Isomeric Ion-Neutral Complexes Generated from Ionized 2-Methylpropanol and *n*-Butanol: the Effect of the Polarity of the Neutral Partner on Complex-Mediated Reactions

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Photoionization was used to characterize the energy dependence of $C_3H_7^+$, $C_3H_6^+$, $CH_3OH_2^+$, and $CH_2=OH^+$ formation from $(CH_3)_2CHCH_2OH^+$ (1) and $CH_3CH_2CH_2CH_2OH^+$ (2). Decomposition patterns of labeled ions demonstrate that close to threshold these products are primarily formed through $[CH_3^+CHCH_3 \cdots CH_2OH]$ (3) from 1 and through $[CH_3CH_2CH_2 \cdots CH_2=OH^+]$ (9) from 2. The onset energies for forming the above products from 1 are spread over 85 kJ mol⁻¹, and are all near thermochemical threshold. The corresponding onsets from 2 are in a 19 kJ mol⁻¹ range, and all except that of $CH_2=OH^+$ are well above their thermochemical thresholds. Each decomposition of 3 occurs over a broad energy range (> 214 kJ mol⁻¹). This demonstrates that ion-permanent dipole complexes can be significant intermediates over a much wider energy range than ion-induced dipole complexes can be. H-exchange between partners in the complexes appears to be much faster than exchange by conventional interconversions of the alcohol molecular ions with their distonic isomers. The onsets for water elimination from 1 and 2 are below the onsets for the complex-mediated processes, demonstrating that the latter are not necessarily the lowest energy decompositions of a given ion when the neutral partner in the complex is polar. (*J Am Soc Mass Spectrom* 1992, 3, 409-416)

Many unimolecular decompositions of ions in the gas phase take place by reactions between electrostatically bound partners created by dissociation of a bond in the initially formed ion [1]. The following expression from the average dipole orientation theory of ion-molecule reactions [2] indicates the components of the interaction potential at the distances that exist between the partners in ion-neutral complexes.

$$U = -\mu_D q \cos \theta / r^2 - \alpha q^2 / 2r^4 + L^2 / q\mu r^2 \quad (1)$$

In this expression μ_D is the dipole moment of the neutral, q is the charge on the ion, θ is the average angle between the dipole moment and the line of collision, r is the distance between the particles, α is the polarizability of the neutral, L is the orbital angu-

lar momentum of the two particles, and μ is the reduced mass of the two particles. When present, a large dipole moment is the major contributor to the attraction between the partners. Therefore, a large dipole moment in the neutral may considerably expand the energy range over which an ion-neutral complex is a significant intermediate [3, 4], a possibility we further explore here.

Complex-mediated reactions include the formation of protonated species from ionized 2-methylpropanol (1), neopentyl alcohol, neopentyl ethers, and neopentyl amines [5]. Such products are much less abundant in the spectra of the isomeric straight chain isomers. Differences in decomposition patterns could stem from formation of the ion-dipole complex $[CH_3^+CHCH_3 \cdots CH_2OH]$ (3) from 1 and the ion-induced dipole complex $[CH_3CH_2CH_2 \cdots CH_2=OH^+]$ (9) from 2. Formation of these isomeric complexes would permit comparison of the energy dependencies of complex-mediated reactions involving polar and nonpolar neutral partners. To broaden our knowledge of these

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energy dependencies, we examined the formation of CH_3OH_2^+ and the mechanistically related products C_3H_7^+ , C_3H_6^+ and $\text{CH}_2=\text{OH}^+$ from **1** and **2**.

Results and Discussion

Fragmentations of ionized 2-methylpropanol. A potential energy diagram representing the reactions of **1** that will be considered is given in Figure 1. A partial mass spectrum of 2-methylpropanol at 12.60 eV photon energy is given in Table 1. At this energy, the dominant fragments are C_3H_7^+ , C_3H_6^+ and CH_3OH_2^+ .

