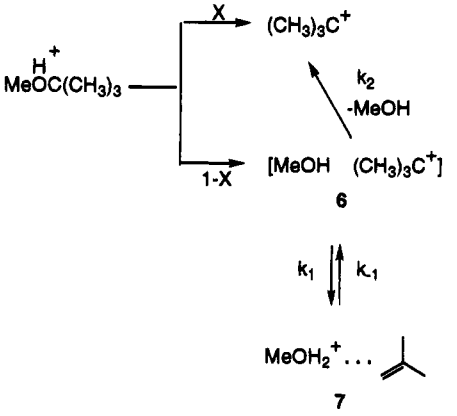
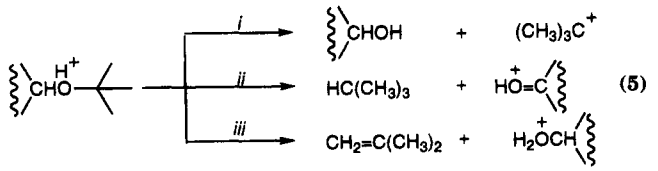


Table 1. Proportions of *tert*-Butyl Cation (Pathway i) and Isobutane Loss (Pathway ii) in the MIKES of Protonated Alkyl *tert*-Butyl Ethers RO(H)C(CH$_3$)$_3^+$ ($T_{0.5}$ Values in meV Given in Parentheses)

R	tBu+ (*m/z* 57)	isobutane loss
CH_3 (**1a**)	1.00 (1.2)	0.00
CH_3CH_2 (**2a**)	0.27 (3.5)	*m/z* 45 0.73 (5)
$(CH_3)_2CH$ (**3**)	0.10 (6.5)	*m/z* 59 0.90 (20)
$CH_3CH_2CH_2$ (**4**)	0.43 (9)	*m/z* 59 0.55 (12)
$(CH_3)_2CHCH_2$ (**5**)	0.49 (10)	*m/z* 73 0.49 (12)

$$R^1OH + R^2O(H)H \xrightarrow{-H_2O} R^1OHR^2 \quad (4)$$

Three general metastable ion decompositions of **1**–**5** are observed: (i) expulsion of a molecule of alcohol to yield *tert*-butyl cation (exemplified by eq 1); (ii) competing expulsion of neutral isobutane (for **2**–**5**) to yield carbonyl conjugate acid ions; and (iii) expulsion of isobutene (for **4** and **5**) to yield alcohol conjugate acid ions. These are represented schematically in eq 5. Pathways i and ii together represent ≥98% of the observed decomposition, and their contributions are summarized in Table 1.



(5)

Pathway ii is not observed for the conjugate acids of MTBE (**1**) since i is less endothermic by approximately

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Table 2. Proportions of Deuterated *tert*-Butyl Cations in the MIKES of Isotopic Analogues of the Conjugate Acid of MTBE. Experimental Uncertainties are ±0.01

parent ion	d_0	d_1	d_2	d_3	d_5	d_6	d_8	d_9
$CH_3O(H)C(CH_3)_3^+$ (**1a**)	1.00							
$CD_3O(H)C(CH_3)_3^+$ (**1b**)	1.00							
$CH_3O(D)C(CH_3)_3^+$ (**1c**)	0.44	0.55						
$CH_3O(H)C(CH_3)_2CD_3^+$ (**1d**)			0.30	0.70				
$CH_3O(H)C(CD_3)_2CH_3^+$ (**1e**)					0.50	0.50		
$CH_3O(H)C(CD_3)_3^+$ (**1f**)							0.65	0.35

Table 3. Proportions of Deuterated Acetaldehyde Conjugate Acid Ions (*m/z* 45–49) and Deuterated *tert*-Butyl Cations (*m/z* 57–66) in the MIKES of Isotopic Analogues of the Conjugate Acid of Ethyl *tert*-Butyl Ether. Experimental Uncertainties are ±0.01

	m/z											
parent ion	45	46	48	49	57	58	59	60	62	63	65	66
$CH_3CH_2O(H)C(CH_3)_3^+$ (**2a**)	0.73				0.27							
$CD_3CH_2O(H)C(CH_3)_3^+$ (**2b**)			0.66		0.34							
$CH_3CD_2O(H)C(CH_3)_3^+$ (**2c**)		0.55			0.45							
$CH_3CHDO(H)C(CH_3)_3^+$ (**2d**)	0.24	0.38			0.38							
$CD_3CD_2O(H)C(CH_3)_3^+$ (**2e**)				0.42	0.58							
$CH_3CH_2O(D)C(CH_3)_3^+$ (**2f**)	0.54	0.16			0.07	0.23						
$CH_3CH_2O(H)C(CH_3)_2CD_3^+$ (**2g**)	0.38	0.19					0.17	0.27				
$CH_3CH_2O(H)C(CD_3)_2CH_3^+$ (**2h**)	0.17	0.31							0.33	0.19		
$CH_3CH_2O(H)C(CD_3)_3^+$ (**2i**)	0.04	0.39									0.46	0.10

75 kJ mol^{-1}. For the larger homologues, however, i is more endothermic than ii, and ii is the major decomposition route. Pathway iii contributes <2% of the fragmentation in the cases where it is observed at all. These three decomposition routes are the only ones detected except in the case of **5**, where a small amount of water loss (comparable in intensity to iii) is also seen. Since water loss constitutes the main decomposition for protonated di-*tert*-butyl ether, **9**, we conclude that isomerization of **5** to **9** is negligible. For pathway i the kinetic energy releases are small, but increase monotonically with the size of the alkyl group. This is what would be expected for a reaction that has no activation barrier above the thermodynamic threshold. The microsecond lifetimes of the precursor ions result from a kinetic shift attributable to energy randomization among the internal degrees of freedom. The larger the molecule, the greater the number of degrees of freedom; hence, the higher the average internal energy of the ions whose decompositions are observed by MIKES.

For pathway ii the kinetic energy releases are greater. The value of $T_{0.5}$ achieves its maximum value for **3**, where expulsion of isobutane forms protonated acetone. Since ketones are more basic than aldehydes, this is the least endothermic of all the decompositions examined in this homologous series. For pathway i to compete with the energetically more favorable pathway ii, the latter must have an activation energy significantly above its thermochemical threshold. We surmise that this is due to an intrinsic barrier for hydride abstraction from the α-carbon of the smaller alkyl group by a *tert*-butyl cation.

Both i and ii are preceded by unimolecular exchange between the methyls of the *tert*-butyl and the O–H hydrogen. Table 2 summarizes the results for deuterated analogues of MTBE. We interpret the exchange in terms of two noncovalently bonded intermediates, **6** and **7**, which are depicted in Scheme 1.

