
A Photoionization Study of the Ion-Neutral Complexes $[\text{CH}_3\text{CH}^+\text{CH}_3 \cdots \text{CH}_2\text{CH}_3]$ and $[\text{CH}_3\text{CH}_2\text{CH}^+\text{CH}_3 \cdots \text{CH}_3]$ in the Gas Phase: Formation, H-Transfer and C—C Bond Formation between Partners, and Channeling of Energy into Dissociation

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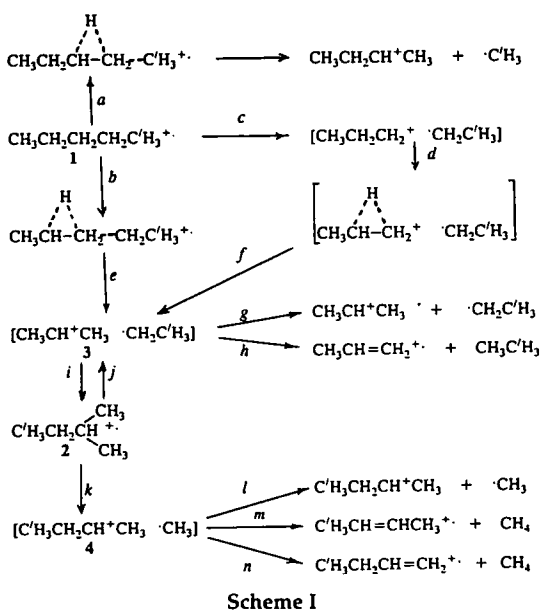
Photoionization mass spectrometry was used to investigate the dynamics of ion-neutral complex-mediated dissociations of the *n*-pentane ion (1). Reinterpretation of previous data demonstrates that a fraction of ions 1 isomerizes to the 2-methylbutane ion (2) through the complex $[\text{CH}_3\text{CH}^+\text{CH}_3 \cdots \text{CH}_2\text{CH}_3]$ (3), but not through $[\text{CH}_3\text{CH}^+\text{CH}_2\text{CH}_3 \cdots \text{CH}_3]$ (4). The appearance energy for C_3H_7^+ formation from 1 is 66 kJ mol^{-1} below that expected for the formation of *n*- C_3H_7^+ and just above that expected for formation of *i*- C_3H_7^+ . This demonstrates that the H shift that isomerizes C_3H_7^+ is synchronized with bond cleavage at the threshold for dissociation to that product. It is suggested that ions that contain *n*-alkyl chains generally dissociate directly to more stable rearranged carbenium ions. Ethane elimination from 3 is estimated to be about seven times more frequent than is C—C bond formation between the partners in that complex to form 2, which demonstrates a substantial preference in 3 for H abstraction over C—C bond formation. In $1 \rightarrow \text{CH}_3\text{CH}^+\text{CH}_2\text{CH}_3 + \text{CH}_3$ by direct cleavage of the C1—C2 bond, the fragments part rapidly enough to prevent any reaction between them. However, $1 \rightarrow 2 \rightarrow 4 \rightarrow \text{C}_4\text{H}_8^+ + \text{CH}_4$ occurs in this same energy range. Thus some of the potential energy made available by the isomerization of *n*- C_4H_9 in 1 is specifically channeled into the coordinate for dissociation. In contrast, analogous formation of 3 by $1 \rightarrow 3$ is predominantly followed by reaction between the electrostatically bound partners. (*J Am Soc Mass Spectrom* 1996, 7, 73–81)

Ion-neutral complexes (ionic and neutral fragments held together primarily by noncovalent attractions) are often intermediates in low energy dissociations of ions in the gas phase [1–5]. As the energy in an ion is increased toward the threshold for simple dissociation, partial dissociation to noncovalently bound fragments that can react with each other begins to occur [6–8]. Determination of how such reactions depend on energy provides unique information on interactions between ions and neutrals at energies from just below to just above the threshold for separation of the partners—an energy regime that is not readily accessed by other means. Little detailed experimental information exists on such interactions.

To understand better the dynamics of complex-mediated reactions, we undertook a study of the en-

ergy dependence of pertinent dissociations of the isomers ionized *n*-pentane (1) and 2-methylbutane (2). Scheme I, which is similar to one presented by Wendelboe et al. [9], summarizes the reactions we will characterize for this purpose. It includes three possible mechanisms for alkyl isomerization upon dissociation of 1: dissociation to complexes (species enclosed in brackets in Scheme I and throughout this contribution) followed by isomerization of the alkyl ion partner (reactions *c* and *d*) [9], concerted C—C bond cleavage and isomerization (reaction *a*) [10], and complex formation by isomerization–bond scission (reactions *b* and *e*). Simple bond cleavage to form complexes (reactions *j* and *k*), simple dissociation of the partners (reactions *g* and *l*), C—C bond formation between partners in complexes (reaction *i*), and H transfer between the partners (reactions *h*, *m*, and *n*) to produce alkane eliminations (processes we also will characterize) are also represented in Scheme I. This scheme

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rationalizes (see subsequent text) isotope distributions observed [9, 11] in the dissociations of labeled ions.

