J. Phys. Chem. A **2005,** *109,* 3159−3165

Isotope Effects on the Unimolecular Dissociation of Ionized 3-Methyl-2-butanol: Reactions via a Long-Lived C−H−C Hydrogen-Bridged Ion-Neutral Complex

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Received: December 3, 2004; In Final Form: January 28, 2005

A pronounced isotope effect causes metastable $CD_3CHOHCH(CH_3)_2^{+\bullet}$ ions to expell $C_3H_6D_2$ in preference to C_3H_7D in a ratio of ∼33:1; a number of related compounds show similar effects. High-level ab initio calculations suggest that the reactant alcohol molecular ion possesses an extraordinarily long α-carbon−carbon bond and that the reaction proceeds via the formation of an intermediate hydrogen-bridged complex of propane and ionized vinyl alcohol, in which the bridging hydrogen atom is almost midway between the two carbon termini. The isotopic preference reflects the difference between the zero-point vibrational energies of the isotopically different product pairs rather than kinetic isotope effects on the hydrogen atom transfer reactions that precede dissociation.

Introduction

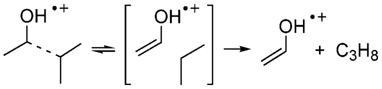
Isotope effects on the unimolecular fragmentation of gas-phase radical cations are nearly always kinetic isotope effects that arise from differences between the zero-point energies of isotopically different transition states.[1,2] The interpretation can be relatively straightforward when the isotope effect affects the last chemical step of the reaction, whereas it may be less easy to interpret the influence of isotopic substitution when the reactant species undergoes further transformation after the step that directly involves the labeled site. An unusual example of this situation is the loss of propane from metastable 3-methyl-2-butanol radical cations (Scheme 1). Previous work[3,4] has shown that the reaction proceeds without skeletal rearrangement and that the two hydrogen atoms on the central propane carbon atom were originally located on the alcohol C(1) and C(3) carbon atoms. The surprising feature is that the 1,1,1-trideuterated analogue expells propane-d_2 more than 30 times more readily than propane-d; other deuterium labeled analogues and their methyl and ethyl ethers show similar behavior. We have examined this reaction more closely, inasmuch as the isotopic specificity observed is not easily explained as the result of a kinetic isotope effect on the hydrogen atom transfer reaction(s) that precede propane loss.

Methods

Mass Spectrometry. The unimolecular ionic gas-phase reactions were studied with a JEOL HX/HX110A mass spectrometer operated in three-sector mode (EBE). In this instrument, the length of the flight path from the ion source to the field-free region is 2.3 m, and the length of the field-free region is 1.4 m. The energy of the ionizing electrons was 70 eV, and the accelerating voltage was 10 kV; the ion-source sample pressure was between 1 and 2×10^{-6} Torr.

The reactions of the metastable molecular ions were examined with mass analyzed ion kinetic energy (MIKE) spectrometry,[5] which makes it possible to selectively monitor those reactions that take place in the field-free region after the magnetic analyzer, that is, the near-threshold dissociation of the molecular ions. Preliminary results were obtained on a VG ZAB-2F instrument at Ecole Polytechnique, Palaiseau, and on an unusually large reverse-geometry double-focusing mass spectrometer (MMM) located at the University of Warwick.

SCHEME 1: Formation of Ion-Neutral Complexes from the 3-Methyl-2-butanol Radical Cation



The relative abundances of the product ions are given in Table 1, based on peak heights. Very accurate determination of the relative ion yield was in some cases not possible, owing to contamination of the molecular ion beam by ^{13}C contributions from $[M - 1]^+$. The $[M - 1]^+$ ions react, inter alia, by loss of C_3H_6, giving rise to product ion signals of a few percent. In the MIKE spectra of the deuterium labeled species, this will give rise to overlapping peaks, and possibly to an overestimation of the relative yield of those ions that give rise to small signals. One example is that the loss of propane-d from $M^{+\bullet}$ and the loss of ^{13}C-propene-d_2 and propene-d_3 from the ^{13}C contribution of $[M - 1]^+$ will give rise to isobaric product ions, and simple measurement of peak heights in turn results in an underestimate of the propane-d_2/propane-d ratio. It is possible that the presence of isobaric product ions is the reason the propane-d_2/propane-d ratio published earlier[3,4] is slightly different from that reported here.

The alcohols and ethers examined were prepared by unexceptional methods, purified by distillation, and examined for identity and purity by gas chromatography−mass spectrometry and ^{13}C NMR spectroscopy.