The H-transfers that form methanol suggest that the main pathway from **1** to CH_3OH_2^+ is $1 \rightarrow 3 \rightarrow 4 \rightarrow 5$ (Scheme I). At $\sim 2 \times 10^{-11}$ s CH_2DOH is specifically eliminated from 1-3,3,3,3',3'-d₆ [6]. This requires methanol formation by H-transfer to C1 in **3** or $[\text{CH}_3\text{CHCH}_3 \text{CH}_2=\text{OH}^+]$, as going by way of $^-\text{CD}_2\text{CH}(\text{CD}_3)\text{CH}_2\text{OHD}^+ \rightarrow [^-\text{CH}_2\text{OHD}^+\text{CD}_2=\text{CHCD}_3]$ (Scheme II) would produce as much CH_3DOD as CH_3DOH (assuming small isotope effects). $[\text{CH}_3\text{CHCH}_3 \text{CH}_2=\text{OH}^+]$ would be less stable than **3** because, in addition to the 23 kJ mol⁻¹ lesser stability of the separated partners, ion-dipole

Table 1. Partial mass spectra of 2-methylpropanol and *n*-butanol

<i>m/z</i>	2-Methylpropanol	<i>n</i> -Butanol
31	0.07	0.14
33	1.00	0.05
42	1.00	0.18
43	0.96	0.19
56	0.09	1.00
74	0.36	0.03

Spectra were obtained on a photoionization mass spectrometer at a photon energy of 12.60 eV.

attractions (eq 1) enhance the stability of **3** relative to that of $[\text{CH}_3\text{CHCH}_3 \text{CH}_2=\text{OH}^+]$. Thus only **3** would be formed near threshold.

An alternate pathway that would account for the exchange is presented in Scheme III. This process can be ruled out however, as reactions such as the first step seem not to occur [7], and ionized *i*-propyl methyl ether does not interconvert with its ylid isomer. Protonated methanol is therefore probably formed by $4 \rightarrow 5$, as $1 \rightarrow 3 \rightarrow 4$ seems demonstrated.

The pathway to water elimination from **1** [8] and a

Figure 1. Potential energy diagram for the reactions of ionized 2-methylpropanol (**1**). The dissociated species and **1** are placed according to the heats of formation in Table 1, except $\text{CH}_3\text{OH}_2^+ + \text{CH}_2\text{CHCH}_2$ is placed according to its appearance energy. $[\text{CH}_3\text{CHCH}_3 \text{CH}_2\text{OH}]^+$ is at $\text{AE}(\text{CH}_3\text{OH}_2^+)$. The transition state for $1 \rightarrow 6$ is at $\text{AE}(\text{C}_4\text{H}_8^+)$. Because $\Delta H_f(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}_2^+)$ is 17 kJ mol⁻¹ below $\Delta H_f(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+)$ [22], **6** is placed 17 kJ mol⁻¹ below **1**. An attraction of 59 kJ mol⁻¹ between polar neutrals and ions was assumed based on $\text{AE}(\text{C}_3\text{H}_7^+) - \text{AE}(\text{CH}_3\text{OH}_2^+)$. On this basis $\Delta H_f(\text{4})$ was placed 59 kJ mol⁻¹ below the combined heats of formation of its separated partners. An attraction of 30 kJ mol⁻¹ was assumed between the thresholds for propyl and propane losses based on a difference of at least 28 kJ mol⁻¹ between the thresholds for propyl and propane losses from ionized 2-methoxypentane [15d].

Scheme I

related potential pathway to CH_3OH_2^+ is given in Scheme II.

The initial H-transfer in Scheme II must precede H_2O elimination, the dominant metastable decomposition of 1 [9] (see below). However, there is no exchange between the hydroxyl and methyl hydrogens of 1 before metastable elimination of water [6], so exchange by $1 \rightleftharpoons 6$ is not significant. This contrasts with substantial exchange of the hydroxyl and methyl hydrogens of 1 prior to formation of both $\text{CH}_3\text{CH}=\text{CH}_2^+$ and CH_3OH_2^+ [5a, 6]. The differences in H-exchange require initiation of water elimination and CH_3OH_2^+ formation from 1 by distinct processes, i.e., CH_3OH_2^+ is produced according to Scheme I and water is eliminated according to Scheme II. CH_3OH_2^+ is probably not formed by $6 \rightarrow 7 \rightarrow 5$ because of competition from the lower energy pathway $1 \rightarrow 3 \rightarrow 4 \rightarrow 5$. ($\Delta H_f(\text{CH}_3\text{CH}=\text{CH}_2) + \Delta H_f(\text{CH}_2\text{OH}_2^+)$ is 62 kJ mol^{-1} above $\Delta H_f(\text{i-C}_3\text{H}_7^+) + \Delta H_f(\text{CH}_2\text{OH})$ and 78 kJ mol^{-1} above $\Delta H_f(\text{CH}_3\text{CH}=\text{CH}_2^+) + \Delta H_f(\text{CH}_3\text{OH})$; heats of formation of the individual species are given in Table 2.) The difference in exchange patterns answers the challenging question [10]: Does exchange in this system occur by intercon-