Although $C_4H_9^+$ is depicted for convenience as a classical 2-butyl species in Scheme I, the potential minima for this ion are H-bridged 2-butene and methyl-bridged propene ions [12], so it is likely that one or both are the ion structures actually present in the complexes.

Although it is clear that ionized *n*-alkanes dissociate to secondary alkyl ions [9-11, 13, 14], there has not been a consensus as to how this and accompanying alkane eliminations occur. Wendelboe et al. [9] concluded that alkane eliminations from ionized *n*-alkanes take place by H-transfer in alkyl ion-alkyl radical complexes. Weitzel et al. [15] inferred from differing dissociation patterns of 1 and 2 "that isomerization of *n*-pentane to *i*-pentane prior to dissociation

does not play an important role" in methane and ethane elimination from 1, but they were uncertain as to the exact nature of the transition state for the ethane elimination. In contrast, Holmes et al. [11] concluded that the data for 1 are best fit by the metastable losses of neutral methyl, methane, ethyl, and ethane that are preceded by $1 \rightarrow 2$. However, this led them to suggest isomerization by "extrusion of C-3 with a concerted H-shift from an adjacent CH_2 group" to explain why only the preexisting methyl radical is lost of the two symmetrically placed methyls that would be present in 2 formed by $1 \rightarrow 2$. Most recently, Weitzel [16] concluded that the rate-limiting step in ethane elimination from 1 has a loose transition state and therefore that the process is complex-mediated. However, he did not address whether 2 is important in the elimination of ethane from 1. Experimental [8, 17-19] and theoretical [20-22] results indicate that most alkane eliminations from radical cations in the gas phase take place through $[R^+ \cdot R']$ complexes. In particular, a recent high level ab initio study [23] of *n*-butane and 2-methylpropane ions, adjacent homologs to the ions studied here, demonstrates quite clearly that elimination of methane by those ions is complex-mediated, so this work will proceed from the assumption that alkane eliminations from 1 and 2 are complex-mediated also.

Substantial energy is sometimes made available by isomerization of ions to more stable structures [24-26]. This has been proposed to influence the dissociations of 1 [9], which leads us to investigate here whether energy made available by isomerization that accompanies bond breaking in 1 to form complexes selectively affects subsequent reactions. Another goal was to characterize competition among simple dissociation, C-C bond formation and H abstraction in 3. Covalent bond formation might be expected to dominate H transfer because the former gives the more stable product (Figure 1). However, this prediction needs exploration