Computational Studies. Heats of formation were derived from total energies calculated with the G3 and G3//B3LYP composite ab initio methods.[6,7] Relative energies were obtained with the G3(MP2) and G3(MP2)//B3LYP methods. These methods have been shown to yield accurate estimates of the thermochemical properties of ions and radicals.[8,9] The calcula-

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10.1021/jp0407425 CCC: $30.25

TABLE 1: Loss of Propane, Propane-*d*, and Propane-d_2 from the Radical Cations of Labeled 3-Methyl-2-propanol and Its Methyl and Ethyl Ethers[a]

		C_3H_8	C_3H_7D	$C_3H_6D_2$
1	$CD_3CHOHCH(CH_3)_2$		<3	100
2	$CHD_2CHOHCD(CH_3)_2$		<3	100
3	$CH_3CHOHCD(CH_3)_2$	<4	100	
4	$CHD_2CHOHCH(CH_3)_2$	<0.1	11	100
5	$CD_3CH(OCH_3)CH(CH_3)_2$		7	100
6	$CD_3CH(OC_2H_5)CH(CH_3)_2$		15	100

[a] From MIKE spectra; relative abundance, including the isobaric ^{13}C contributions from $[M - 1]^+$. The only other peaks in the spectra correspond to the loss of (labeled) methane.

tions were performed with the Gaussian 98 and Gaussian 03 suites of programs,[10] and the 298 K heats of formation were obtained as described by Nicolaides et al.;[11] the required auxiliary thermochemical data were taken from the compilation by Chase.[12] Zero-point vibrational energies (zpve's) were obtained from vibrational frequency calculations performed with the methods and basis sets indicated in Tables 2 and 3. The zpve results are based on unscaled calculated frequencies.

Results and Discussion

The Molecular Ion. Ab initio calculations with the MP2 and DFT methods suggest that ionized 3-methyl-2-butanol may exist in two quite different forms (Figure 1), both of which exhibit an unusually long α-CC bond. In one, **A**, a long bond (1.72 Å) connects the C(1) methyl to the oxygen-bearing carbon, C(2), whereas the other, **B**, possesses a long bond between C(2) and C(3), 1.97 Å; the calculated length of this bond varies somewhat with the method employed; see Table 4.

Long bonds in aliphatic radical cations were first noticed by Bellville and Bauld,[13] and a careful study by Gauld and Radom[14] of the long carbon−carbon bond in the ethanol radical cation provided convincing evidence that this is not a computational artifact. Traeger and Morton[15] reported that the higher homolog, the 2,3-dimethyl-2-butanol radical cation, also possesses a very long bond between C(2) and C(3), and long CC bonds have been reported for α-branched aliphatic amine radical cations.[16]

Ionization energy measurements[4] provide an experimental heat of formation of the 3-methyl-2-butanol radical cation that is not very different from the G3 heat of formation of ions with structure **A**, 634 kJ mol^{-1}. However, it is perhaps open to question whether the measured value corresponds to adiabatic ionization of the neutral alcohol. It was not possible for us to characterize the **A** ions with DFT methods; geometry optimization with B3LYP/6-31G(d) led directly to the other long-bond form, **B**, whose G3 heat of formation is ∼40 kJ mol^{-1} lower (Table 4).

The existence of a lower-energy isomer of the molecular ion, the long-bond **B** ion, vindicates the suggestion made by George and Holmes[4] that the experimentally observed formation of reasonably abundant metastable molecular ions of 3-methyl-2-butanol implies the presence of additional, low-energy isomers.

Loss of Alkane Molecules. The expulsion of neutral methane and propane molecules are the two major reactions observed when metastable 3-methyl-2-butanol radical cations undergo unimolecular fragmentation.[17] The loss of alkane molecules from metastable secondary alcohol and ether molecular ions is often described[3,4,15,18−21] as proceeding via intermediate ion-neutral complexes;[3,22−29] that is, cleavage of the α-carbon−carbon bond does not result in immediate dissociation but is followed by hydrogen atom transfer, to give rise to an enol or enol ether radical cation and an alkane molecule (Scheme 1). When sufficiently exothermic, the H transfer is followed by rapid expulsion of the alkane molecule.[19]

The predominant ion-source reaction of the molecular ion is the loss of isopropyl radicals; the G3 heats of formation of the products show that this reaction requires ∼20 kJ mol^{-1} more than the loss of propane: iso-$C_3H_7^•$, 90; C_3H_8, −106; $CH_2{=}CHOH^{+•}$, 770; $CH_3CH{=}OH^+$, 594 (298 K values, in kilojoules per mole).

