

Decompositions of Ionized Isopropyl Methyl Ether: Complex-Mediated and Direct Processes in Unimolecular Dissociations

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Methane and methyl losses from ionized isopropyl methyl ether (1) were characterized to improve our understanding of ion-neutral-complex-mediated dissociations in the gas phase. Photoionization appearance energies demonstrate that the onsets for the two reactions differ by only 2 ± 1 kJ mol⁻¹, consistent with the two processes being related by a common bond cleavage. Isotope effects confirm that the transition states for bond scission to form the complex and subsequent hydrogen transfer to form methane are at very similar energies. Loss of methane becomes insignificant 20–30 kJ mol⁻¹ above its onset, whereas loss of methyl increases rapidly for at least 100 kJ mol⁻¹ above threshold. From this it is concluded that the decompositions of 1 are complex-mediated near threshold but shift to a direct mechanism at higher energies, i.e., that decomposition is ion-neutral-complex-mediated over only a narrow range of energies just above threshold.

Ion-neutral complexes have been invoked to rationalize a variety of unimolecular ionic decompositions in the gas phase.¹⁻⁷ We use the term complex to describe an electrostatically bound ion and neutral pair formed by scission of a covalent bond.⁸ Others have applied the term to hydrogen-bonded complexes¹ and even covalently bonded species.⁹ The electrostatically bound complexes can be identified with the "orbiting" complexes formed in ion-molecule reactions at low energies,^{10,11} as microscopic reversibility dictates that a dissociation follow in reverse order the steps of the corresponding association.¹⁰ Ion-neutral complex formation in unimolecular dissociations appears to be important over a limited energy range,⁸ but precise characterizations of this range and the factors which determine it are nonexistent. This energy dependence is a potential source of information about the dynamics of ion-neutral-complex-mediated dissociation and forces of attraction between incipient ions and neutrals near the threshold for their dissociation in the gas phase. Therefore we begin here and in the companion paper the exploration of the behavior of such reactions as a function of ion internal energies.

Alkane eliminations from ions in the gas phase are thought to be ion-neutral-complex-mediated processes.^{1&8} It has been argued from appearance energies and reported isotope effects that bond cleavage to generate complexes and hydrogen transfers to form the alkane molecules eliminated take place in separate steps.⁸ The threshold for formation of complexes containing alkyl radicals can be at least 20–25 kJ mol⁻¹ below the threshold for simple dissociation.⁸ This correlates reasonably with theoretical predictions that the incipient fragments in simple ionic dissociations begin to rotate freely relative to each other about 10–20 kJ mol⁻¹ below the threshold for complete dissociation.^{10,11} However, this difference increases markedly with increasing polarity of the neutral partner, as CH₂CH₂O⁺H₂ forms a water-ethylene ion complex about 80 kJ mol⁻¹ below the threshold for dissociation to CH₂=CH₂^{•+} + H₂O.¹² We have suggested¹³ that in the absence of reverse activation energy barriers the transition states for unimolecular formation and dissociation of ion-neutral complexes correspond to entropy bottlenecks associated respectively with bond fission and the centrifugal barrier in ionic fragmentations.^{10,11}

Ionized ethyl *sec*-butyl ether loses predominantly ethane upon metastable decomposition, but such ions formed at slightly higher energies by isomerization from ionized ethyl *n*-butyl ether lose almost exclusively ethyl.¹⁴ This was attributed to the presence of an isolated electronically excited state, but it is the behavior later ascribed⁸ to ion-neutral-complex-mediated alkane elimina-

tion. Therefore ether ions should provide useful systems for examining whether alkane eliminations generally occur through ion-neutral complexes and, if so, for exploring the properties of such dissociations. We present here a study of methane elimination from ionized isopropyl methyl ether (1).

Results

The metastable and collision-induced (CAD)¹⁵ decomposition

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TABLE I: Metastable Spectra of Ionized Methyl Isopropyl Ether^a

ion	mode	species lost						
		CH ₃	CH ₄	CH ₃ D	CHD ₂	CH ₂ D ₂	CD ₃	CHD ₃
CH ₃ O ⁺ CH(CH ₃) ₂ (1)	U	3 ^b	97					
CD ₃ O ⁺ CH(CH ₃) ₂ (1a)	U	4 ^b	96					
	C	100	<0.3 ^c					
CH ₃ O ⁺ CH(CD ₃)CH ₃ (1b)	U	23 ^b		16				61
	C	70	<0.07 ^c	<0.04 ^c			30	0.03 ^c
CH ₃ O ⁺ CH(CHD ₂) ₂ (1c)	U				6	91		3
	C				100	<0.6 ^c		

^aData are based on peak areas. U = unimolecular; C = collision induced. ^bCorrected for a collision-induced contribution. ^cCorrected for unimolecular contributions.

TABLE II: Photoionization Appearance Energies from Isopropyl Methyl Ethers

	IE, eV	neutral fragments			
		CH ₃	CH ₄	CD ₃	CD ₃ H
1	9.50	9.71	9.69		
1a	9.49	9.68	9.66		
1b	9.49	9.68		9.68	ca. 9.7 ^a

^aIt was impossible to obtain precise onsets for the CH₃D and CD₃H losses from **1b** due to a poor signal to noise ratio.