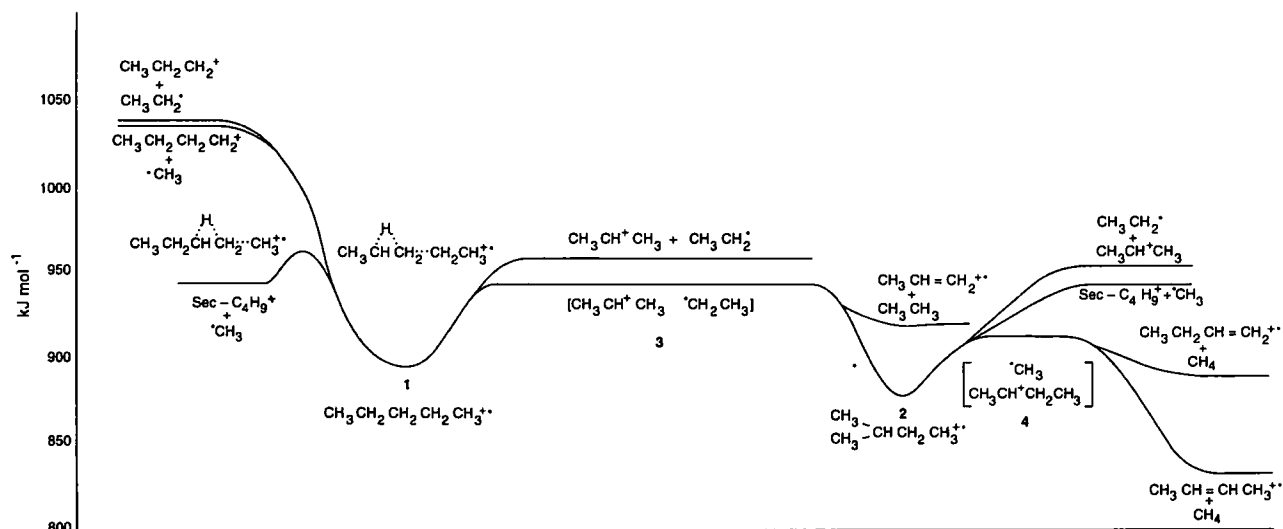


Figure 1. Potential energy surface for the decompositions of ionized *n*-pentane and 2-methylbutane. The surface was drawn based on 0-K heats of formation in Table 2 and appearance energies in Table 1.

because C—C bond formation appears to be less frequent than H transfer in $[\text{CH}_3\text{CH}_2\text{CH}=\text{OH}^+\text{CH}_3]$ [27]. We will address the following questions:

1. Are the isomerizing 1,2-H shifts in Scheme I synchronized with C—C bond cleavage, as proposed for $i\text{-C}_3\text{H}_7^+$ formation from the n -butane ion [10] or are bond cleavage and isomerization separate steps?
2. How do reactions between the partners in $[\text{R}^+\text{R}']$ complexes compete with each other?
3. Does the potential energy that is converted to vibrational and internal rotational energy during the n -alkyl to sec -alkyl isomerizations specifically influence the associated dissociations?

We answer these questions by using photoionization mass spectrometry to determine the energy dependence of dissociations of **1**, deuterated forms thereof, and **2**. We have used photoionization to study other complex-mediated dissociations [6-8, 28, 29].

Experimental

Photoionization efficiency (PIE) curves were obtained as described previously [30] with a microcomputer-controlled photoionization mass spectrometer. 0-K appearance energies (AEs) were obtained by linear extrapolation of the 298-K PIE curves to the abscissa in the region close to onset and then correcting for the thermal energy in the precursor molecules [30, 31]. The corrections used were $+17.6 \text{ kJ mol}^{-1}$ for n -pentane and $+14.9 \text{ kJ mol}^{-1}$ for 2-methylbutane; these values were obtained by using the formula $\text{AE}(0 \text{ K}) = \text{AE}(298 \text{ K}) + [\text{H}_{298} - \text{H}_0](\text{alkane}) - 5/2(298 \text{ R})$ [30a]. 0-K values were used to provide a potential surface (Figure 1) that depicts precisely the energy requirements for the processes examined. The differential PIE curves presented in the figures were obtained from the experimental data by using a 20-point Fourier transform filter for smoothing with the program Horizon (Star Blue Software, Inc.) before a simple first derivative was taken.

n -Pentane-2,2-D₂ was prepared by reduction of 3-pentanone with LiAlD_4 , conversion of the resulting 3-pentanol to the tosylate with tosyl chloride, and reduction of the tosylate with LiAlD_4 in diglyme. n -Pentane-1,1,1,5,5,5-D₆ was prepared by addition of 2 moles of $\text{CD}_3\text{CH}_2\text{MgBr}$ to ethyl formate, followed by conversion of the resulting alcohol to the tosylate with tosyl chloride. The tosylate was reduced with $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$. Trace amounts of alkene were removed from this product by treatment with Br_2 followed by distillation.

Mechanism of the Isomerization 1 → 2

Deuterium labeling unequivocally establishes that **1** → **2** and/or **1** → **3** precedes all of the ethane elimination from metastable **1** [9, 11]. Holmes et al. [11] demon-

strated that only C1, C3, and C5 are present in methyls and methanes lost in metastable decompositions of **1**, but they could not rationalize fully why C3 but no C2 and C4 was present in the methyl radicals and methane lost by **1**. However, this puzzle is easily solved: The observed pattern is caused by formation of **2** exclusively by a 1,2-ethyl shift; this shift places C3 and C1 or C5 but not C2 or C4 in positions to be lost in methyl and methane (Scheme 1). That is, **1** → **3** → **2** precedes the ejections of methane- and methyl-containing internal carbons, but the methyl shift **1** → **4** → **2** does not occur.

Methyl radicals lost from ionized n -butane contain predominantly terminal carbons [10], and the penultimate carbons are the only ones not lost in methyl at low energy by ionized n -heptane [13] and other ionized alkanes [14]. Thus isomerizations by shifts of terminal methyls generally are disfavored strongly in n -alkane ions.