TABLE 2: Calculated Zero-Point Vibrational Energies[a]

	HF/6-31G(d)		HF/6-31++G(d,p)		MP2/6-31G(d)		B3PW91/6-31G(d)		B3LYP/6-31G(d)	
	zpve	Δ[b]	zpve	Δ[b]	zpve	Δ[b]	zpve	Δ[b]	zpve	Δ[b]
$CH_3CH_2CH_3$	290.3	0	287.5	0	280.3	0	273.9	0	273.3	0
CH_3CHDCH_3	281.1	9.2	278.4	9.1	271.3	9.0	265.1	8.8	264.6	8.7
$CH_3CD_2CH_3$	271.7	18.6	269.1	18.4	262.3	18.0	256.3	17.6	255.8	17.5
$CH_2{=}CHOH^{+•}$	159.3	0	158.7	0	151.1	0	149.0	0	148.5	0
$CHD{=}CHOH^{+•}$	150.9	8.4	150.4	8.4	143.0	8.1	141.1	7.9	140.6	7.9
$CD_2{=}CHOH^{+•}$	142.4	16.9	141.9	16.8	134.8	16.3	133.0	16.0	132.5	16.0
CH_3CHCH_3	248.2	0	245.9	0	239.8	0	233.2	0	232.6	0
CH_3CDCH_3	240.1	8.1	237.8	8.1	231.9	7.9	225.5	7.7	224.9	7.7
$CH_3CH{=}OH^+$	193.4	0	192.5	0	183.8	0	180.8	0	180.2	0
$CH_2DCH{=}OH^+$	184.4	9.0	183.6	8.9	175.2	8.6	172.3	8.5	171.8	8.4
$CHD_2CH{=}OH^+$	175.6	17.8	175.1	17.4	167.0	16.8	164.3	16.5	163.8	16.4
$CD_3CH{=}OH^+$	167.0	26.4	166.4	26.1	158.6	25.2	156.2	24.6	155.7	24.5

[a] kilojoules per mole; values not scaled. [b] zpve(unlabeled) − zpve(labeled).

TABLE 3: Sum of the Zero-Point Vibrational Energies of the Possible Products Formed by Dissociation of the $CD_3CHOHCH(CH_3)_2$ and $CH_3CHOHCD(CH_3)_2$ Radical Cations[a]

	HF/6-31G(d)		HF/6-31++G(d,p)		MP2/6-31G(d)		B3PW91/6-31G(d)		B3LYP/6-31G(d)	
	zpve	Δ[b]	zpve	Δ[b]	zpve	Δ[b]	zpve	Δ[b]	zpve	Δ[b]
$CD_3CH{=}OH^+ + {}^•CH(CH_3)_2$	415.2	0.5	412.3	0.6	398.4	0.5	389.4	0.4	388.3	0.4
$CHD_2CH{=}OH^+ + {}^•CD(CH_3)_2$	415.7		412.9		398.9		389.8		388.7	
$CD_2{=}CHOH^{+•} + CHD(CH_3)_2$	423.5		420.3		406.1		398.1		397.1	
$CHD{=}CHOH^{+•} + CD_2(CH_3)_2$	422.6	0.9	419.5	0.8	405.3	0.8	397.4	0.7	396.4	0.7
$CH_2DCH{=}OH^+ + {}^•CH(CH_3)_2$	432.6	0.9	429.4	0.9	415.0	0.7	405.5	0.8	404.4	0.7
$CH_3CH{=}OH^+ + {}^•CD(CH_3)_2$	433.5		430.3		415.7		406.3		405.1	
$CHD{=}CHOH^{+•} + CH_2(CH_3)_2$	441.2		437.9		423.3		415.0		413.9	
$CH_2{=}CHOH^{+•} + CHD(CH_3)_2$	440.4	0.8	437.1	0.8	422.4	0.9	414.1	0.9	413.1	0.8

[a] kilojoules per mole; values not scaled. [b] Energy difference favoring the more stable product pair.

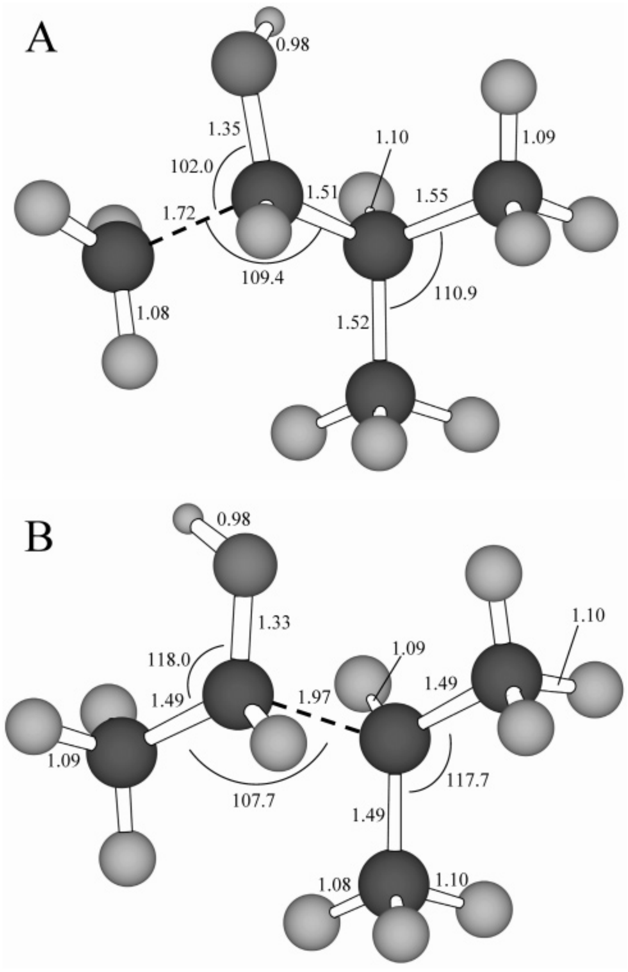


Figure 1. Long-bond 3-methyl-2-butanol radical cations.