patterns of (1) and several labeled forms thereof are given in Table I. The unimolecular decompositions took place about 1.4×10^{-5} s after initial ionization. Most of the metastable decompositions were dominated by methane loss, with an associated much weaker methyl loss being present. A recent communication¹⁶ has presented evidence that loss of CH₃ from metastable 1 and labeled forms thereof is totally collision-induced. However, we believe the corrected metastable peak intensities that we report do represent unimolecular decompositions because (a) extrapolation of the abundances of peaks representing losses of CD₃ and CH₃ from **1b** to zero pressure left residual intensity for the peak corresponding to the former but not that representing the later process, and (b) the translational energy release distributions derived from the raw peaks were markedly bimodal, the translational energy release associated with the narrow component being 7–8 times less than that associated with the corresponding collision-induced dissociation. We conclude from (a) that **1b** has a significant unimolecular loss of CH₃ but not CD₃ at long lifetimes. The CAD spectrum of C₃H₆O⁺ formed in both the ion source and the first field-free region contained peaks at m/z 15, 26, 27, 28, 29, 31, 42, 43, and 57 with intensities greater than 20% of that of the most abundant peak. This pattern is consistent with the published CAD spectrum of CH₃OCH=CH₂⁺.¹⁷ CD₃OCH(CH₃)₂⁺ (**1a**) lost no CD₃ in either unimolecular or collision-induced decompositions, so there was no loss of the methoxy methyl. CH₃OCH(CD₃)CH₃⁺ (**1b**) lost only CH₃, CH₃D, and CD₃H in unimolecular decompositions, demonstrating that both the methyl and the additional hydrogen in the methane eliminated come from the isopropyl methyls.

The unimolecular CD₃ loss from **1b** was at most 2% of the accompanying unimolecular CH₃ loss, so the methyl losses were subject to a very strong secondary isotope effect. This effect persisted up to energies substantially above the threshold for simple fragmentation, as **1b** lost more than twice as much CH₃ as CD₃ following collision. This ratio was 1.2 in the 70 eV electron impact spectrum of **1b**. CH₃OCH(CHD₂)₂⁺ (**1c**) lost CH₂D₂ about 30 times as often as it lost CHD₃, demonstrating the presence of a substantial primary isotope effect on methane elimination. The loss of methyl increased dramatically relative to the loss of methane with increasing ion internal energy, as collision-induced losses of methane were negligible.

Photoionization ion efficiency (PI) curves were determined to define more precisely the energy dependence of the decompositions

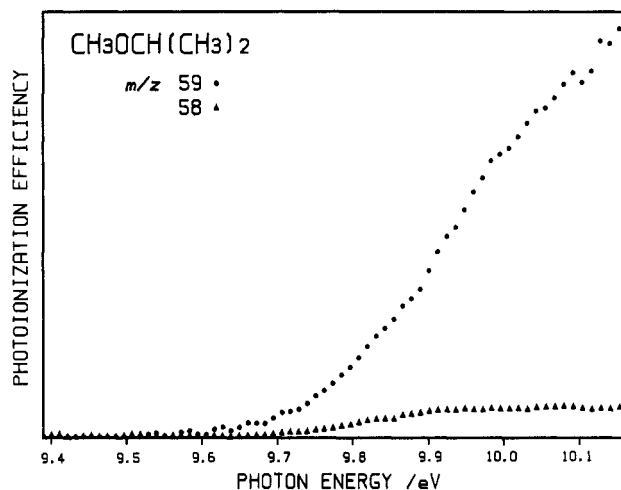


Figure 1. Photoionization efficiency curves for the losses of methyl (upper curve) and methane (lower curve) from ionized isopropyl methyl ether.

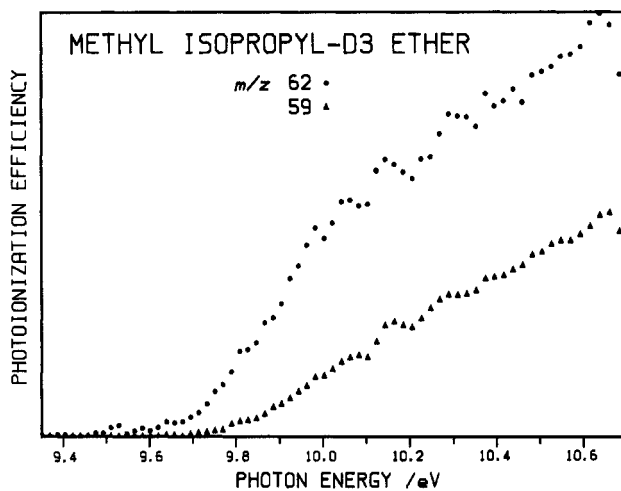


Figure 2. Photoionization efficiency curves for the losses of CH₃ (upper curve) and CD₃ (lower curve) from CH₃OCH⁺(CD₃)CH₃.

studied. Decomposition thresholds are given in Table II, and PI curves are given in Figures 1–3. The curves for losses of methane plateaued at 9.9–10.0 eV, indicating that methane loss becomes quite weak at 20–30 kJ mol⁻¹ above its onset.¹⁸ The plateau cannot be attributed to further decomposition of the product CH₃OCH=CH₂⁺, as the threshold for decomposition of that species is about 160 kJ mol⁻¹ above its heat of formation,¹⁹ but it is formed from **1** only about 20–50 kJ mol⁻¹ above the product

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TABLE III: Average Translational Energies^a Released in the Decompositions of Isopropyl Methyl Ether Ions

ion	mode	species lost						
		CH ₃	CH ₄	CH ₃ D	CHD ₂	CH ₂ D ₂	CD ₃	CD ₃ H
CH ₃ O ⁺ CH(CH ₃) ₂	U	1.0	4.1					
CD ₃ O ⁺ CH(CH ₃) ₂	U		3.7					
CH ₃ O ⁺ CH(CD ₃)CH ₃	C	8.1						
	U	0.74			7.6			5.6
CH ₃ O ⁺ CH(CHD ₂) ₂	C	5.2					8.6	
	U							5.3
	C				3.4	4.3		

^aDetermined by the method of Holmes and Osborne (*Int. J. Mass Spectrom. Ion Phys.* **1977**, *23*, 189). Values are kJ mol⁻¹.