The data in Table 1 can be used for a steady state kinetic analysis, as described in the Appendix. The number of independent measurements does not permit a solution that embraces all the conceivable isotope effects, so the simplifying assumption is made that the mole fraction X is independent of the degree of deuteration. The resulting set of equations can be solved to get a branching ratio $X/(1 - X) = 30:70$ and an isotopic partition factor for the exchange equilibrium C–D + O–H → C–H + O–D of $k_1^D\, k_{-1}^H/k_1^H\, k_{-1}^D = 2.0$. To a good approximation, the fraction of **1** that undergoes hydrogen exchange (mole fraction 1 − X) completely randomizes hydrogen between the *tert*-butyl group and oxygen (subject to weighting by the isotopic partition factor).

The situation for the higher homologues is more complicated, since pathways i and ii are in competition. Hydrogen exchange between oxygen and the *tert*-butyl group is extensive prior to both decompositions. Results from the conjugate acid ions of ethyl *tert*-butyl ether, **2**, are summarized in Table 3 (in which the experimental uncertainties of the relative intensities are ±0.01). Hydrogen randomization between the *tert*-butyl and the oxygen results in there being two path ii products from **2f–i**. One (*m/z* 45) is the product of hydride abstraction from CH_3CH_2OH, the other (*m/z* 46) from CH_3CH_2OD. If we use an isotopic fractionation factor that is slightly smaller than that calculated for **1** (1.6 instead of 2.0) and assume complete randomization, a consistent set of values is obtained for the mole fraction of **2** that decomposes directly, $X = 0.09 \pm 0.02$.

As can be seen from Table 3, the proportion of decomposition of **2** to *tert*-butyl cation increases with increasing deuteration of the *tert*-butyl group. As will be discussed below, this is contrary to thermochemical expectations. Two alternative explanations can be advanced to account for this result. One is that deuteration alters the kinetic shift. Since MIKES detects ion decompositions within a narrow time window (*i.e.* those ions that survive for a microsecond before dissociating, which then decompose on the 10^{-5} s time scale), this technique samples a slice of internal energies within a much broader energy distribution. Deuteration might conceivably shift the energy slice that is monitored. This shift might consequently result in an alteration of the branching ratio between pathways i and ii. If the kinetic shift hypothesis if correct, then isotopic effects ought to have the same result regardless of where deuterium is substituted into the parent ion. To test this hypothesis we have examined protonated ethyl *tert*-amyl ether (**8**) and its deuterated analogues. This higher homologue of **2**

Table 4. Proportions of *tert*-Amyl Cation (Homologous to Pathway i) and 2-Methylbutane Loss (Homologous to Pathway ii) in the MIKES of Protonated Ethyl *tert*-Amyl Ethers $CH_3CH_2O(H)R^+$ Containing Deuterated Methyl Groups

R	*tert*-amyl$^+$ (*m/z* value)	isobutane loss (*m/z* value)
$(CH_3)_2CCH_2CH_3$ (**8a**)[a,b]	0.93 (71)	0.07 (45)
$(CH_3)_2CCH_2CD_3$ (**8b**)[a]	0.92 (74); 0.01 (73)	0.068 (45); 0.002 (46)
$CH_3(CD_3)CCH_2CH_3$ (**8c**)[b]	0.63 (74); 0.315 (73)	0.038 (45); 0.018 (46)
$(CD_3)_2CCH_2CH_3$ (**8d**)[b]	0.373 (77); 0.58 (76)	0.015 (45); 0.032 (46)

[a] Protonated ether prepared by chemical ionization of the neutral ether by H_3O^+. [b] Protonated ether prepared by eq 4 from ethanol and the corresponding *tert*-amyl alcohol.

shows the same two pathways (*mutatis mutandis*) as does protonated ETBE, and the branching ratio is the same regardless of whether the conjugate acid ion is prepared by protonation of the ether or via the ion–molecule reaction represented in eq 4. The effect of deuterating the α-methyl groups parallels what is seen for **2**: the proportion of cleavage to a tertiary carbocation increases from 93% to 94.5% when one α-methyl is perdeuterated and to >95% when both α-methyls are per-deuterated. By contrast, deuteration of the β-methyl of the *tert*-amyl (**8b**) does not alter the relative proportions of the two pathways, as Table 4 summarizes. Since the kinetic shift hypothesis predicts the same variation for both d_3 isomers, **8b** and **8c**, contrary to what is observed, this interpretation can be ruled out. The alternative explanation is that deuterium exerts kinetic isotope effects on competition between product-determining steps (as outlined in the Discussion and detailed in the Appendix).

Ion–Molecule Reactions. Possible reactions within ion–neutral complexes can be explored by examination of the bimolecular chemistry of the corresponding partners. Using FT-ICR we have probed whether hydride abstraction might be reversible. There are two major differences between an ion–neutral complex that is formed via unimolecular decomposition and the analogous complex formed in a bimolecular collision. While both can be viewed as encounters within the gas phase analogue of a solvent cage (which lives long enough for a variety of relative orientations to be explored before further reaction takes place),[16] the internal energy content of the latter has to be sufficient (in the absence of radiative emission or a third-body collision) for the complex to return to the reactants that formed it. By contrast, the enthalpy of an ion–neutral complex formed unimolecularly might be well below the heat of formation of the separated partners. The second major difference is that net angular momentum distributions of the two types of complexes may differ considerably. Nevertheless, if an ion–molecule reaction does not take place under bimolecular conditions, it is probable that it will also not occur within an ion–neutral complex that is formed from a unimolecular decomposition.

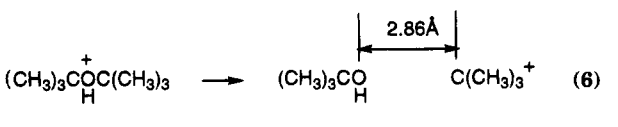
In its reaction with primary alcohols, *tert*-butyl cation exchanges hydrogen with the OH of those whose proton affinity is lower than that of isobutene. We have not been able to measure the rate of exchange of one hydrogen under single-collision conditions, but multiple collisions with CH_3OD or CH_3CH_2OD convert the *tert*-butyl cation reactant (*m/z* 57) into a cluster of peaks from *m/z* 57 to 66 with a Poisson distribution. In competition with this exchange, *tert*-butyl cation abstracts hydride from ethanol. The observed product of the reaction between $(CH_3)_3C^+$ and CH_3CD_2OH is $CH_3CD{=}OH^+$ (*m/z* 46), with no detectable *m/z* 45, *m/z* 47, or isotopically exchanged *tert*-butyl cations.

We also inquire whether protonated acetaldehyde reacts with saturated hydrocarbons. In particular, we have looked to see if $CH_3CH{=}OD^+$ exhibits any observable chemistry with isobutane. No bimolecular reaction was observed. In particular, there is no exchange of D for H. This is consistent with the fact that *tert*-butyl cation does not yield any *m/z* 45 when it reacts with CH_3-CD_2OH.