Results and Discussion

Isomerization and C—C Bond Cleavage in 1

The potential energy surface on which the reactions of **1** and **2** occur needs to be defined to characterize those reactions. Figure 1 gives the pertinent region of this surface derived by combination of the present AEs to form C_3H_6^+ , C_3H_7^+ , C_4H_8^+ , and C_4H_9^+ from **1** and **2** with thermochemical information at 0 K (Table 2). Our AEs largely agree with results of previous photoionization measurements [33].

As noted in previous studies [9-11], all AEs measured for dissociations of **1** are in a narrow energy range and most are above those predicted thermochemically (Table 1), consistent with a common rate-determining step, that is, **1** → **3**, in all of those dissociations. In contrast to **1**, the dissociations of **2** examined

Table 1. Photoionization appearance energies (kilojoules per mole) for dissociations of ionized n -pentane and 2-methylbutane^a

m/z	n -Pentane ⁺	2-Methylbutane ⁺
72 ($\text{C}_5\text{H}_{12}^+$)	1001 (999 ^b)	985 ($\leq 986^b$)
57 (C_4H_9^+)	1071 (1066 ^c)	1058 (1075 ^c)
	1054 ^{d,e} 1137 ^{d,f}	1059 ^{d,e} 1142 ^{d,f}
56 (C_4H_8^+)	1066 (1057 ^c)	1034 (1035 ^c)
	936 ^{d,g}	941 ^{d,g}
43 (C_3H_7^+)	1074 (1071 ^c)	1067 (1075 ^c)
	1061 ^{d,e} 1140 ^{d,f}	1066 ^{d,e} 1145 ^{d,f}
42 (C_3H_6^+)	1063 (1060 ^c)	1029 (1046 ^c)
	1023 ^d	1027 ^d

^a The first value in each group was determined in present work and corrected to 0 K (see Experimental).

^b Reference 32.

^c Reference 33.

^d Thermochemical threshold predicted at 0 K from data given in Table 2.

^e Value expected for sec or i product.

^f Value expected for n -product.

^g Assuming formation of $(E)\text{-CH}_3\text{CH}=\text{CHCH}_3$.

other than to $C_4H_8^+$ begin close to their thermochemical thresholds. $AE(1 \rightarrow C_4H_8^+)$ and $AE(1 \rightarrow C_3H_6^+)$ are above those for the corresponding dissociations that start from 2, so there is an activation energy barrier in the pathway $1 \rightarrow 2$. The location of the top of the barrier is given by the difference between the AEs for dissociations that follow $1 \rightarrow 2$ and those for dissociations of 2. Correcting our AEs for the 4.6 kJ mol⁻¹ difference between the ΔH_f s of the neutral pentanes (Table 2) places the threshold for $1 \rightarrow 2$ 34 kJ mol⁻¹ [from $AE(1 \rightarrow C_3H_6^+) - AE(2 \rightarrow C_3H_6^+)$] to 37 kJ mol⁻¹ [from $AE(1 \rightarrow C_4H_8^+) - AE(2 \rightarrow C_3H_6^+)$] above the threshold for $2 \rightarrow C_3H_6^+$. This excess energy previously was estimated to be 34-38 kJ mol⁻¹ [9].

One of the questions we set out to address is whether bond cleavage and isomerization in 1 are consecutive steps or are concerted. This is resolved by the AEs for formation of the alkyl ions and associated alkane eliminations from 1; formation of transient *n*-alkyl-containing complexes would require more energy than direct formation of *sec*-alkyl-containing complexes. $AE(C_3H_7^+)$ from 1 is only 13 kJ mol⁻¹ above that expected for *i*- $C_3H_7^+$ formation and is about 66 kJ mol⁻¹ below that required for dissociation to *n*- $C_3H_7^+$ (Table 1). Similarly, $AE(C_4H_9^+)$ is just above that expected for *sec*- $C_4H_9^+$ formation and 67 kJ mol⁻¹ below the value predicted for dissociation to *n*- $C_4H_9^+$. The AEs demonstrate dissociation to secondary ions without passage through primary structures in both cases. The energy required to dissociate alkyl ion-alkyl radical partners in a complex is about 13 kJ mol⁻¹ [23], much too small to accommodate formation of complexes that contain *n*-alkyl ions. Therefore, $[CH_3CH_2CH_2^+ \cdot CH_2CH_3]$ and $[CH_3CH_2CH_2CH_2^+ \cdot CH_3]$

do not intervene in the dissociations of 1 near threshold.