Scheme II

sion of complexes (Scheme I) or by reversible isomerization (Scheme II)? It occurs by interconversion of complexes.

By $\sim 4 \times 10^{-10}$ s, near randomization of methyl and hydroxyl hydrogens accompanies CH_3OH_2^+ formation [6]. This is considerably faster than H-exchange by interconversion of distonic ions, which can take 10^{-8} – 10^{-7} s to become appreciable [11]. This suggests that complex-mediated H-exchange can be orders of magnitude faster than conventional H-transfers in ions.

Exchange of the C1 hydrogens is much slower than exchange of the hydroxyl and methyl hydrogens in 1 [5a, 6]. This presumably reflects a higher rate of $4 \rightleftharpoons 5$ than of $4 \rightleftharpoons 3$. Such a higher rate is plausible, because 5 is more stable than 3 (Figure 1). The dominant exchange could also reflect a preferred orientation of the negative end of the dipole of methanol toward the charged partner in 4, as such a preferred orientation is reflected in low energy ion-molecule reactions of methanol [12]. The alternative exchange mechanism, $4 \rightleftharpoons [\text{CH}_3^+\text{CHCH}_3 \cdots \text{OCH}_3]$ is less likely because the last complex would be about 41 kJ mol^{-1} ($\Delta H_f[\text{CH}_3\text{O}^\cdot] - \Delta H_f[\text{CH}_2\text{OH}]$) higher in energy than 3.

Energy dependence of the complex-mediated fragmentations of 1. We obtained the onsets and energy dependen-

Table 2. Pertinent heats of formation

$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	-283.6	$(\text{CH}_3)_2\text{CHCH}_2\text{OH}^+$	692
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	-275	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}^+$	696
$\text{CH}_3^+\text{CHCH}_3$	93.3	$\text{CH}_3^+\text{CHCH}_3$	798.9
$\text{CH}_3\text{CH}_2\text{CH}_2^\cdot$	100.5	$\text{CH}_3\text{CH}_2\text{CH}_2^+$	881
$\text{CH}_3\text{CH}=\text{CH}_2$	20.2	$\text{CH}_3\text{CH}=\text{CH}_2^+$	959
$\text{CH}_2\text{CH}_2\text{CH}_2$	53.3	$\text{CH}_2\text{CH}_2\text{CH}_2^+$	1004
$\text{CH}_2\text{CHCH}_2^\cdot$	165.2 ^a	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2^\cdot$	924
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^+$	985	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}_2^\cdot$	874
$\text{CH}_3\text{CHCH}_2\text{CH}_2^+$	938	H_2O	-241.8
CH_2OH	-25.9	$\text{CH}_2=\text{OH}^+$	703
CH_3OH	-201.6	CH_3OH^+	845.3
CH_2OH_2^+	815	CH_3OH_2^+	567
$\text{CH}_3\text{O}^\cdot$	15.5		

^a Value from ref 21; all other values from ref 22.

Scheme III

cies of the reactions examined here by determining photoionization efficiency curves [13]. Our results (Table 3) are in reasonable agreement with ones from an earlier study [14], except that our $\text{AE}(\text{C}_3\text{H}_7^+)$ is 27 kJ mol^{-1} below that previously reported, and our $\text{AE}(\text{C}_3\text{H}_6^+)$ is 26 kJ mol^{-1} lower. The onsets of C_3H_7^+ , C_3H_6^+ , CH_3OH_2^+ , and $\text{CH}_2=\text{OH}^+$ formation from 2-methylpropanol (1) cover an 85 kJ mol^{-1} energy range. However, all are close to corresponding thermochemical thresholds (see Table 3). If Scheme I is correct in assuming that the second and third species are formed through 3, that complex must form down to at least 59 kJ mol^{-1} ($\text{AE}[\text{C}_3\text{H}_7^+] - \text{AE}[\text{CH}_3\text{OH}_2^+]$) below the threshold for dissociation of 3. This indicates much stronger attractions in 3 than in ion-nonpolar neutral complexes, as eliminations through the latter usually begin no more than about 20–30 kJ mol^{-1} below the threshold for simple dissociation of the initial partners [15].