Ab Initio Calculations. SCF computations on protonated alkyl *tert*-butyl ethers suggest that a variety of isomers interconvert in the gas phase. It will be most convenient first to present the results for the symmetrically substituted case, the conjugate acid of di-*tert*-butyl ether, **9**. In this system there are three potential energy minima whose calculated heats of formation are close to one another. The calculations described below attempt to evaluate the relative stabilities of isomeric ions. Reported electronic energy differences are corrected for basis set superposition error (BSSE) by means of counterpoise.[17]

In structure **9** one bond length is 1.555 Å and the other 1.564 Å, considerably longer than we calculate at the same level for protonated dimethyl ether, Me_2OH^+ (1.48 Å). The stretching of the C–O bonds in **9**, as well as the fact that the two bond lengths differ by nearly 0.01 Å, can be ascribed to steric crowding. The C–O–C angle of **9** is 137°, larger than the experimental (and computational) value reported for neutral di-*tert*-butyl ether, 131°.[18] The electronic energy for dissociation of **9** to *tert*-butyl cation plus *tert*-butyl alcohol is D_e = 70 kJ mol^{-1}. When zero-point energies (computed at 3-21G//3-21G) are taken into consideration, the calculated dissociation energy of the C–O bond is only D_0 = 50 kJ mol^{-1}.

In addition to the conventional, covalently bonded species **9**, SCF calculations exhibit a potential energy minimum corresponding to valence isomer **10**, in which one of the C–O bonds is nearly twice as long as the other. Steric hindrance is responsible for the fact that valence isomer **10** corresponds to a potential energy minimum. The C–O–C bond angle of **10** is 144°, which indicates that strain is relieved in eq 6. The O–H hydrogen in **9**



9 **10** (6)

is 0.37 Å out of the C–O–C plane, while in **10** this hydrogen is essentially coplanar with the oxygen and the two carbons. While the geometry of **10** was optimized without any symmetry constraint, the minimum energy structure acquires a mirror plane of symmetry, as eq 7

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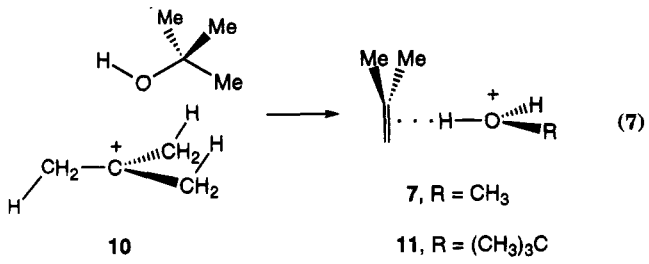
endeavors to represent. One *tert*-butyl group is nearly planar, while the remainder of the molecule is superimposable on neutral *tert*-butyl alcohol (with a C–O bond length of 1.44 Å). The electronic energy change for eq 6 is +19 kJ mol^{-1}. When zero-point energies (calculated at 3-21G//3-21G) are taken into consideration, eq 6 is calculated to be only 6.5 kJ mol^{-1} endothermic.



10 7, R = CH_3 11, R = $(CH_3)_3C$ (7)

A tautomer of **10** also corresponds to a potential energy minimum: the hydrogen-bonded complex of isobutene with protonated *tert*-butyl alcohol, **11**. Energetically **11** lies within 2 kJ mol^{-1} of **10**. Dissociation of **11** to isobutene and protonated *tert*-butyl alcohol is uphill by D_e = 50 kJ mol^{-1} (D_0 = 45 kJ mol^{-1} when 3-21G//3-21G zero-point energies are taken into consideration). Structures **10** and **11** correspond to what we have termed an α-complex and a β-complex, respectively.[10]

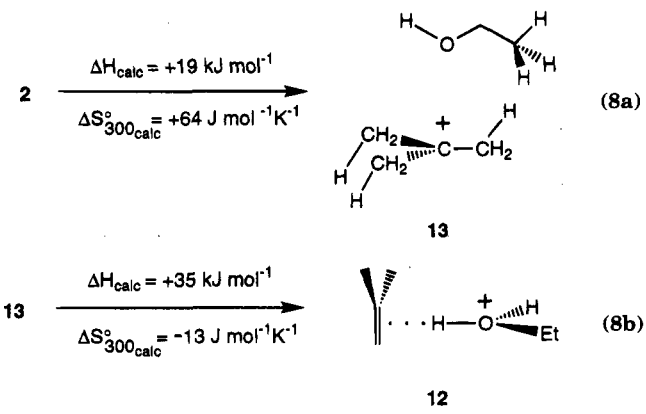
As would be expected for MTBE (given the different electron demands of a methyl and a *tert*-butyl group), the two C–O bond lengths of **1** differ to a greater extent than in **9**: 1.46 Å for the methyl–oxygen bond and 1.585 Å for the *tert*-butyl–oxygen bond. The C–O–C bond angle is 125°, much larger than that reported for neutral MTBE (116°)[18] and also larger than what we calculate for Me_2OH^+ (119°). The oxygen atom in **1** is much more pyramidal than that of **9**, with its hydrogen 0.56 Å out of the C–O–C plane, about the same as we calculate for Me_2OH^+ (0.58 Å).

In contrast to the di-*tert*-butyl system, we cannot locate a potential energy minimum corresponding to a methanol/*tert*-butyl cation complex on the 6-31G** SCF energy surface. We have explored a half-dozen different initial geometries and find that they all collapse to the covalent structure **1**. This is analogous to what we have reported for 3-21G calculations on methanol/isopropyl cation: there is no stable structure corresponding to the α-complex.[10] The electronic energy of the protonated ether increases rapidly as the C–O bond is stretched to approximately 2.5 Å and then increases much more gradually (but still monotonically) out to 5 Å, beyond which the energy curve is well fit as a point charge–point dipole potential.

While protonated MTBE does not enjoy a local potential energy minimum homologous to **10**, there is a stable isomer, **7**, that is a lower homologue of **11** and corresponds to a β-complex. Geometry is largely conserved in going from **7** to **11** and resembles the β-complex from protonated methyl isopropyl ether.[10] The isobutene skeleton remains virtually planar, and one of the O–H bonds points directly toward the C=C double bond. The structures all have the appearance of being hydrogen bonded aggregates between a protonated alcohol and a molecule of isobutene, $ROH_2^+\cdots CH_2{=}C(CH_3)_2$. The other OH bond is not far from being parallel to the plane of the isobutene (making an angle in the range 10–20° with that plane). We likewise compute a similar geometry for the complex between protonated ethanol and isobutene, **12**, whose structural features are intermediate between those of **7** and **11**.