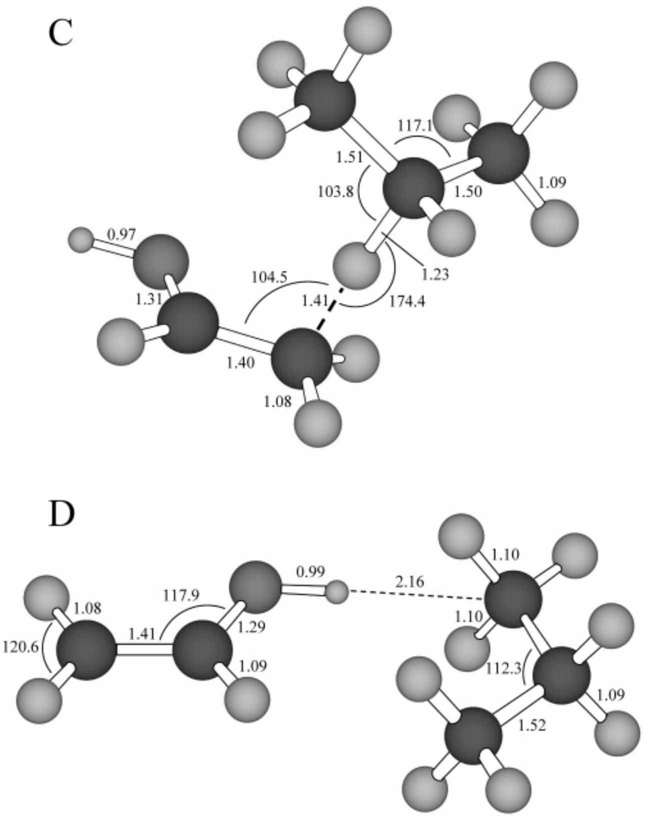


Figure 2. Propane−vinyl alcohol$^{+\bullet}$ complexes.

The Intermediate Complexes. The reactions of ionized (1,1,1-D_3)-3-methyl-2-butanol, **1**, illustrate that dissociation need not follow immediately when the hydrogen atom transfer is almost thermoneutral[3,19] and that a long-lived complex of ionized vinyl alcohol with propane exists. The computational results suggest that several such complexes may be formed. These fall into two distinct groups, one, **C**, where the two components are sandwiched over one another, with the vinyl alcohol CC bond almost parallel to one of the propane CC bonds, so that the two methylene groups are relatively close to each other, and another, **D**, where the vinyl alcohol OH group points toward the propane and the CH_2 away (Figure 2).

DFT, MP2, and CCSD calculations with a variety of basis sets suggest that the structure of the typical **C** complex is quite similar to that expected for a transition state for hydrogen atom transfer between the methylene groups of the vinyl alcohol and the propane (Figure 2). The two components are connected by a C−H−C hydrogen atom bridge, in which the C−H distances are approximately 1.25 and 1.42 Å, respectively, and the C−H−C grouping is almost linear; the exact values are somewhat dependent upon the method and basis set (Table 5). Determination of the vibrational frequencies with each of the various MP2 and DFT methods employed confirms that complex **C** is a proper minimum on the potential energy surface, even though there is in each case at least one very low calculated mode (below 30 cm^{-1}).

The results obtained with all methods employed suggest that the potential energy surface in the vicinity of **C** is quite flat. There is a small barrier (<2 kJ mol^{-1}) toward 360° rotation of propane with respect to the vinyl alcohol. Likewise, variation of the C−H bond lengths of the bridging hydrogen atom changes the electronic energy very little: partial B3LYP/6-31G(d) optimization with the CH_2−H bond length fixed at values between 1.25 and 1.85 Å at 0.05 Å intervals shows <4 kJ mol^{-1} variation of the electronic energy of the complex. The distance between the two methylene carbon atoms varies as the H atom is moved; it is 2.67 Å in the unconstrained complex and increases to ∼3 Å when the H is furthest from the equilibrium position. The results of CCSD(T)/6-31G(d) single-point energy

TABLE 4: Long-Bond 3-Methyl-2-butanol Molecular Ions[a]