Eliminations through ion-nonpolar neutral complexes rapidly diminish in importance as the energy in the system rises above the threshold for simple dissociation of the initial partners [15–17]. Significant evidence for this is that PIE curves for eliminations involving H-abstractions by alkyl radical partners level off just above the thresholds for simple dissociation of complexes [15]. Because the threshold law for photoionization is a step function for each product state, the number of ions formed containing the energy

$h\nu - \text{IE}$ is proportional to the slope of the PIE curve [18]. The PIE curves for C_3H_6^+ and CH_3OH_2^+ formed from 1 rise without leveling up to at least 181 and 214 kJ mol^{-1} above their onsets (Figure 2). This demonstrates that H-transfers in 3 and 4 take place well above the thresholds for their simple dissociation. Therefore ion-dipole complexes can be significant intermediates over a much wider energy range than can ion-induced dipole complexes. Recent photoionization efficiency curves for fragmentations through alcohol-containing [3] and alkoxy-containing [4] complexes support this conclusion.

Ionized n-butanol (2). Like 1, ionized *n*-butanol (2) fragments to C_3H_7^+ , C_3H_6^+ , CH_3OH_2^+ , and $\text{CH}_2=\text{OH}^+$, although the abundance of CH_3OH_2^+ is lower and the loss of water dominant (see Table 1). In contrast to formation of 3 from 1, the charge might go to either fragment during complex-forming alpha cleavage of 2 near threshold. Based on the heats of formation of the dissociated partners and estimated binding energies, the complex containing $\text{CH}_2=\text{OH}^+$ should be the more stable one (Figure 3), although either complex is energetically accessible at the threshold for forming $\text{CH}_3\text{CH}_2\text{CH}_2^+ + \text{CH}_2=\text{OH}^+$.

Assuming that concerted eliminations do not occur at low energies, the distribution of labels in protonated methanols produced from deuterated forms of 2 (Table 4) demonstrates that $2 \rightarrow 9$ occurs. Although there was H-transfer from all positions in the propyl to both O and C of the protonated methanol daughter, there was a preference for transfer from C3 to the carbon and from C4 (numbering as in 2) to the oxy-

Table 3. Photoionization appearance energies for butanols (kJ mol^{-1})

<i>m/z</i>	2-Methylpropanol			<i>n</i> -Butanol		
	Present	Predicted	Ref 14	Present	Expected	Ref 14
74	971 ± 3		967 ± 5	964 ± 3		964
56	1000 ± 2	916 ^a , 980 ^b	997 ± 3	981 ± 2	971 ^b , 1018 ^c , 957 ^d	982
43	1061 ± 5	1057 ^e	1088 ± 3	1084 ± 5	1048 ^e , 1130 ^f	
42	1035 ± 3	1041 ^g , 1086 ^h	1061 ± 3	1074 ± 5	1032 ^g , 1077 ^h	
33	1002 ± 3	1012	1006 ± 3	1069 ± 5	1003	
31	1087 ± 3	1080 ⁱ		1088 ± 3	1078 ⁱ	

Products associated with the predicted thresholds

^a $\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}_2^+$

^b $\text{CH}_3\text{CHCH}_2\text{CH}_2^+$

^c $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^+$

^d $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2^+$

^e $\text{CH}_3^+\text{CHCH}_3$

^f $\text{CH}_3\text{CH}_2\text{CH}_2^+$

^g $\text{CH}_3\text{CH}=\text{CH}_2^+$

^h $\text{CH}_2\text{CH}_2\text{CH}_2^+$

ⁱ CH_3CHCH_3

^j $\text{CH}_3\text{CH}_2\text{CH}_2^+$

ΔH_{corr} , a statistical mechanical correction factor for the thermal energy content of the fragments [13], is typically 18 kJ mol^{-1} for these decompositions. Thus, all predicted AEs should be lowered by about that amount.