The conclusion that **7**, **11**, and **12** are hydrogen-bonded is reinforced by the existence of a 30 kJ mol^{-1} barrier to switching the positions of the two O–H hydrogens (the energy, relative to **7**, of a structure in which the C–O–C plane bisects the H–O–H angle and serves as a mirror plane of symmetry). This potential energy maximum (which corresponds to a barrier to internal rotation by 70° about the methyl–oxygen bond of **7**) implies a degree of directionality consistent with hydrogen bonding.[13] Other geometrical features also support the inference that the alkene is acting as a hydrogen-bond acceptor. The oxygen is on the order of 3 Å from the plane of the isobutene (2.92 Å for **7**, 2.95 Å for **12**, and 3.04 Å for **11**). The vector from the disubstituted sp^2-carbon to the oxygen makes a fairly constant angle with that plane (66° for **7** and **12**, 68° for **11**). The length of the nonbridging O–H bond remains 0.95 Å , while the bridging O–H becomes progressively shorter as the alkyl group gets larger (1.00 Å for **7**, 0.99 Å for **12**, 0.98 Å for **11**), suggesting that steric bulk reduces the strength of the hydrogen bond. There is also a large difference between the two calculated O–H stretching frequencies, which becomes smaller as the size of the alkyl group increases, $\Delta\nu$ = 1010 cm^{-1} for **7** versus $\Delta\nu$ = 870 cm^{-1} for **12** (the value of $\Delta\nu$ calculated for free protonated alcohols is on the order of 100 cm^{-1}). This progression is accompanied by a corresponding decrease in dissociation energies to free ROH_2^+ plus isobutene, D_0 = 70 kJ mol^{-1} for **7**, 60 kJ mol^{-1} for **12**, and 45 kJ mol^{-1} for **11**.

It turns out that the stability of the *tert*-butyl cation/alcohol complexes is a function of steric hindrance. The failure of methanol to form a stable, noncovalent potential energy minimum with *tert*-butyl cation can be attributed to the lack of any obstacle to its collapse. By contrast the α-complex **10** is stable because one of the *tert*-butyl alcohol methyl groups hangs up on the pair of cation hydrogens pointing toward it, as represented in eq 7. We test this assertion by looking at two different conformational isomers of the *tert*-butyl cation/ethanol system. Ethanol has a pair of distinguishable rotamers in the gas phase, *trans* and *gauche* with respect to its C–O bond.[19] The *trans* (which possesses a plane of symmetry) has a methyl that experiences steric hindrance with a methyl of the *tert*-butyl and gives a stable complex, **13**, as depicted in eq 8a. The *gauche* rotamer encounters no steric barrier when it attacks *tert*-butyl cation. The collapse of the ion and the *gauche* neutral to form **2** proceeds with a monotonic decrease in electronic energy.



2 ΔH_{calc} = +19 kJ mol^{-1}, $\Delta S°_{300_{calc}}$ = +64 J mol^{-1}K^{-1} 13 (8a)

13 ΔH_{calc} = +35 kJ mol^{-1}, $\Delta S°_{300_{calc}}$ = -13 J mol^{-1}K^{-1} 12 (8b)

The energy gap between **2** and **13** is greater than that between **9** and **10**, as eq 8a notes. Dissociation of **2** to *tert*-butyl cation plus ethanol is endothermic by $D_0 = 62$ kJ mol^{-1}, while dissociation of **13** is endothermic by $D_0 = 43$ kJ mol^{-1}. Energies of isomerization of gaseous **2** (including 6-31G** zero-point energies, corrected by a factor of 0.9) are summarized in eqs, parts 8a and 8b. The vibrational entropy differences (assuming harmonic oscillators) are also given, although loose vibrations (particularly in **12** and **13**) are more appropriately treated as hindered internal rotors.[20] Nonharmonic considerations probably do not greatly influence the anticipated entropy difference between **13** and **12**, since both have a comparable number of loose rotors. Such considerations probably do affect the entropy difference between **2** and **13**, but probably not so much as to alter the conclusion that the free energy change $\Delta G_{2\rightarrow 13}$ is close to zero at room temperature and becomes negative at higher temperatures.

The calculated endothermicity of path i (**2** → tBu$^+$) relative to path ii (**2** → MeCH=OH$^+$) agrees well with the experimental value[21] ($\Delta\Delta H = 16$ kJ mol^{-1} *vs* $\Delta\Delta H = 10$ kJ mol^{-1}). Isotope effects on the energetics can be estimated from shifts in calculated zero-point energies. When one of the methyl groups of the *tert*-butyl is fully deuterated, the endothermicity of path i is predicted to become 0.60 kJ mol^{-1} greater relative to path ii. When two of the methyl groups are fully deuterated the increment is twice as large, 1.18 kJ mol^{-1}. When the *tert*-butyl group is fully deuterated, the calculated increment is 1.76 kJ mol^{-1}. Ab initio calculations thus support the supposition that secondary isotope effects on the *relative* rates of paths i and ii are multiplicative. This inference has great importance on our evaluation of mechanistic hypotheses regarding the number of transient intermediates in the unimolecular decomposition of **2**.

The definition of an α-complex has to be refined in treating the decomposition of **2**. As originally conceived, this terminology designates a noncovalent aggregate of an alkyl cation with an alcohol, regardless of whether it corresponds to a minimum on the potential energy surface. In the case of protonated ETBE, however, the experimental results appear to require the reversible formation of an ion–neutral complex, [EtOH tBu$^+$], in addition to **12** and **13**. Complexes of this form intervene even when there is no potential energy well corresponding to the vibrational zero-point of the noncovalent structure, as in the published example of [MeOH iPr$^+$][10] and the present example of [MeOH tBu$^+$]. In the case of protonated ETBE the term α-complex will be restricted to the stable geometry **13**. The ion–neutral complexes [MeOH tBu$^+$] and [EtOH tBu$^+$] must represent aggregates where the partners are inhibited from collapsing instantaneously by an entropic barrier, which comes from restricting the free rotation of the ion within the complex.

Discussion

The conjugate acids of *tert*-butyl ethers decompose in the gas phase to yield free *tert*-butyl cations. Exchange takes place between the hydrogen bound to oxygen and the hydrogens of the *tert*-butyl. The experimental results indicate that some of the ions (mole fraction X) decompose directly without exchange, but the majority behave as though ten hydrogens randomize (subject to weighting by an isotopic fractionation factor, which favors deuterium attached to oxygen relative to deuterium attached to carbon). Scheme 1 summarizes our interpretation. In the discussion that follows, species that are implicated as intermediates by our kinetic analysis, but which do not correspond to minima on the ab initio potential energy surface, are represented as enclosed in brackets. Other intermediates are drawn so as to represent qualitative geometries of stable SCF potential energy minima.

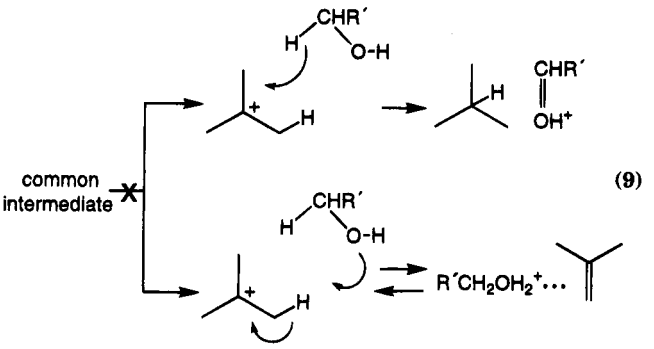
The internal hydrogen exchange for the conjugate acids of MTBE, **1**, requires two transient intermediates. (In the present context, "intermediate" specifically designates a species that forms reversibly.) A kinetic analysis (outlined in the Appendix) of observed ion intensity ratios leads to the conclusion that interchange between intermediates **6** and **7** is fast compared to the decomposition of the intermediate complex (corresponding to rate constant k_2). However, our ab initio calculations locate only structure **7** as a local minimum on the 6-31G** SCF potential energy surface. We propose that intermediate **6** is an ion–neutral complex, [MeOH tBu$^+$], which does not correspond to a potential energy well but which is prevented from instaneous collapse by an entropic bottleneck.