		C(1)−C(2)	C(2)−C(3)	ΔH_f	method/basis
A	CH_3−CHOHCH(CH_3)$_2$	1.73	1.52		MP2/6-31G(d)
		1.72	1.51	634	MP2(fu)/6-31+G(d,p)
B	CH_3CHOH−CH(CH_3)$_2$	1.49	1.96		MP2/6-31G(d)
		1.49	1.97	592[b]	MP2(fu)/6-31+G(d,p)
		1.50	1.99		CCSD/6-31G(d)
		1.50	1.98		QCISD/6-31G(d)
		1.49	2.09	590	B3LYP/6-31G(d)
		1.49	2.14		B3LYP/6-311G(d,p)

[a] CC distances in angstroms; G3 (respectively G3//B3LYP) 298 K heats of formation in kilojoules per mole. [b] Calculated using MP2 frequencies, scaled by 0.9434, as suggested by Scott and Radom, ref 38.

TABLE 5: Propane−Vinyl Alcohol$^{+\bullet}$ Complexes[a]

C	$(CH_3)_2CH-H-CH_2CHOH^{+\bullet}$		C−H−C	ΔH_f	
	1.23	1.43	174		MP2/6-31G(d)
	1.23	1.41	174	629	MP2(fu)/6-31+G(d,p)
	1.23	1.42	173		MP2/6-311G(d,p)
	1.22	1.45	173		CCSD/6-31+G(d,p)
	1.23	1.45	173		CCSD/6-311G(d,p)
	1.22	1.47	172		QCISD/6-311G(d,p)
	1.26	1.45	171	629	B3LYP/6-31G(d)
	1.29	1.39	171		B3LYP/6-31+G(d,p)
	1.28	1.42	171		B3LYP/6-311G(d,p)
TS(**B** → **C**)				661	MP2(fu)/6-31+G(d,p)
TS(**C** → **C**)				642	B3LYP/6-31G(d)
D	$(CH_3)_2CH_2,HOCH{=}CH_2^{+\bullet}$			626	MP2(fu)/6-31+G(d,p)

[a] Typical CH distances in angstroms, angles in degrees; G3 (respectively G3//B3LYP) 298 K heats of formation in kilojoules per mole.

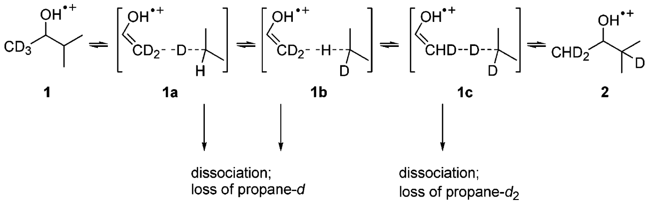
calculations at each of these intermediate situations also show ~4 kJ mol^{-1} variation, which confirms that the electronic energy of the complex only changes little as the hydrogen atom is moved between the two components. Furthermore, the CCSD(T) energy shows a mininum at a CH_2-H distance of ~1.45 Å, which indicates that the hydrogen-bridged form would be a proper minimum on the potential energy surface also when examined with methods incorporating very high levels of electron correlation. However, our computational resources do not allow us to examine this possibility in more detail for systems of this size. The calculated C−H stretching frequency for the bridging hydrogen is ~1600 cm^{-1}, in reasonable agreement with the empirical relationship between bond length and harmonic stretching frequency known as Badger's rule.[30]

The G3 heat of formation of the **C** complex, 629 kJ mol^{-1}, is close to that of one of the molecular ion isomers, **A**, midway between that of the long-bond form of the molecular ion (**B**) and that of the separated products. The ionized vinyl alcohol component of **C** is the anti form; the calculated heat of formation of the complex incorporating the syn form is some 9 kJ mol^{-1} higher, about the same energy difference as that between the two conformers of ionized vinyl alcohol.[31]

The calculated heats of formation of the various **D** complexes are almost the same, close to that of complex **C**; the electronic energy of the **D** complexes is well below that of the **C** complexes (by ~15 kJ mol^{-1}), but that is offset by the difference between the zero-point vibrational energies. The structure of **D** is such that the methylene groups of the two components are about as far from each other as possible, and considerable reorganization would be required for these complexes to be directly involved in the hydrogen exchange reactions or otherwise contribute to the transformations that cause **1** to expel propane. The **D** complexes of *syn*-vinyl alcohol$^{+\bullet}$ are also some 9 kJ mol^{-1} higher in energy than those incorporating the anti form; the CC bond of the *syn*-vinyl alcohol is almost parallel to the propane C(1)−C(3), that is, ~90° different from that shown in Figure 2. This indicates that the ion-induced dipole interactions in the syn and anti complexes are quite different.