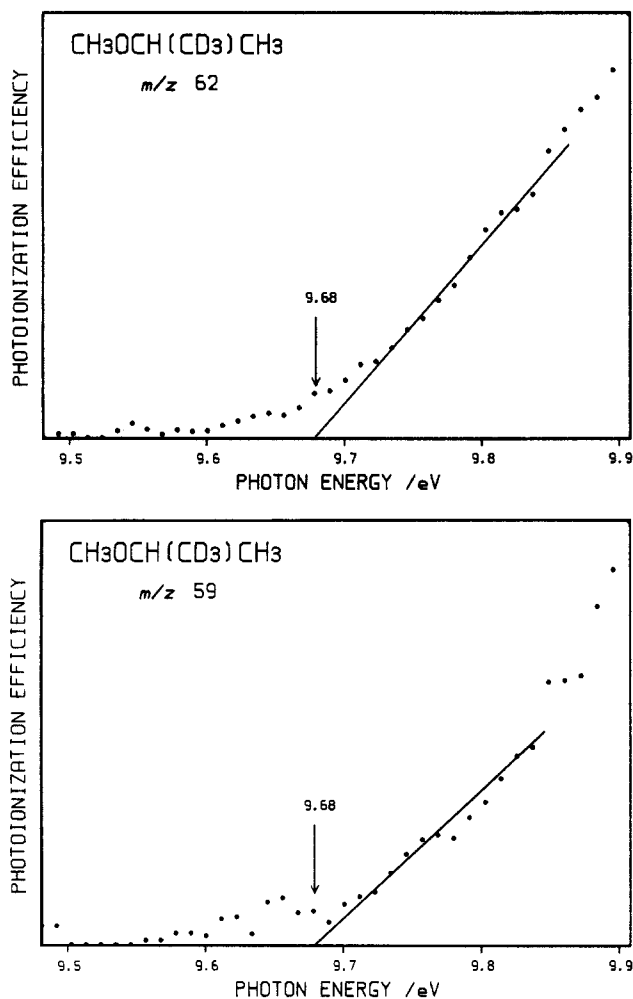


Figure 3. Threshold regions for losses of (a, top) CH₃ and (b, bottom) CD₃ from CH₃O⁺CH(CD₃)CH₃.

heats of formation (see below). In contrast to the curves for methane elimination, the curves for methyl loss rose dramatically with photon energy up to at least 1 eV above threshold.

The stationary electron convention and the following formula²⁰ were used to derive heats of formation at 298 K from appearance energies for the process AB + hν → A⁺ + B + e: ΔH_{f,298}(A⁺) = AE₂₉₈(A⁺) + ΔH_{f,298}(AB) - ΔH_{f,298}(B) + ΔH_{cor}. The adiabatic ionization energy of CH₃OCH(CH₃)₂ was measured here to be 9.50 ± 0.02 eV, which is slightly above the value of 9.42 eV reported previously.²¹ The photoelectron spectrum indicated a vertical ionization energy of 9.60 eV, with no defined onset that could be assigned to the adiabatic transition. Our value of 9.50 eV was the first step in the PIE curve that gave a prethreshold

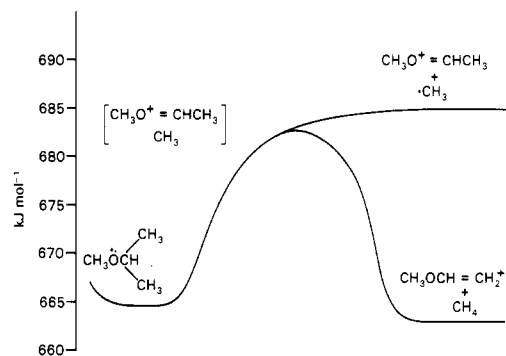


Figure 4. Potential energy diagram for the decompositions of metastable isopropyl methyl ether ions. The onset of complex formation is taken to be at the divergence of the curves leading to the two sets of products. The reactant and products were placed at AE - ΔH_f (isopropyl methyl ether). To allow for the reverse activation energy AE (CH₃OCH=CH₂⁺⁺ + CH₄) was calculated according to the formula²⁰ AE(A⁺) = ΔH_f(A⁺) - ΔH_f(AB) + ΔH_f(B) - ΔH_{cor}.²⁶

tail consistent with the expected hot band structure. Combining this with ΔH_f(CH₃OCH(CH₃)₂) = -252 kJ mol⁻¹²⁰ gives ΔH_{f,298}(1) = 664.6 kJ mol⁻¹. AE(CH₃O⁺=CHCH₃ + ·CH₃), 9.71 eV, was very close to AE(CH₃OCH=CH₂⁺⁺ + CH₄), 9.69 eV. The first value is significantly below the 9.82 eV previously reported for the same process.²² AE(-CH₃) and AE(-CD₃) from 1b were identical (Figure 3), so secondary isotope effects had little influence on the thresholds for methyl loss. ΔH_f(CH₃O⁺=CHCH₃), 561 kJ mol⁻¹, derived from present results using ΔH_{cor} = 20 kJ mol⁻¹²³ and ΔH_f(CH₃) = 143.9 kJ mol⁻¹,²⁰ is slightly higher than values derived previously both experimentally without utilizing ΔH_{cor} (552 kJ mol⁻¹)²² and computationally (553 kJ mol⁻¹).²⁴ We measured IE(CH₃OCH=CH₂) to be 8.92 eV, in excellent agreement with a previous value of 8.93 eV.¹⁹ Assuming that ΔH_f^o(CH₃OCH=CH₂) = -107.0 kJ mol⁻¹²⁵ results in ΔH_f^o(CH₃OCH=CH₂⁺⁺) = 753.7 kJ mol⁻¹, which is slightly higher than a theoretical estimate of 742 ± 11 kJ mol⁻¹.²⁶ ΔH_f for a C₃H₆O⁺⁺ produced by loss of CH₄ from 1 based on AE-(C₃H₆O⁺⁺), ΔH_f(CH₃OCH(CH₃)₂) = -252 kJ mol⁻¹²¹ and ΔH_f(CH₄) = -74.5 kJ mol⁻¹ and ΔH_{cor} = 18.0 kJ mol⁻¹²⁶ is 775 kJ mol⁻¹. From kinetic energy releases, we estimate ΔH_f(C₃H₆O⁺⁺) formed from 1 to be about 765 kJ mol⁻¹ (see Discussion, Isotope Effects). Based on ref 27, CH₃CH₂CHO⁺⁺ and