Figure 2. Photoionization efficiency curves for the formation of $C_4H_8^+$, $C_3H_7^+$, $C_3H_6^+$, $CH_3OH_2^+$, and CH_2OH^+ from ionized 2-methylpropanol. Note that only the $C_4H_8^+$ curve levels off with increasing photon energy, indicating that each of the other processes is important up to the energy at the upper limit of the measurements.

gen. By analogy to arguments given above for complex-mediated elimination of methanol and formation of protonated methanol from 1, formation of protonated methanol is attributed to $2 \rightarrow 9 \rightarrow 4 \rightarrow CH_3OH_2^+$. The specificity of the initial H-transfers could be substantially obscured by exchange by $4 \rightleftharpoons 5$ and $4 \rightleftharpoons 3$, as happens in the dissociations of 1 [6]. This (Scheme IV) or isomerization of $n-C_3H_7^+$ in a complex (Scheme V) may precede reactions such as H transfer from C2 and C4 (numbering as in 2) of the propyl to C in the generation of $CH_3OH_2^+$.

$i-C_3H_7^+$ is formed from 2, as $AE(C_3H_7^+)$ is 46 kJ mol $^{-1}$ below the predicted $AE(CH_3CH_2CH_2^+)$ (see Table 3). $i-C_3H_7^+$ and $CH_3OH_2^+$ could be formed through $[CH_3CH_2CH_2^+ \cdot CH_2OH^+]$, as shown in Scheme IV. $i-C_3H_7^+$ could also form through 10 (see Scheme V), as primary alkyl ions usually isomerize before dissociation of complexes [19] because such ions do not exist in potential minima.

$AE(C_3H_6^+)$ and $AE(CH_3OH_2^+)$ are within experimental uncertainty of each other and about 16 kJ mol $^{-1}$ below $AE(CH_2=OH^+)$. This meets expectations for decomposition of 2 through $[CH_3CH_2CH_2^+ \cdot CH_2=OH^+]$ because the thresholds for ion-nonpolar

neutral complex-mediated processes are usually no more than 20–30 kJ mol $^{-1}$ below the threshold for simple dissociation of the complex [15]. The narrow range of the onsets of the decompositions of 2 contrasts with the larger differences between the onsets for the corresponding decompositions of 1. The onsets for $C_3H_6^+$, $CH_3OH_2^+$, and $C_3H_7^+$ formation from 2 are, respectively 42, 66, and 36 kJ mol $^{-1}$ above their thermochemical thresholds (see Table 3). Onsets of complex-mediated dissociations can be significantly above the product heats of formation when the latter are more stable than the products of simple dissociation of the partners in the complex [15d]. "Conventional" mechanisms (e.g., Scheme III) would predict similar threshold behavior for the corresponding products from 1 and 2; the contrasts observed are added evidence for the occurrence of the proposed complex-mediated processes.

The PIE curve for $CH_3OH_2^+$ formation from 2 rises continuously for at least 145 kJ mol $^{-1}$ above onset without signs of leveling, in contrast to expectations for formation of $CH_3OH_2^+$ through an ion-nonpolar neutral complex such as 9. This suggests that $[CH_3CH_2CH_2^+ \cdot CH_2OH^+]$ becomes important at higher energies (see Scheme V). The polarity of the neutral partner in this complex would expand the energy range upward, as in the decompositions of 1.

One of our objectives was to determine why much more $CH_3OH_2^+$ is formed from 1 than from 2. One reason for this is that, relative to 2, $CH_3OH_2^+$ is generated from 1 starting much further below the onset of simple dissociation of the partners in the complex. Thus more $CH_3OH_2^+$ is formed from 1 than from 2 because $CH_3OH_2^+$ is formed from 1 over a wider energy range. This is attributable to differences between the energy dependencies of reactions in ion-induced dipole complexes and ion-dipole complexes.