The collision experiments reported previously[3,4] show that the loss of propane is among the efficiently collision-induced reactions of the undecomposed $C_5H_{12}O^{+\bullet}$ ions, which demonstrates that a considerable proportion of these ions have been converted to propane−vinyl alcohol$^{+\bullet}$ complexes prior to collision. We are not suggesting that the relative yield of the collision-induced dissociation reactions will provide a reliable measure of the composition of the reactant ion population, but it ought to provide a reasonable guide in this case, inasmuch as it is unlikely that propane loss will contribute in a major way to the collision-induced reactions of intact molecular ions, since propane loss is not among the prominent ion-source reactions of the ionized parent alcohol. We note in this context that the calculated heats of formation of the propane−vinyl alcohol complexes are close to the experimentally determined heat of formation of the molecular ion; it follows that nearly all the $C_5H_{12}O^{+\bullet}$ species will possess sufficient internal energy to undergo conversion to the intermediate complexes.

SCHEME 2: Reactions of the Metastable (1,1,1-D$_3$)-3-Methyl-2-butanol Radical Cation, 1



H/D Exchange. The initial CC cleavage of **1** followed by D transfer yields the propane-*d* and vinyl alcohol-$d_2^{+\bullet}$ pair (**1a** and **1b** in Scheme 2). However, H/D permutation must precede dissociation, inasmuch as propane-d_2 is the predominating neutral product[3,4] (Table 1); that is, further isomerization to produce **1c** precedes dissociation. The occurrence of multiple hydrogen atom transfer reactions demonstrates that dissociation of the [propane/vinyl alcohol]$^{+\bullet}$ complex is less rapid than reversal of the hydrogen atom transfer (Scheme 2).

Permutation of the initial positions of the deuterium atoms between C1 and C3 does not change the outcome of the reactions. The radical cation of (1,1,3-D$_3$)-3-methyl-2-butanol, **2**, expells propane-*d* and propane-d_2 in approximately the same ratio as does **1**. The CC cleavage and hydrogen transfer reactions of **2** will initially give rise to **1b** or **1c**.

The deuterium labeled methyl and ethyl ethers, **5** and **6**, behave similarly, losing predominantly propane-d_2 (Table 1). Correspondingly, the loss of propane-*d* from the monodeuterated alcohol, **3**, is preferred over the loss of unlabeled propane, and the loss of propane-d_2 is the preferred reaction of the dideuterated alcohol, **4**. The labeled analogues examined by George and Holmes[4] also exhibit a strong preference for the inclusion of deuterium in the neutral propane molecule.

The hydrogen atom exchange involves three distinct steps: conversion of the long-bond molecular ion to a propane−vinyl alcohol complex by hydrogen atom transfer from protonated acetaldehyde to the isopropyl radical (formed by attempted α-cleavage), interchange of the bridging hydrogen and the remaining hydrogen of the propane methylene group, and interchange of the bridging hydrogen and the hydrogen atoms of the vinyl alcohol methylene group. All three steps are reversible.

It appears[3,4,32] that also the initial CC cleavage of the molecular ion is a reversible process, inasmuch as the collision-induced reactions of the deuterium labeled molecular ions include elimination of methyl and isopropyl radicals that have undergone hydrogen atom exchange, presumably via the reversible formation of propane−vinyl alcohol$^{+\bullet}$ complexes. Furthermore, George and Holmes[4] point out that the collision-induced loss of methyl radicals gives rise to an unexpectedly weak signal. This observation is consistent with reversible (re)formation of molecular ions of structure **B**, which would not be expected to readily expel methyl radicals.

H transfer between the methylene groups of complex **C** requires only little reorganization. However, many attempts notwithstanding, our calculations have not allowed us to unambiguously identify transition states for the hydrogen atom interchange, nor a transition state for the formation of **C** from **B** (or **A**). A possible transition state for the formation of complex **C** from the long-bond molecular ion **B** was located with MP2 methods; however, it was not possible to find a related structure with DFT methods. A frequency calculation showed one imaginary frequency, and IRC calculations confirmed that the transition state connects **B** and **C** ions. The G3 heat of formation is only a few kilojoules per mole below that of the final products (Table 5); the zpve difference between transition states for the transfer of H and D in deuterium-containing ions was 0.6 kJ mol^{-1}.

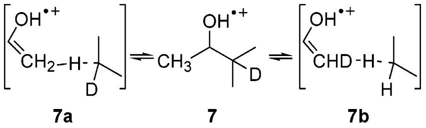
A possible transition state for permutation of the two hydrogen atoms of the propane methylene group in complex **C** was located at the B3LYP/6-31G(d) level. A frequency calculation showed one imaginary frequency, and IRC calculations confirmed that the transition state connects two **C** type complexes. The structure is without very unusual bond lengths; the CH distances in the propane methylene group are both ∼1.10 A, and the distances to the terminal vinyl alcohol carbon atom are both ∼2.50 A. The G3//B3LYP heat of formation is 13 kJ mol^{-1} higher than that of the **C** complex. We did not succeed in locating a related structure with MP2 methods.