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(25) A "best estimate" for ΔH_f(CH₃OCH=CH₂) is derived as follows: -107 kJ mol⁻¹ based on the average between (a) -108.5 kJ mol⁻¹ from ΔH_f(ethyl vinyl ether) = -140.9 kJ mol⁻¹ + 32.4 kJ mol⁻¹, the difference between ΔH_f(CH₃OCH₂CH₃) (-216.4 kJ mol⁻¹) and ΔH_f(CH₃OCH₃) (-184.0 kJ mol⁻¹), and (b) -105.6 kJ mol⁻¹ from ΔH_f(CH₃OCH₂CH₃) (-216.4 kJ mol⁻¹) + ΔH_f(CH₃CH₂OCH=CH₂) (-140.9 kJ mol⁻¹) - ΔH_f(C₂H₅OC₂H₅) (-251.7 kJ mol⁻¹). Combining with IE₂₉₈(CH₃OCH=CH₂) = 8.92 eV gives ΔH_{f,298}(CH₃OCH=CH₂⁺⁺) = 753.7 kJ mol⁻¹.

(26) Calculated by using the vibrational frequencies for methyl vinyl ether (Cadioli, B.; Gallinella, E.; Pincelli, V. *J. Mol. Struct.* **1982**, *78*, 215-228) and CH₄ (JANAF Tables NSRDS-NBS 37).

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perhaps $\text{CH}_2=\text{CHCH}_2\text{OH}^{++}$, $\text{CH}_3\text{COCH}_3^{++}$, $\text{CH}_2=\text{C}(\text{OH}_2)-\text{CH}_2^{++}$, and $\text{CH}_3\text{CHOCH}_2^{++}$ also have heats of formation within reasonable range of 765 kJ mol^{-1} . However, only $\text{CH}_3\text{OCH}=\text{CH}_2^{++}$ seems mechanistically plausible, because of the structures of the reactants and products and because the methanes lost consisted exclusively of a methyl and a β -hydrogen from the isopropyl group. CAD spectra, thermochemical measurements, and decomposition patterns of labeled ions all indicate that **1** loses methane to form $\text{CH}_3\text{OCH}=\text{CH}_2^{++}$. The identity of the products, lack of isotopic exchange prior to metastable decomposition, and distinction of the metastable decompositions from those of a variety of isomers²⁸ demonstrate that decomposition occurs without isomerization to other structures. We believe that the one isomer which cannot be rigorously excluded due to lack of experimental data, $\text{CH}_3\text{O}^+\text{HCH}(\text{CH}_2)\text{CH}_3$, is not an intermediate because the critical energy for the required 4-membered ring H transfer in ether ions should be similar to that of ionized ethanol, about 147 kJ mol^{-1} ,²⁹ well above the threshold for the metastable decompositions of (**1**), and we predict this isomer would decompose to $\text{CH}_3\text{OH} + \text{CH}_3\text{CH}=\text{CH}_2^{++}$ or $\text{CH}_3\text{OH}_2^+ + \text{CH}_2\dot{\text{C}}\text{HCH}_2$. A potential diagram summarizing the preceding information is presented in Figure 4.

Average translational energies ($\langle T \rangle$) released in the decompositions of the ionized ethers are given in Table III. Correction for collision-induced contributions gave a relatively small value for the loss of methyl, 1.0 kJ mol^{-1} . Energies released in the losses of methane were 6–10 times larger than those for the losses of methyl. The energy releases were subject to substantial primary and secondary isotope effects, as $\langle T \rangle$ for CH_3D loss from **1b** was 36% greater than that accompanying CD_3H loss, and $\langle T \rangle$ associated with CD_3 loss upon collision was nearly twice that of the accompanying CH_3 loss.

Discussion

The Characteristics of Methane Elimination Are Those of Ion-Neutral-Complex-Mediated Processes. Several criteria have been proposed^{8,28} for recognizing when a reaction involves an ion-neutral complex, including (a) such a reaction will have the lowest critical energy of the decompositions of the fragmenting ion, (b) decompositions via complexes are restricted to a narrow range of energies just above the threshold for forming the complex, and (c) the ion formed by the simple bond cleavage required to form the complex will be very abundant at energies appreciably above threshold. More recent work³⁰ indicates that the first criterion only applies precisely to complex-mediated metastable decompositions. Its appearance energy and dominance of the metastable spectra establish that methane elimination is the lowest energy decomposition of **1**. The plateauing of the PI curves for methane elimination 20–30 kJ mol^{-1} above the threshold for decomposition and the absence of methane loss following collision demonstrate that methane elimination is significant over only a narrow energy range. Losses of methyl dominate the high energy, ion source decompositions, and the CAD spectra of ionized isopropyl methyl ethers. Therefore the losses of methane characterized here fit the above profile, and behave similarly to the alkane eliminations from alcohols,³¹ ketones,^{30,31} amines,³¹ and alkanes.³²

(27) Derived by calibrating the computed relative $\text{C}_3\text{H}_6\text{O}^{++}$ heats of formation in Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 2246–2252 with the experimentally determined²¹ $\Delta H_f^\circ(\text{CH}_3\text{C}(\text{O}^+)=\text{CH}_2)$ and $\Delta H_f^\circ(\text{CH}_3\text{CH}_2\text{CHO}^+)$.