Water elimination: competition of a lower energy conventional isomerization with complex-mediated elimination. The threshold for H_2O elimination from 1 is 2 kJ mol $^{-1}$ below that for $CH_3OH_2^+$ formation (see Table 3). This small difference causes loss of water to be the major and $CH_3OH_2^+$ the minor metastable decomposition of 1 [9]. The $C_4H_8^+$ threshold is just above that for forming ionized methylcyclopropane, the main product of water elimination from 1 [8]. The slope of the PIE curve for this process becomes close to zero less than 20 kJ mol $^{-1}$ above threshold. Therefore, $1 \rightarrow 6$ is confined to very low energies [18]. This and the difference in H-exchange accompanying the two fragmentation pathways (see above) suggest that $1 \rightarrow 6$ occurs largely below the threshold for complex formation $1 \rightarrow 3$. Loss of water is also the lowest energy decomposition of 2, in this instance by about 90 kJ mol $^{-1}$. The methylcyclopropane ion is also a major product of water elimination from 2, even following $2 \rightarrow \cdot CH_2CH_2CH_2CH_2OH_2^+$, whereas the cyclobutane ion is not detectable [8]. $AE(C_4H_8^+)$ is that expected

Figure 3. Potential energy diagram for the dissociations of ionized *n*-butanol (2). The dissociated species and 2 are placed according to the values in Table 1. 6 is placed 17 kJ mol⁻¹ below 2 based on $\Delta H_f(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+) - \Delta H_f(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}_2^+)$ [22]. Attractions of 59 and 30 kJ mol⁻¹ were assumed between charged and polar and nonpolar neutral partners, respectively. (See legend to Figure 1.)

for the methylcyclopropane ion (see Table 3). The formation of CH_3OH_2^+ from 2 demonstrates that some complex formation competes with the H-transfer that leads to water loss and that complex-mediated processes can compete with substantially lower energy hydrogen transfers. This contrasts with a conclusion [17] that ion-nonpolar neutral complex-mediated reactions are generally not competitive with lower threshold processes. The ability to compete with other types of reactions well above the threshold for simple dissociation of the partners is thus another difference between the reactions of complexes containing polar versus those containing nonpolar neutral partners.

Summary

Several significant conclusions emerge from the present study. First, complex-mediated reactions occur

over wide energy ranges when the neutral partner is polar, in contrast to the very narrow energy range of such reactions when the neutral partner is small and nonpolar [15–17]. Second, ion-polar neutral complex-mediated reactions can compete with lower energy isomerizations. Finally, H-exchange between partners in an ion-neutral complex can be very fast.

Experimental

Photoionization efficiency curves were determined with a microprocessor-controlled photoionization magnetic sector mass spectrometer, as described elsewhere [13]. AE values were obtained by linear extrapolation of the initial rising portion of the curve to the abscissa. Corrections for influences of thermal energy on the curves were made by comparisons to the PIE

Table 4. Protonated methanol formation from labeled *n*-butanol ions^a

	CH ₃ OH ₂ ⁺	CH ₃ OHD ⁺	CH ₂ DOH ₂ ⁺	CH ₂ DOHD ⁺	CH ₃ OD ₂ ⁺
2-2,2-d ₂	62	21	17		
2-3,3-d ₂	44	19	34	3 ^b	
2-4,4,4-d ₃	19	55	17	4	5

^a Abundances determined from the peak heights in the normal mass spectrum of each species and the areas of the peaks representing C(H,D)₃⁺ products of the collision-induced dissociation of protonated methanol.

^b Composite intensities of CH_2DOHD^+ and CH_3OD_2^+ .

Figure 4. Photoionization efficiency curves for the formation of $C_4H_8^+$, $C_3H_7^+$, $C_3H_6^+$, $CH_3OH_2^+$, and CH_2OH^+ from ionized *n*-butanol. Note that none of the curves level off with increasing photon energy. Therefore, each of these processes is important up to the upper limit of the measurements.

curves for the corresponding molecular ions. The AE measurements are reproducible to ± 1 kJ mol $^{-1}$, but the uncertainties due to the contribution of thermal energy can be larger.

Collision-induced dissociation was achieved by pressurizing with helium the collision cell between the magnetic sector and second electric sector of a mass spectrometer of the geometry electric sector-magnetic sector-electric sector [20]. The ions that were collided were produced by ionization with 70 eV electrons in the ion source of the mass spectrometer. Spectra were recorded by scanning the voltage on the second electric sector following sample admission and pressurization of the collision cell.

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