Dissociation to free *tert*-butyl cation (albeit via more than one pathway) is the sole reaction of protonated MTBE observed in the MIKES. By contrast, protonated ETBE exhibits an additional pathway, expulsion of isobutane to yield the conjugate acid of acetaldehyde. The unimolecular decompositions of conjugate acid ions from ETBE, **2**, appear to require no fewer than three transient intermediates to account for the MIKES data quantitatively. In part, this is necessitated by the observation that the competition between the two decompositions of **2** (pathways i and ii in eq 5) is sensitive to deuterium substitution of the *tert*-butyl group in a fashion contrary to thermochemical expectation. A kinetic analysis (outlined in the Appendix) illustrates this in greater detail. It is worth noting that only two plausible intermediates can be located on the SCF potential energy surface, which correspond to structures that have been called α- and β-complexes.[10] We suppose that the additional required intermediate corresponds to an ion–neutral complex, [EtOH tBu$^+$], which represents a species distinct from the α- and β-complexes, despite the fact that it does not correspond to a separate potential energy minimum.

All the primary alkyl *tert*-butyl ether conjugate acids in this study form protonated aldehyde products via pathway ii. It is tempting to surmise that the intermediate that gives rise to hydrogen transposition is also the direct antecedent to hydride transfer. While it is mechanistically plausible that a common intermediate partitions irreversibly between these two pathways, neither theory nor experiment supports such an economical explanation, depicted by eq 9. As a candidate for such a branch point, structure **13** does not possess the requisite geometry for the upper pathway in eq 9, since the methylene hydrogens of the alcohol in **13** are pointed away from the *tert*-butyl group. Thus, while the oxygen lone pairs are appropriately oriented for the interconversion of **13** with **12** via proton transfer, **13** does not have a suitable geometry for hydride transfer. The

(19) Lovas, F. J. *J. Phys. Chem. Ref. Data* **1982**, *11*, 251–276.
(20) Midland, M. M.; Morton, T. H. *J. Am. Chem. Soc.* **1993**, *115*, 9596–9601.
(21) (a) Lias, S. G.; Bartmess,. J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Supplement 1. (b) Szulejko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 7839–7848. (c) Smith, B. J.; Radom, L. *Chem Phys. Lett.* **1994**, *231*, 345–351.

kinetic analysis in the Appendix confirms the inadequacy of eq 9 to account for the observed ion intensity ratios.



(9)

We interpret the MIKES data with the aid of the steady state kinetic approximation. As is well known, unimolecular reactions in the mass spectrometer do not necessarily obey first-order kinetics, since ions are formed with a range of internal energies, and they dissociate much faster than they exchange energy intermolecularly. Consider a hypothetical collection of ions formed with a broad distribution of internal energies. The intensity of each subset of ions with a given internal energy ought to decay with a characteristic first-order rate constant k, but different energies will correspond to different values of k. Suppose, as a simple example, there is a collection of ions such that the probability of a given value of k, $P(k)$, decreases exponentially. The most probable rate will be zero. That means that some of the ions will never decompose. By assuming that the internal energies are distributed such that $P(k) = e^{-\lambda k}$ (where λ has units of time so that the exponent will be dimensionless), the expression for the intensity of ions in the collection that decompose becomes the Laplace transform of the expression for first-order decay. If the intensity of this fraction of the ions is called I, the time dependence of I is given by

$$I(t) = \frac{\int_0^\infty (e^{-\lambda k})(e^{-kt})\,dk}{\int_0^\infty e^{-\lambda k}\,dk} = I_0\lambda/(\lambda - t) \qquad (10)$$

where I_0 is concentration at time = zero. In other words, the result of the integration gives a function that corresponds to second-order kinetics, even though the decay process is strictly unimolecular.

Steady state analysis, which involves dividing branching ratios by one another, is appropriate for any energetic subset of ions that obeys first-order kinetics but may not be a good approximation for systems such as the hypothetical case outlined above. However, the validity of kinetic analyses based upon quotients of branching ratios is not limited to strictly first-order regimes. As we have pointed out elsewhere,[12] if a quotient, when averaged over the collection of ions that decompose within a given time frame, is equal to the quotient of the average branching ratios over the same time frame, then steady state analysis is valid and can be used to test mechanistic hypotheses. It is reasonable to suppose that MIKES, which samples ions that decompose in a 10^{-6} s time window after having had 10^{-5} s to react, falls within a domain where steady state analysis is appropriate, and this has been used to test mechanistic hypotheses in other MIKES studies.[11] Such a kinetic analysis rules out eq 9.

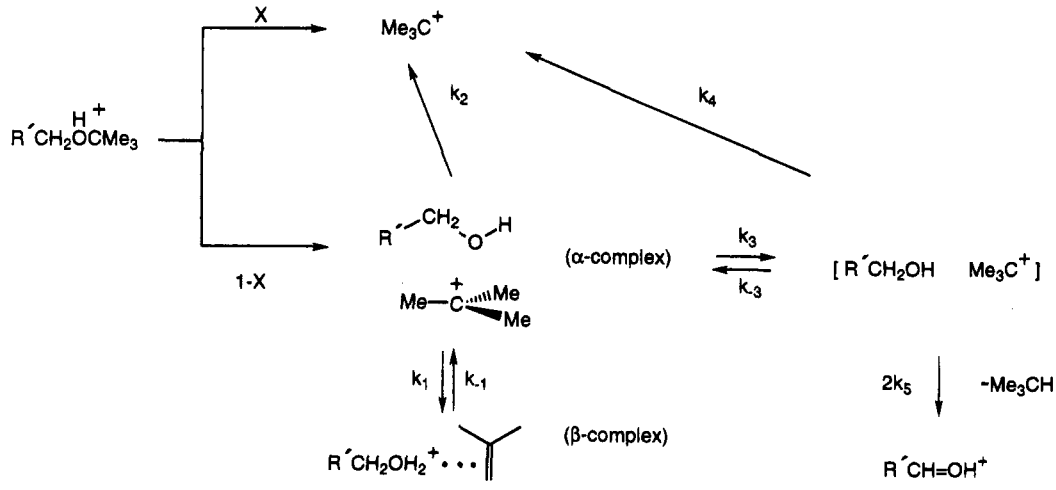
The defects of positing a common intermediate in the decompositions of protonated ETBE are revealed by solving the steady state equations in the Appendix for the effects of deuterating the *tert*-butyl. This can be summarized qualitatively as follows. Our ab initio calculations show that the isotopic shift of the *relative* endothermicities of paths i and ii scales linearly with the number of deuteria (when zero-point energies of all the positional isomers are averaged). Therefore we expect that the net secondary kinetic isotope effect (kie) on the rate of hydride transfer *relative* to simple dissociation of the intermediate ought to be $(k_H/k_D)^n$ for a precursor ion with n deuteria in its *tert*-butyl (where k_H/k_D is the kie for a single deuterium). A steady state analysis based on eq 9 gives three independent measures for the net effect of deuterating a methyl in the series **2g**–**i**. The three values for $(k_H/k_D)^3$ that are extracted from the observed ion intensities differ considerably from one another. If we are correct in supposing that secondary kie values for a ratio of rate constants are multiplicative, eq 9 must be rejected as a complete mechanism. It is necessary to introduce another reversible step, as Scheme 2 depicts, with an additional intermediate.