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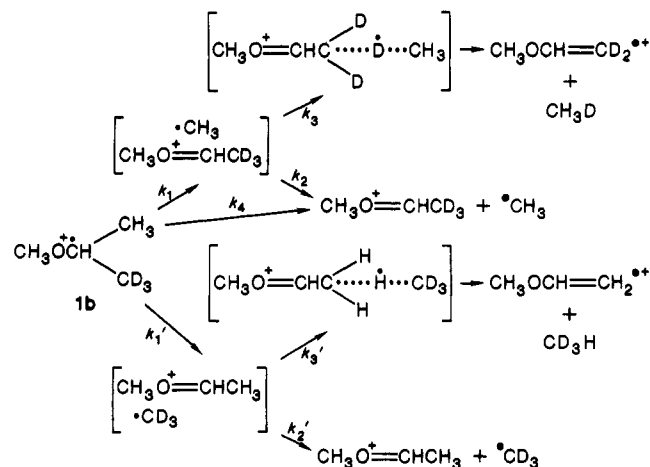
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SCHEME I



These characteristics are inconsistent with expectations for concerted 1,2-eliminations, which have high reverse activation energies and are accompanied by substantial translational energy releases when they occur.³³ Proposed decompositions of **1b** are given in Scheme I in which the first species in brackets in each decomposition pathway represents an ion-radical complex and the second the transition state for hydrogen transfer to produce alkane elimination. Weiske and co-workers¹⁶ have recently concluded that isopropyl methyl ether ions do not decompose through methane-ionized methyl vinyl ether complexes because the products of methane elimination are substantially lower in energy than the transition state for methane elimination (see Figure 4). However, hydrogen migrations prior to alkane elimination from ionized ketones appear to take place by reversible formation of substituted ketone ion-alkane complexes.³⁴ The potential surface for alkane-ketone complex formation³⁰ from ketone ions is much more favorable than is the case of the system studied here. Weiske and co-workers are likely correct in the point they make. However, the main issue is whether methyl/oxonium ion complexes are involved in the decomposition (Scheme I), an issue they did not comment on.

Energetics of the Decomposition of Ionized Isopropyl Methyl Ether. The AE measurements place the threshold for methane elimination $2 \pm 1 \text{ kJ mol}^{-1}$ below that for methyl elimination. Its very small $\langle T \rangle$ demonstrates that the methyl loss takes place at its thermochemical threshold. The larger $\langle T \rangle$ values for the methane eliminations suggest that the latter reactions may have small reverse activation energies. $\Delta H_f^\circ(\text{CH}_3\text{OCH}=\text{CH}_2^{++})$ derived from our AE measurements, 775 kJ mol^{-1} , is 21 kJ mol^{-1} above $753.7 \text{ kJ mol}^{-1}$, our estimate of the actual value (see Results). The 2 kJ mol^{-1} between the onsets of methyl loss and methane loss is much less than the largest observed differences of 20–25 kJ mol^{-1} between thresholds for other associated methane and methyl losses.⁸ We attribute this to the onset of methyl loss being only 20 kJ mol^{-1} above $\text{IE}(\text{CH}_3\text{OCH}(\text{CH}_3)_2^{++})$. Some covalent bonding of the isopropyl methyls in **1** should exist, raising the threshold for complex formation above $\text{IE}(\mathbf{1})$ and apparently bringing it close to the threshold for methyl loss. The close correlation of the onset of methane elimination with the energy required to cleave the C–C bond rather than the total heat of formation of the products supports our belief that C–C bond cleavage is a step in the elimination of methane. A common transition state for methyl and methane losses was probably first suggested in 1967 by Chupka and Berkowitz³⁵ based on identical

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appearance energies for those two decompositions of ionized *n*-butane.

It is interesting that, while the rates of methyl and methane loss near threshold are quite similar in the ion source photoionization studies, the methane losses are strongly dominant after ca. 10^{-5} s. This seems to indicate that the decomposition of ions very near threshold change with ion lifetime. This is not a unique situation because ionized acetone displays similar behavior.³⁰ The threshold for methane elimination could be slightly below that for methyl loss, causing methane loss to dominate because most ions with enough energy to lose methyl decompose prior to reaching the field-free region. More interestingly, it could be due to ions in low rotational states dissociating rapidly, predominantly by methyl loss, and to ions in higher rotational states dissociating more slowly by loss of methane. The centrifugal barrier to methyl loss would increase with increasing rotational energy, discriminating against that process. Also, the distance to the centrifugal barrier decreases as the rotational quantum number increases, perhaps holding the methyl more often in a region in which hydrogen transfer can occur. The energy released in the formation of methane in the complex (ca. 20 kJ mol⁻¹ based on the difference between the best value of $\Delta H_f(\text{CH}_3\text{OCH}=\text{CH}_2^{*+})$ and its apparent ΔH_f based on $\text{AE}(\text{C}_3\text{H}_6\text{O}^{*+})$ from **1** might drive methane over this barrier.

Isotope Effects. There are very strong primary isotope effects on the metastable methane losses, as **1c** loses CH_2D_2 30 times oftener than it loses CHD_3 . Correcting for the 2:1 D:H availability gives a primary isotope effect of 60. Primary isotope effects on alkane losses can be as large as 100–200.³² The primary isotope effect on the unimolecular decompositions of **1b** is probably opposed by the strong secondary isotope effect evident in the methyl losses, as the $-\text{CD}_3\text{H}/-\text{CH}_3\text{D}$ ratio for **1b** is only 3.8, far below the expected ca. 60, whereas its $-\text{CH}_3/-\text{CD}_3$ ratio is at least 50. The much stronger loss of CH_3 from **1b** relative to the other metastable ions could result from inhibition of D abstraction in the complex by the primary isotope effect as well as more facile cleavage of the C– CH_3 than the C– CD_3 bond. According to previous interpretations,⁸ combined strong primary and secondary isotope effects indicate that the transition states for C–C bond cleavage to form the complex and subsequent H abstraction are at very similar energies. The small differences between the measured thresholds for methyl and methane losses are consistent with this interpretation, as alkane eliminations usually have thresholds 20–30 kJ mol⁻¹ below those for associated alkyl losses when the product heats of formation permit it.^{8,30}