Isotope Effects. The preference observed for the loss of propane-d_2 from ion **1** either can reflect isotope effects on the formation or interconversion of complexes with propane-*d* or propane-d_2 (Scheme 2) or may show that the rates of dissociation via **1a** (or **1b**) and **1c** differ as the result of isotopic substitution.

The involvement of three D atoms and one H atom in the hydrogen atom exchange reactions of **1** should in the absence of isotope effects result in an equal probability for loss of propane-d_2 and propane-*d*, quite different from that observed, 33:1. The dissociation of the 1,1-dideuterated alcohol, **4**, results in a 9:1 preference for losing propane-d_2 over propane-*d* and virtually no loss of unlabeled propane (Table 1). However, the isotopic preference is in fact the same as that for **1**, inasmuch as the reciprocal hydrogen transfer reactions of **4** involve two D atoms and two H atoms, and the formation of complexes with one D atom in each component is in turn 4 times as likely as forming a complex with two D atoms in the propane molecule.

To bring about such a remarkable preference for the transfer of D rather than H to the isopropyl radical, an inverse isotope effect of unusual magnitude would be required. However, hydrogen atom abstraction in closely related systems is subject to normal primary isotope effects, and the discrimination against the transfer of D can be quite pronounced. McAdoo and coworkers[18] reported a primary isotope effect of approximately 60 on the hydrogen atom abstraction involved when methane is expelled from methyl isopropyl ether radical cations, and normal primary hydrogen isotope effects have also been reported for the alkane loss from other alcohol and ether radical cations.[22,28,29,33]

SCHEME 3: Loss of Propane from the 1-D-3-Methyl-2-butanol Radical Cation, 7



Zero-Point Vibrational Energy Differences. Alternatively, the preference for the loss of propane-d_2 from **1** could reflect the properties of the intermediate complexes of propane and ionized vinyl alcohol. In particular, the hydrogen-bridged complex, **C**, might exhibit isotope-dependent properties that would influence the formation and dissociation of these intermediates. Considering the interconverting species **1a**, **1b**, and **1c**, the difference between the zero-point vibrational energies is such that the H-bridged ion, **1b**, is lower in energy than the D-bridged ions, **1a** and **1c**, by ∼3 kJ mol^{-1}. The results of the collision experiments[4] are consistent with this, inasmuch as the undecomposed molecular ions (*m*/*z* 91, ions that may be present as **1**, **2**, **1a**, **1b**, or **1c**) upon collisional activation dissociate by the loss of propane-*d* to a considerably greater extent than by the loss of propane-d_2. This implies that **1b** (**1a**) is present in greater amounts than **1c**. The observation that the predominant spontaneous reaction of the metastable **1** ions nonetheless is dissociation via **1c** could in turn be taken to reflect that the C−D−C bond in **1c** is less strong than the C−H−C bond in **1b**. However, the reactions of the monodeuterated analogue, **7**, reported by Georges and Holmes[4] demonstrate that the isotopic preference is just as strong when the complex that will yield the more abundant products is not of necessity D-bridged. Ion **7** eliminates propane-*d* to a much greater extent than unlabeled propane, even though the lower-energy forms of the intermediate complexes, **7a** and **7b**, are both H-bridged rather than D-bridged (Scheme 3).

The interconversion of the propane−vinyl alcohol$^{+\bullet}$ complexes is, as noted above, more rapid than the dissociation of the complexes. The ubiquitous preference for the incorporation of deuterium into the propane will therefore reflect differences between the transition states for the final dissociation, inasmuch as the loss of propane from 3-methyl-2-butanol ions does not appear to involve isotope sensitive steps that have pronounced enthalpy barriers.

The simple separation of the components of an electrostatically bonded ion-neutral complex should not involve significant reverse activation barriers,[19,24,34,35] and any (small) barrier present should influence the dissociation of the isotopically different complexes equally. However, the isotopic substitution will cause the zero-point vibrational energy (zpve) contribution to the potential energy of each of the separated product pairs to be different. It follows that the transition states for dissociation will differ in energy by an amount that is close to the difference between the zpve's of the incipient product pairs. We have calculated the zpve's of the various isotope labeled ions and neutrals involved in the reactions of **1** with a variety of quantum mechanical procedures (Table 2) and found that the zpve of the propane-d_2/vinyl alcohol-*d* pair is lower than the zpve of the propane-*d*/vinyl alcohol-d_2 pair. The difference is on the order of 1 kJ mol^{-1} (Table 3).

RRKM Calculations. To examine if critical energy differences this small can resonably be expected to account for the isotopic preferences observed, we have used a simple RRKM model to describe the competing dissociation reactions of **1** that result in the loss of propane-*d* and propane-d_2, employing previously described programs[36] to calculate state sums and densities of state, and the derived relative probabilities of reaction in the field-free region (which correspond to the observed abundance ratios).