It is possible to fit the observed ion ratios for **2b**–**i** using Scheme 2 by assuming secondary kie's to be multiplicative. While it is not always valid to suppose that changes in ΔH and ΔS resulting from deuterium substitution are additive,[22] ab initio estimates of isotope effects on the thermodynamics of protonated **2** with respect to its decomposition products suggest, in the present case, this to be a reasonable assumption (*vide infra*). Our ab initio calculations predict that isobutane expulsion becomes thermodynamically more favorable with increasing deuteration, but the opposite trend is observed experimentally. As one passes from the undeuterated to the d_3, d_6, and d_9 *tert*-butyl ethers (**2a**, **2g**, **2h**, and **2i**, respectively), the proportion of cleavage to *tert*-butyl cation increases from one-third to nearly two-thirds. This manifestation of kinetic control reinforces our conclusion that there is a barrier to hydride transfer that exceeds the endothermicity of that reaction. At first glance, it might be imagined that the kinetic control reflects an isotope effect on the mole fraction, X, of direct cleavage. But, as the data reveal, this is not the case. To a good approximation, hydrogen is completely randomized in the fraction of **2** that does not decompose directly. After statistical correction the value of X is on the order of 0.1. The mole fraction of direct cleavage is not large enough to account for the attenuation of pathway ii that results from deuteration of the *tert*-butyl, even if X were isotope-dependent (which it does not appear to be, to any significant extent). Consequently it is clear that the direction of the secondary kie for hydride transfer is opposite to what would have been observed had that reaction operated under thermodynamic control (the ab initio zero-point energy difference favors d_1-isobutane + $MeCH{=}OH^+$ over isobutane + $MeCD{=}OH^+$ by 0.5 kJ mol^{-1}).

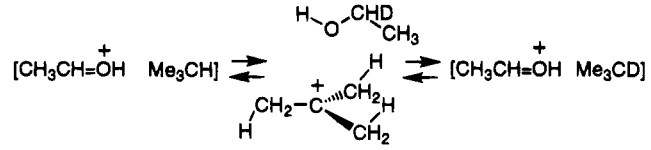
To what structure does the additional intermediate in Scheme 2 correspond? One option is that hydride transfer might be reversible. Without question there is a potential energy minimum corresponding to the aggregate of a protonated carbonyl with isobutane, and it is conceivable that this might correspond to an ion–neutral complex, $[R'CH{=}OH^+\ (CH_3)_3CH]$, which could

(22) Saunders, M.; Cline, G. W. *J. Am. Chem. Soc.* **1990**, *112*, 3955–3963.

Scheme 2



interconvert with **13**, as eq 11 portrays. The experimen-



(11)

tal data, however, argue against such a hypothesis. The bimolecular chemistry of $CH_3CD{=}OH^+$ with isobutane exhibits no transposition of D for H (nor any other detectable reaction). Moreover, *tert*-butyl cation abstracts deuterium from CH_2CD_2OH without any exchange. Finally, the decomposition of ion **2c** manifests a large preference for H-transfer over D-transfer (1.65:1), which is not what would be expected if the interconversion in eq 11 went to equilibrium. The exclusion of other reasonable alternatives leaves us with the ion–neutral complex represented as [EtOH tBu^+] in Scheme 2. Some ion–neutral complexes have been viewed as vibrationally excited forms of stable structures.[20] In the present case, however, our mechanistic interpretation stipulates that [EtOH tBu^+] be a discrete intermediate distinct from the α-complex **13**. The increasing yield of *tert*-butyl cation with increasing deuteration in the series **2g–i** can be accounted for in terms of secondary isotope effects on k_4 and k_5, as well as a large effect on the k_4/k_5 ratio that results from O-deuteration.

The proportions of ions from ETBE analogues with deuterated ethyl groups are interpreted using Scheme 2. The observed relative ion abundances in the MIKES of **2a–e** can be fit within experimental uncertainty using the mole fraction for direct decomposition inferred from **2f–i** ($X = 0.1$), the relative rate constants $k_4/k_5 = 0.32 \pm 0.05$ and $k_2/k_3 = 0.07 \pm 0.03$, and the following isotope effects on k_5 resulting from deuteration of the ethyl group: a β-secondary isotope effect of 1.8 ± 0.2 for Me = CH_3 versus Me = CD_3, an α-secondary isotope effect of $k_H/k_D = 1.4 \pm 0.05$ for deuterium substitution of the methylene group, and a primary isotope effect of $k_H/k_D = 2.2 \pm 0.1$ for hydride abstraction versus deuteride abstraction. The secondary isotope effects agree with the shifts in thermochemistry predicted ab initio. The calculated zero-point energy increases by 2.8 kJ mol^{-1} for **13** → isobutane plus protonated acetaldehyde. When the methyl group of the ethyl is trideuterated, that reaction becomes 0.6 kJ mol^{-1} more endothermic.

The above analysis of the experimental data requires the assumption that isotope effects be multiplicative (otherwise there are too many unknowns). While ab initio calculations of zero-point energy differences support this supposition for ratios of rate constants (such as k_4/k_5), such is not the case for individual rate constants. On the one hand, the zero-point energy difference corresponding to monodeuterated **13** → *m/z* 46 is 0.39 kJ mol^{-1} greater than for **13** → *m/z* 45. On the other hand, the zero-point energy difference corresponding to dideuterated **13** → *m/z* 46 is 0.46 kJ mol^{-1} greater than for monodeuterated **13** → *m/z* 45. If isotope effects were strictly multiplicative, these two calculated shifts in zero-point energy differences should have been the same. Thus, the quantitative kie values based on steady state analysis of observed fragment ion abundances are subject to a systematic error. The magnitude of the normal primary isotope effect favoring hydride transfer over deuteride transfer (which is the opposite direction from the shift in net thermochemistry) is probably not greatly affected by this error.

Conclusion

The unimolecular dissociation of protonated MTBE to *tert*-butyl cation proceeds by two competing types of simple bond fission: direct cleavage *vs* formation of an ion–neutral complex, [MeOH tBu^+]. The latter leads to randomization of ten hydrogens via interconversion with the hydrogen-bonded aggregate $MeOH_2^+ \cdots CH_2{=}C(CH_3)_2$ prior to decomposition. The hydrogen-bonded aggregate, which we call a β-complex, corresponds to a local minimum on the potential energy surface, while the ion–neutral complex does not.