Isotope effects influence the translation energy releases (Table III) as well as the branching ratios. Isotope effects on metastable decompositions are usually attributed to elevations of the critical energy for the decomposition.³⁶ A primary isotope effect would raise the critical energy for CH_3D loss by at most 4.8 kJ mol⁻¹ relative to CD_3H loss.³⁷ $\langle T \rangle$ is 20 kJ mol⁻¹ higher for the former than the latter transition, so at least 42% of the increased energy due to the isotope effect appears to become translational energy. If the energy released in the methane losses is close to this portion of the overall excess energy, then $\Delta H_f(\text{CH}_3\text{OCH}=\text{CH}_2^{*+} + \text{CH}_4)$ is about 10 kJ mol⁻¹ below the threshold for their formation from **1**. This predicts a heat of formation near 765 kJ mol⁻¹ for $\text{CH}_3\text{OCH}=\text{CH}_2^{*+}$, in reasonable agreement with a ΔH_f of 753.7 kJ mol⁻¹ (Results).

The differences in $\langle T \rangle$, 3.4 kJ mol⁻¹, between CH_3 and CD_3 losses following collision of **1b** is startlingly large. The increases in $\langle T \rangle$ relative to those for unimolecular decompositions indicate that on average the collision-induced methyl losses take place well above threshold. The ratio $-\text{CH}_3/-\text{CD}_3$ in Figure 2 decreases from 4.5 at 9.7 eV to 2.2 at the highest energy data point taken. Therefore, we attribute the larger $\langle T \rangle$ to stronger suppression of CD_3 loss at low than at high internal energies.

The identical thresholds for the CH_3 and CD_3 losses from **1b** imply that the different frequencies and energy releases of the

two processes are not caused by a difference in their critical energies. Differences in angular momentum should discriminate against the products of lower reduced mass,³⁸ the opposite of the observed results. It seems unlikely that there is a greater tendency of bound CH_3 than CD_3 to be impacted upon collision, as the cross-sectional areas of the two groups do not differ by more than a few percent. Existence of more $[\text{CH}_3\text{O}^+=\text{CHCD}_3\cdot\text{CH}_3]$ than $[\text{CH}_3\text{O}^+=\text{CHCH}_3\cdot\text{CD}_3]$ prior to collision with each complex losing its loose methyl upon collision could explain the differences. This could occur if isotope effects favor the formation of the former complex, which seems plausible in light of the influence of isotopes on the losses of methyl.

The Dynamics of Methane and Methyl Loss. Longevialle and Botter have rationalized the ability of a moiety from one end of a steroid nucleus to be eliminated together with a hydrogen from the other end following ionization by proposing that fragmentation occurs through an ion-neutral complex, as the distance is too great for the elimination to involve a bent, stretched bond.³ Proton transfer occurs only after bond cleavage and rotation of the fragments into a configuration in which proton transfer can occur, a process calculated to take 10^{-11} s.^{3a} This is perhaps the most direct evidence to date that associated ion-neutral pairs are fully formed intermediates in some unimolecular decompositions.

Complex-mediated dissociations correspond to the second halves of low-energy ion-molecule reactions. The dynamics of ion-molecule reactions generally change from complex-mediated at low energies to direct with increasing energy.³⁹ Complexes by experimental definition rotate to the extent that no memory of the trajectories of the reactants is displayed in the direction of dissociation of the products. At the other extreme, at high energies some ion-molecule reactions occur by the transfer of an atom without significantly altering the trajectory of the remainder of the molecule to which it was initially bound.⁴⁰ Ion-molecule reactions tend to change from the former type of dynamics to the latter with increasing relative translational energy. Utilizing the relationship $E = 1/2(RT)$, assuming a temperature of 525 K and using the approach of Longevialle and Botter^{3a} indicates that it would take $\text{CH}_3\text{O}^+=\text{CHCH}_3$ about 10^{-12} s on average to rotate to a position where H transfer to the accompanying methyl could occur. Therefore all methyls "escape" from $\text{CH}_3\text{O}^+=\text{CHCH}_3$ in less than 10^{-12} s when the energy in the system exceeds threshold by more than 20–30 kJ mol⁻¹. By analogy to ion-molecule reactions, we will use this as the experimental criterion for a direct process. We conclude that the rapid decrease in the loss of methane with increasing energy represents a transition from complex-mediated to direct dynamics. Complex formation at the higher energies examined here would require that return to **1** take place before 10^{-12} s has elapsed. However, return in less than 10^{-12} s would be a vibration rather than passage through a transition state. The disappearance of the atom-transfer reaction with increasing energy in the present reactions contrasts with the persistence of such reactions, despite dynamic changes, with increasing energy in ion-molecule reactions. This difference is due to the ability of the reactants to find configurations permitting atom transfer in bimolecular interactions, but not upon rapid unimolecular dissociation.