To estimate the magnitude of the isotope effects on the dissociation reactions within a simple RRKM framework, it is necessary to know the energy distribution of the reacting ions, in particular the upper limit to the excess energy in the transition state, the critical energy of each of the isotopically different reactions, and the vibrational frequencies of the reactant and the transition states.

If small critical energy differences are to be significant, the reacting ions must possess a narrowly delimited and quite low internal energy. It is possible to assess the energy distribution in the present case by considering that the rate constants of the simple cleavage reactions of ions such as **1** will increase very rapidly with the internal energy of the ion, because the critical energies of these reactions,[4] loss of methyl and isopropyl radicals, are only a few tenths of an electronvolt. It follows that most of those molecular ions that do not dissociate already in the mass spectrometer ion source will not possess sufficient energy to undergo the simple cleavage reactions. In other words, the energy distribution of the metastable molecular ions will be upwardly delimited by the energy required by the simple cleavage reactions that take place in the ion source.

The reaction to take into account is the simple cleavage reaction that involves the loss of isopropyl radicals. The 20 kJ mol^{-1} difference between the sum of the G3 heats of formation of the products when an isopropyl radical is lost and when propane is lost is taken as an estimate of the upper limit to the excess energy in the transition state. An even lower value would be obtained if the estimate were based on the energy required for the loss of methyl radicals from the molecular ion. However, for the long-bond molecular ion **B**, this reaction would not be a straightforward simple cleavage; $k(E)$ for methyl loss would therefore not be expected to rise rapidly with increasing E, and the depletion of the reactant ion population would not be as efficient. These considerations are in agreement with the observation[4] that the loss of $CH_3^{\bullet}$ contributes much less to the mass spectrum than does the loss of $C_3H_7^{\bullet}$, even though the latter reaction has the higher appearance energy.

The critical energy of loss of propane in the absence of isotopic substitution can be derived directly from the calculated heats of formation of the reactant and the products, and the calculated vibrational frequencies yield the difference between the critical energies, that is, the difference between the zero-point vibrational energy of the isotopically different product pairs (Table 3). The transition state frequencies are taken to be the vibrational frequencies of the products, together with the five low-frequency modes of the complex that become the external degrees of freedom as the dissociation completes; the values adopted for these frequencies are half the numerical value[35,37] of the five lower-frequency modes of the **D** complex (in which there are no C−H−C interactions).

RRKM calculations based on the values described above predict a propane-d_2/propane-*d* ratio of 17, which compares reasonably well with the experimental value 33. However, this correspondence is to some extent fortuitous, inasmuch as the application of a model that treats all degrees of freedom as vibrations and does not take into account rotational effects and anharmonicity cannot be expected to yield reliable quantitative information, even though these deficiencies will be less serious when the model is used to derive ratios of rate constants rather than absolute rate constants. This allows us to use such a model to examine whether order-of-magnitude agreement can be obtained and to conclude that it is indeed physically reasonable to suggest that a 1 kJ mol^{-1} critical energy difference is sufficient to cause quite large differences in relative ion yield for two very closely related competing reactions.

Conclusions

At least three reciprocal hydrogen atom transfers are required to form the predominating products, the neutral propane-d_2 and vinyl alcohol-*d* radical cations, when metastable 3-methyl-2-butanol-d_3 molecular ions dissociate. The H exchange demonstrates the interconversion of intermediate ion-neutral complexes, and the computational results suggest that these intermediates possess quite unusual C−H−C hydrogen bridging. However, the competition between the loss of propane-*d* and propane-d_2 is determined not by the isotope-dependent properties of the ion-neutral complexes but by the relative energies of the two transition states for the final dissociation. The two transition states will very much resemble the incipient products, and the transition state leading to the lower-energy products will in turn be the lower-energy transition state. The zero-point vibrational energy difference between the product pairs gives rise to a kinetic isotope effect. We note that in a sense the two possible propane/vinyl alcohol product pairs are not formed by dissociation of the same reactant. However, a system of interconverting complexes separated by relative low barriers will in a very real sense behave like a covalently bonded system at internal conformational equilibrium and can be considered as a single system with two exit channels.

Comparison of the behavior of isolated, nonthermal systems with that of systems that obey equilibrium thermodynamics is full of pitfalls, but we notice that an energy difference of 1 kJ mol^{-1} for a thermal system at equilibrium at 40 K translates into an equilibrium constant of 20. We take this to illustrate that a transition state energy difference this low can indeed have remarkable effects on the competing reactions of any system with sufficiently low internal energy, and we find that the reactions of the metastable molecular ions of 3-methyl-2-butanol provide an illustrative example.

Acknowledgment. We gratefully acknowledge illuminating exchanges of views with Dr. T. I. Sølling and professor P. J. Derrick, and we thank professor Derrick and Dr. H. E. Audier for instrument time during the early stages of this investigation.

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