In higher homologues steric hindrance confers stability upon α-complexes, such as **12** from protonated ETBE, which interconvert with β-complexes to randomize ten hydrogens. If there is a hydrogen geminal to oxygen, hydride transfer from the alcohol to tBu^+ competes with dissociation to free tBu^+. Hydride transfer also takes place in bimolecular reactions of alcohols with tBu^+. This takes place via [ROH tBu^+] ion–neutral complexes that are distinct from the α-complexes and which permit the neutral alcohol to turn so that the hydrogen to be transferred points toward the cationic partner. The transition state for hydride transfer is the subject of continuing inquiry.

Experimental Section

Methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and deuterated ethanols were purchased from Aldrich and used without any additional purification. Isopropyl, *n*-propyl, isobutyl, d_3-methyl, and deuterated ethyl *tert*-butyl ethers and ethyl *tert*-amyl ether are known compounds and were prepared as described in the literature. The parent neutral of ion **8b**, $CD_3CH_2C(CH_3)_2OCH_2CH_3$, was synthesized by $LiAlD_4$ reduction of ethyl 3-ethoxyisovalerate, $EtOOCCH_2C(CH_3)_2OEt$, followed by conversion to the tosylate and reduction with $LiD/LiAlD_4$ in refluxing THF. Ethyl 3-ethoxyisovalerate was in turn prepared (in a $r \approx 2{:}1$ mixture with unreacted starting material) by refluxing ethyl 3,3-dimethylacrylate in ethanol containing 1 *M* sodium ethoxide.

Where appropriate, samples were purified by preparative GLPC. Mass-resolved ion kinetic energy spectra (MIKES) were measured on a VG ZAB-2F double-focussing mass spectrometer equipped with a modified chemical ionization source. FT-ICR mass spectra were recorded on a Bruker CMS-47X FT-ICR. Ab initio calculations were performed using the SPARTAN[23] and GAUSSIAN 92[24] programs on a Silicon Graphics Personal Iris computer and the San Diego Supercomputer Center Cray C90, respectively. Calculated harmonic vibrational frequencies and zero-point energies are scaled by a factor of 0.9.

For MIKES experiments ions **1a–c**, **2a–f**, **3**, **4**, and **5** were prepared by chemical ionization of the corresponding neutral ethers using H_2O or D_2O reagent gas. Additionally, ions **1a,b**, **2a–e**, and **3** were also prepared from the corresponding alcohols by eq 4 in the ZAB source to confirm that the MIKES does not depend on the origin of the parent ion. Ions **1d–f** and **2g–i** were prepared from the corresponding alcohols by eq 4 in the ZAB source. Relative fragment ion abundances were determined from the areas of MIKES peaks.

Appendix

Steady State Kinetic Analysis of Scheme 1 Using $MeO(H^+)C(CD_3)_2CH_3$ (1e) as an Example. Consider the three intermediates for exchange: [MeOH d_6-tBu$^+$], [MeOHD$^+$ d_5-isobutene], and [MeOD d_5-tBu$^+$]. If only the primary isotope effects on k_{-1} and k_1 are treated (symbolizing the values of k_H/k_D as w and z, respectively) the steady state concentrations for the latter two intermediates are

$$[\text{MeOD } d_5\text{-tBu}^+] = \frac{k_{-1}[\text{MeOHD}^+ \, d_5\text{-isobutene}]}{k_2 + 4k_1} \quad \text{(A1)}$$

and

$$[\text{MeOHD}^+ \, d_5\text{-isobutene}] = \frac{6wk_1[\text{MeOH } d_6\text{-tBu}^+] + 4wzk_1[\text{MeOD } d_5\text{-tBu}^+]}{zk_{-1}(1+w)} \quad \text{(A2)}$$

Call $k_1/k_2 = q$ and solve to get the steady state result

$$[\text{MeOD } d_5\text{-tBu}^+] = \frac{6qw[\text{MeOH } d_6\text{-tBu}^+]}{z(1+4q+w)} \quad \text{(A3)}$$

Assuming a first-order decay law get the following ratio of ion intensities,

$$\frac{m/z\ 63}{m/z\ 62} = \frac{z(1+4q+w)+6qwX}{6qw(1-X)} \quad \text{(A4)}$$

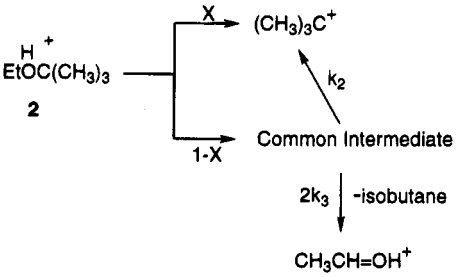
In like fashion, get the following results for **1c**, **1d**, and **1f**:

for **1c** $$\frac{m/z\ 57}{m/z\ 58} = \frac{qw+wz+z+9qzX}{9qz(1-X)} \quad \text{(A5)}$$

for **1d** $$\frac{m/z\ 60}{m/z\ 59} = \frac{z(1+7q+w)+3qwX}{3qw(1-X)} \quad \text{(A6)}$$

for **1f** $$\frac{m/z\ 66}{m/z\ 65} = \frac{z(1+q+w)+9qwX}{9qw(1-X)} \quad \text{(A7)}$$

Scheme 3



Steady State Analysis for 2 That Turns Out To Require More Than Two Intermediates. Suppose that protonated ETBE were to decompose by a pathway analogous to Scheme 1 with a common intermediate for exchange and hydride transfer, as eq 9 portrays. The corresponding kinetic scheme (omitting the exchange steps) would look as depicted in Scheme 3.

Call $k_2/k_3 = y$. The steady state solution for the proportion of isobutane expulsion should be

for **2a** $$m/z\ 45 = [2(1-X)]/(2+y) \quad \text{(A8)}$$

Symbolize the primary and secondary isotope effects on k_3 as u and v, respectively. The 1-d_1 ion exhibits loss of both isobutane and d_1-isobutane. The ratio and proportion of these should be

for **2d** $$\frac{m/z\ 45}{m/z\ 46} = \frac{v}{u} \quad \text{(A9)}$$

and $$m/z\ 45 + m/z\ 46 = [(u+v)(1-X)]/(uvy+u+v) \quad \text{(A10)}$$

For the 1,1-d_2 ion the proportion of d_1-isobutane loss should be

for **2c** $$m/z\ 46 = [2(1-X)]/(uvy+u+v) \quad \text{(A11)}$$

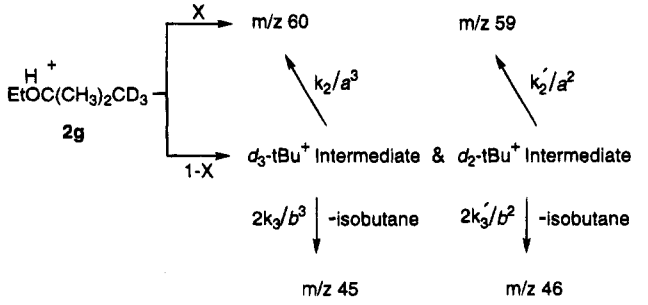
This set of equations can be fit within experimental error by $X = 0.10$, $y = 0.50$, and reasonable values for the isotope effects, $u = 2.08$ and $v = 1.33$. This value of X accords with the value independently determined based on isotopic randomization in **2g–i**.