Calculated and Observed Decomposition Rates of 1. A complex can be defined theoretically as a region of high probability between reactants and products from which return to the reactants through a minimum flux region or continuation to products can occur.⁴¹ RRKM calculations were carried out with the initial intention of exploring this model. Resulting rate constants are given in Table IV and a description of the calculations in the Appendix. Applying the steady-state assumption to the complex and assuming that all reactions pass through the complex gives

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TABLE IV: Calculated Rate Constants for Reactions of Ionized Isopropyl Methyl Ether^a

rate const	$E^* - \Delta H_f(1)$	
	21 kJ mol ⁻¹	45 kJ mol ⁻¹ ^b
k_1^c	2.3×10^{11}	1.6×10^{12}
k_2^d	1.4×10^{12}	5.5×10^{12}
k_3^e	5.4×10^{11}	7.5×10^{11}
k_4^f	1.5×10^{11}	2.5×10^{12}
k_5^g	2.0×10^{10}	2.0×10^{11}

^aDimensions are s⁻¹; E^* = the total energy content of the system; reactions represented by each rate constant except k_5 are given in Scheme I. ^bThe energy of the onset of the plateau, i.e., the upper limit of the energies at which significant methane elimination occurs. ^cFour free rotors assumed in the reactant and three in the transition state (rotation about the O-C(CH₃)₂ bond inhibited by developing π character as decomposition progresses), a degeneracy of 2, and a critical energy (e_0) of 17 kJ mol⁻¹. ^dFive free rotors assumed in reactant and five in the transition state, $e_0 = 3$ kJ mol⁻¹. ^eAssuming five free rotors in the reactant and three in the transition state (loss of two free rotations of the methyl radical) $e_0 = 1$ kJ mol⁻¹. ^fAssuming four free rotors in the reactant, five in the transition state, a degeneracy of two, and $e_0 = 20$ kJ mol⁻¹. ^gFor "direct" methane elimination assuming four free rotors in reactant and three in the transition state.

the following overall rate expressions (see Scheme I for association of rate constants to reactions)

$$\frac{d[\text{CH}_3\text{OCH}=\text{CH}_2^+]}{dt} = \frac{k_1 k_3 [1]}{k_{-1} + k_2 + k_3}$$

$$\frac{d[\text{CH}_3\text{O}^+=\text{CHCH}_3]}{dt} = \frac{k_1 k_2 [1]}{k_{-1} + k_2 + k_3}$$

These expressions cannot be evaluated exactly without knowing k_{-1} , which we could not calculate. The rate of return from the complex is likely to be very high even at threshold, since that reaction is energetically downhill. The maximum physically meaningful rate constant would be less than 10^{14} s⁻¹. Substituting this value together with results from Table IV into the first of the above expressions gives an overall rate constant of 1.2×10^9 s⁻¹ for methane elimination; smaller values of k_{-1} give higher rates. Utilizing $k_{-1} = 10^{14}$ s⁻¹ in the second of the above expressions gives an overall rate of methyl loss of about 3.2×10^9 s⁻¹. Lowering k_{-1} to 1×10^{10} s⁻¹ so that its influence becomes negligible raises the rate of methyl loss to 1.6×10^{11} s⁻¹. Using critical energies of 18 and 20 kJ mol⁻¹ for methane and methyl losses and lowering the number of reactant free rotors to 4 to represent direct decomposition from **1** gave calculated rate constants for methyl and methane losses at 21 kJ mol⁻¹ of about 1.5×10^{11} s⁻¹ and 2×10^{10} s⁻¹, respectively.

The calculated decomposition rates are 5–6 orders of magnitude too high to produce the observed metastable decompositions assuming direct dissociation and about 4 orders too high if complex-mediated dissociation is assumed. However, one of these types of mechanisms must be correct (see Results). Reasonable variations in vibrational frequencies or numbers of free rotors did not greatly alter the computed rates. A discrepancy between observed and calculated decomposition rates of ionized methane has been removed by including the effects of tunneling in the calculation.⁴² A similar difference between calculated and observed rates for the butanoic acid ion has been attributed to isomerization to lower energy, longer lived intermediates.⁴³ Finally, observations similar to the ones we report here for ion-permanent dipole complexes have been attributed to a very high density of states in the reactant due to lowering of the vibrational frequency of the ion-dipole bond as it elongates.⁴⁴ None of these explanations seems applicable

TABLE V: Frequencies (cm⁻¹) Utilized for RRKM Calculations on CH₃O⁺CH(CH₃)₂

2990	2820	1460	900
2990	1480	1450	900
2965	1480	1400	850
2960	1480	1385	850
2960	1460	1385	450
2905	1460	1350	400
2880	1460	1300	400
2820	1460	1200	400
2865	1460	1160	

here. A similar mismatch between observed and calculated lifetimes has been encountered by Rosenstock and co-workers in the decomposition of 2-bromopropane ions.⁴⁵ Decomposition by an alternate pathway involving an isomerization also appears to be impossible for the near-threshold decompositions of ionized 2-bromopropane. One of the possible explanations they suggested for their observations was that their decomposition was slow because of weak coupling between vibrational modes. Calculations including the effect of the rotational barrier and conservation of angular momentum in the products are needed to see if they can better reproduce the results.

The mismatch between the observed and calculated decay rates may have another source. The rate of energy flow decreases markedly with decreasing internal energy and randomization must fail for all species at low enough energies.⁴⁶ The density of states in **1** at 21 kJ mol⁻¹ found by the program used for the RRKM calculations was about 300 states per cm⁻¹. However, energy no longer moves freely through molecules below densities of states of about 1000 states per cm⁻¹.⁴⁷ Below this point the equilibrium between reactant and activated complex assumed in RRKM theory would no longer be maintained, and actual rates of reaction could drop far below calculated rates. Modes with frequencies above 1756 cm⁻¹, 10 of those in Table V, would not be excited at 21 kJ mol⁻¹, which might inhibit energy flow. We have previously suggested that ionic dissociations with very low critical energies might be a good place to look for nonstatistical behavior.⁴⁸

A second problem encountered when comparing RRKM-calculated rates and experimental observations was that the calculated rates of methyl and methane loss changed slowly relative to each other with increasing energy, in contrast to the switch from strong dominance by methane elimination to its disappearance over an energy range of 20–30 kJ mol⁻¹. Methane loss would dominate below the threshold for methyl loss, i.e., below the energies in Table IV. At 21 kJ mol⁻¹, the calculated rate of complex-mediated methyl loss was 2.7 times the rate of methane elimination, reasonably consistent with the threshold region of the P1 curves. However, the computed rate of methyl loss was only 7.3 times that of methane elimination in ions containing 45 kJ mol⁻¹ excess energy, whereas observations indicate a much higher ratio. Assuming "direct" rather than complex-mediated processes did not appreciably improve the correlation between observed and calculated relative rates. However, we concluded above that it would take about 10⁻¹² s for the ion in the complex to rotate to the point where methane formation would become possible, and the calculated rate constant for methyl loss from the complex (k_2) was 5.5×10^{12} s at 45 kJ mol⁻¹. Although this method of calculating rates of decomposition of the complex may be inappropriate for such a fleeting species, the results are consistent with the departure of the methyl being too fast for formation of methane to occur. The only obvious way the discrepancy between the computed and observed energy dependences of the relative rates can be resolved is by assuming methane elimination occurs through a configuration that cannot be reached at higher energies. Therefore, we conclude that with increasing internal energy **1** first goes through a region

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where complex-mediated decomposition dominates, a transition region where complex-mediated and direct decomposition both occur, and finally a high-energy region in which only direct decomposition occurs.

Experimental Section

Metastable decomposition spectra were obtained for decompositions occurring in the third field-free region of a mass spectrometer of the geometry electric sector–magnetic sector–electric sector⁴⁹ by scanning the potential on the third sector. CAD spectra were obtained by raising the pressure of helium in a collision cell in the third field-free region until the beam was attenuated to the desired degree. Unimolecular contributions to CAD spectra were corrected for by applying a potential to the collision cell such that peaks representing decompositions inside the cell were deflected from their normal positions. The fraction of decompositions occurring inside the cell relative to the total were determined at base pressure and under CAD conditions. The former fraction and the intensity of decomposition outside the cell were utilized to correct the intensities of CAD decompositions inside the cell for unimolecular components.⁵⁰ Average translational energy releases were determined utilizing the method of Holmes and Osborne.⁵¹ These determinations were made from decompositions within a short cell near the middle of the field-free region, which give energy releases 14% smaller than those from conventionally recorded peaks.⁵² We believe the results from deflected peaks on the instrument utilized to be closer to the true energy releases.

Photoionization ion efficiency curves were obtained with a microcomputer-controlled photoionization efficiency mass spectrometer, which has been described in detail elsewhere.²⁰ The photon beam used in the present experiments was produced from the hydrogen pseudocontinuum with a wavelength resolution of 0.125 nm corresponding to an energy resolution of 0.01 eV at 10.0-eV photon energy. Calibration of the energy scale with known atomic emission lines indicated that it is accurate to better than 0.003 eV. Experiments were performed at a source temperature of 297 K with sample pressures of 10^{-3} Pa in the ionization region. Appearance energies were derived from linear extrapolations to the abscissa which yielded hot band structures consistent with those observed for the relevant molecular ions.

The ethers were prepared by treatment of the appropriate 2-propanol with NaH in diglyme and then the appropriate labeled methyl iodide. CD₃I was prepared by reaction of CD₃OD with H₃PO₄/KI. CD₃CH(OH)CH₃ was prepared by adding CD₃MgI to acetaldehyde. (CHD₂)₂CHOH was prepared by the reduction of hexyl formate with LiAlD₄ to produce CHD₂OH, conversion to CHD₂I with KI/H₃PO₄ and addition of the Grignard to hexyl formate.

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Appendix

Parameters Used in RRKM Calculation. RRKM computations on decompositions of **1** were performed utilizing the computer program of Bunker and Hase.⁵³ Critical energies determined here of 18 and 20 kJ mol⁻¹ were utilized for losses of methane and methyl, respectively. Vibrational frequencies were assigned to an assumed structure by considering stretches as separate internal coordinates along with independent combinations of bending coordinates⁵⁴ and free internal rotations. Values for the vibrational frequencies were adopted from those available in the literature for analogous molecules or analogous regions of molecules or ions. External rotations were treated as adiabatic at temperature of 500 K. Moments of inertia for the molecular ion were assumed to be those of the parent molecule.⁵⁵ These were increased slightly for the ion–molecule complex and transition states.

Most frequencies for the methyl isopropyl ether molecular ion were adapted from those tabulated for methyl *n*-propyl ether,²³ but methine rocking frequencies were based on tabulated C–H deformations,⁵⁶ and methine heavy atom deformations were based on an assumed 400-cm⁻¹ C–C–C bends for C₆H₈⁺.⁵⁷ Our model assumed four free internal rotations for **1**, one per methyl, and one about the isopropyl C–O. Frequencies utilized to represent **1** are given in Table IV.

The ion–radical complex was assumed to be a methyl radical associated with a CH₃O⁺=CHCH₃ ion.²⁴ Twenty-five vibrations and two methyl free rotations were assumed for the CH₃O⁺=CHCH₃ part of the complex. Methyl contributed three C–H stretches and five independent bends to the model. An ion–radical stretch of 400 cm⁻¹ and free rotation of the radical about its threefold symmetry axis were assumed. The set of coordinates was completed by either (a) two low-lying methyl translation-like “wags” or (b) two additional free internal rotations.

Losses of methyl were assumed to occur with no reverse activation energy. Thus the CH₃O⁺=CHCH₃ ion and methyl radical were used to represent the transition state for these reactions. Three free rotations were assumed for the radical and two for the bonded methyls. The reaction coordinates were (1) the appropriate C–C stretch for direct loss and (2) the radical–ion stretch for reaction from the ion–induced dipole complex.

The model transition state for loss of methane from the complex assumed that the ion framework was transitional between CH₃O⁺=CHCH₃ and CH₃OCH=CH₂⁺ with a terminal hydrogen shared by the incipient radical cation and a somewhat tetrahedral methyl. The model reported here assumed that both C–O torsions are free internal rotations and included a third free rotation for methane methyl.

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