Now consider the effect of deuterating the *tert*-butyl upon the partition between k_2 and k_3. Starting with **2g** there will be two intermediates corresponding to Scheme 4: one with a d_3-*tert*-butyl (and an O–H) and the other with a d_2-*tert*-butyl (and an O–D). The statistical ratio

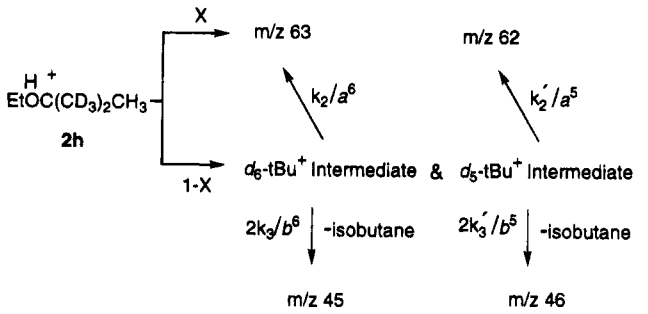
(23) SPARTAN, Wavefunction Inc., Irvine, CA. This program optimizes geometries by EF minimization, as described in Baker, J.; Hehre, W. J. *J. Comput. Chem.* **1991**, *12*, 606–610.

(24) GAUSSIAN 92, Revision B. Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA.

Scheme 4



Scheme 5



is expected to be 13:6, weighted by the isotopic partition factor. The corresponding mechanism is depicted by Scheme 4.

The secondary isotope effect (per carbon-bound deuterium) on k_2 will be designated as $k_H/k_D = a$, while the secondary isotope effect (per carbon-bound deuterium) on k_3 will be designated as $k_H/k_D = b$. (The effects of O-deuteration correspond to the rate constants labeled as k_2' and k_3'.) Assuming secondary isotope effects to be multiplicative (as inferred from the additivity of zero-point energy differences calculated ab intio), the ratio of d_3-*tert*-butyl cation to $CH_3CH{=}OH^+$ is

$$\text{for } \mathbf{2g} \qquad \frac{m/z\ 60 - X}{m/z\ 45} = \frac{k_2/a^3}{2k_3/b^3} = \frac{y}{2}(b/a)^3 \qquad \text{(A12)}$$

The experimental values (using $X = 0.10$ and $y = 0.50$ from our treatment of Scheme 3) gives the result $(b/a)^3 = 1.79$.

Starting with **2h** the analogous mechanism is represented by Scheme 5, where the statistical ratio of the two intermediates is 2:3 (weighted by the isotopic partition factor). The ratio of d_6-*tert*-butyl cation to $CH_3CH{=}OH^+$ is predicted to give

$$\text{for } \mathbf{2h} \qquad \frac{m/z\ 63 - X}{m/z\ 45} = \frac{k_2/a^6}{2k_3/b^6} = \frac{y}{2}(b/a)^6 \qquad \text{(A13)}$$

The experimental values (again using $X = 0.10$ and $y = 0.50$) give the result $(b/a)^3 = 1.46$. In like fashion the ratio of d_5-*tert*-butyl cation to $CH_3CH{=}OD^+$ is predicted to be

$$\text{for } \mathbf{2h} \qquad \frac{m/z\ 62}{m/z\ 46} = \frac{k_2'/a^5}{2k_3'/b^5} \qquad \text{(A14)}$$

and the corresponding ratio of d_8-*tert*-butyl cation to $CH_3CH{=}OD^+$ from **2i** is predicted to be

$$\text{for } \mathbf{2i} \qquad \frac{m/z\ 65}{m/z\ 46} = \frac{k_2'/a^8}{2k_3'/b^8} \qquad \text{(A15)}$$

The quotient of A15 and A14 gives yet another value, $(b/a)^3 = 1.11$. These discrepancies in the value of b/a lie outside the range of experimental uncertainty.

Steady State Analysis of Scheme 2 for ETBE (R' = Ethyl). For Scheme 2 call $k_4/k_{-3} = r$, $k_2/k_3 = s$, and $k_5/k_{-3} = t$. The proportion of isobutane expulsion is

$$\text{for } \mathbf{2a} \qquad m/z\ 45 = \frac{2t(1 - X)}{r + 2t + s\,(1 + r + 2t)} \qquad \text{(A16)}$$

Call the β-secondary isotope effect on hydride transfer that results from methyl substitution $k_{CH_3}/k_{CD_3} = p$. The proportion of isobutane expulsion from **2b** is then

$$m/z\ 48 = \frac{2t(1 - X)}{pr + 2t + s(p + pr + 2t)} \qquad \text{(A17)}$$

Call the primary isotope effect on hydride transfer $k_H/k_D = m$ and the α-secondary isotope effect $k_H/k_D = n$. The proportion of C_4H_9D expulsion from **2c** is then

$$m/z\ 46 = \frac{2t(1 - X)}{mnr + 2t + s(mn + mnr + 2t)} \qquad \text{(A18)}$$

The m/z 46:m/z 45 ratio from **2d** gives

$$\frac{m}{n} = \frac{0.38}{0.24} \qquad \text{(A19)}$$

and the proportion of combined C_4H_{10} and C_4H_9D expulsion from **2d** gives

$$m/z\ 45 + m/z\ 46 = \frac{t(m + n)(1 - X)}{mnr + t(m + n) + s(mn + mnr + mt + nt)} \qquad \text{(A20)}$$

Finally, the proportion of C_4H_9D expulsion from **2e** is

$$m/z\ 49 = \frac{2t(1 - X)}{mnpr + 2t + s(mnp + mnpr + 2t)} \qquad \text{(A21)}$$

Using $X = 0.10$ equations A16–21 can be fit within experimental uncertainty by the values $m = 2.29$, $n = 1.48$, $p = 1.76$, $r = 278$, $s = 0.07$, and $t = 823$. The values of r and t are particularly sensitive to the precise values used for experimentally determined ratios, with a systematic error that varies over 2 orders of magnitude. The ratio $r/t = 0.34$ remains fairly constant, however.

The observed ion ratios for **2f–i** can be fit within experimental uncertainty by assuming five additional independent secondary isotope effects on k_2–k_5. While ab initio calculations support the inference that the isotope effect on k_4/k_5 should be multiplicative (*i.e.* should scale as $(k_H/k_D)^n$ for a *tert*-butyl group containing n deuteria), they suggest that the secondary isotope effects on individual rate constants should not be multiplicative. Thus we do not ascribe much significance to the numerical values from such a fit. If multiplicativity cannot be assumed, Scheme 2 presents too many unknowns for the

steady state equations to be solved using the experimental data.

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Supporting Information Available: NMR of isobutyl *tert*-butyl ether, and ab initio geometries and harmonic vibrational frequencies for ions **1**, **2**, **7**, **12**, and **13** (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page or ordering information.

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