Ionized alkanes have easily elongated C—C bonds [34-36], so it is likely that as such a C—C bond is further stretched, simultaneous initiation of a Wagner-Meerwein-like 1,2-H shift facilitates bond breaking. The absence of an activation energy for conversion of primary alkyl cations to isomeric forms, for example, *n*- $C_3H_7^+ \rightarrow i$ - $C_3H_7^+$ [37], enables an H shift to anchimerically assist bond cleavage and to lower the barrier to C—C bond breaking in 1. This may be additionally aided by H shifts to form proton-bridged 2-butene or methyl shift to form methyl-bridged propene (Scheme II)—the most stable forms of $C_4H_9^+$. Either or both might be formed, because according to theory [12] they differ in energy by only about 2 kJ mol⁻¹. As the bond to the terminal methyl breaks and a 3,4-H shift occurs, complexes that contain different $C_4H_9^+$ isomers may form by respective migrations of H versus CH_3 . In support of concerted isomerization-bond cleavage, ab initio studies [23] demonstrate that H shift and bond cleavage are synchronized in ionized *n*-butane.

AE measurements demonstrate that formation of secondary or tertiary $C_nH_{2n+1}^+$ ions from precursors that contain *n*-alkyl groups is a general phenomenon—a conclusion supported by a variety of other observations [10, 38-42]. Early [34] and recent [23] theoretical studies of the dissociations of ionized *n*-butane demonstrate that H migration accompanies dissociation of that ion to *i*- $C_3H_7^+ + \cdot CH_3$. Chronister and Morton [41] placed the point of complex formation in ionized *n*-propyl phenyl ether close to the point of isomerization of *n*- to *i*-propyl, and Veith and Gross [42] demonstrated by interpretation of isotope effects that a 1,2-H shift in a propyl is the rate-determining step in complex-mediated propene eliminations from di-*n*-propylmethylene immonium ions. Harnish and Holmes [39] inferred that the rate-determining step for alkene eliminations from ionized primary alkyl phenyl ethers involves a 1,2-H shift. Finally, Nibbering and co-workers [43] concluded that C—S bond cleavage in the ethyl propyl thioether ion is assisted by a 1,2-hydride shift to give dissociation to *i*- $C_3H_7^+$.

Energy Dependence of the Fragmentations of 1 and 2

Insight into the dynamics of complex-mediated dissociations is provided by the energy dependencies of

Table 2. Applicable heats of formation^a

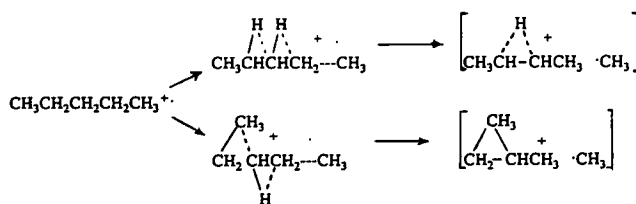
Species	0 K (kJ mol ⁻¹)	298 K (kJ mol ⁻¹)
$CH_3CH=CH_2^+$	977 ^b	959
$CH_3CH^+CH_3$	817	799
$CH_3CH_2CH_2^+$	896	881
(E)- $CH_3CH=CHCH_3^+$	889 ^b	866
$CH_3CH_2CH=CH_2^+$	947 ^c	924
$CH_3CH^+CH_2CH_3$	791 ^d	766
$CH_3CH_2CH_2CH_2^+$	874 ^d	849
$CH_3CH_2CH_2CH_2CH_3^+$ (1)	884	852
$(CH_3)_2CHCH_2CH_3^+$ (2)	≤ 867	≤ 832
$\cdot CH_3$	149.0	145.8
CH_4	-66.8	-74.5
CH_3CH_2	130	118
$\dot{C}H_3CH_3$	-68.4	-84.0
$CH_3CH_2CH_2CH_2CH_3$	-114.2	-146.5
$(CH_3)_2CHCH_2CH_3$	-118.8	-153.8

^a Values are from ref 32 unless otherwise indicated.

^b From ref 15.

^c Estimated from the 298-K value for this ion and $\Delta H_{1298} - \Delta H_{10}$ for $CH_3CH=CHCH_3^+$.

^d Value estimated by adding 25 kJ mol⁻¹ to ΔH_{1298} from ref 32 based on a difference of that amount between ΔH_{10} and ΔH_{1298} for $CH_3CH^+CH_2CH_3$.



Scheme II

those processes [6, 7, 28]. Such energy dependencies can be derived from photoionization efficiency (PIE) curves for the ionic products. The rate of dissociation at a particular ion internal energy (photon energy minus the ionization energy of the molecule) is proportional to the slope of the PIE curve at the corresponding photon energy, so a first differential PIE curve gives the relative extent of a reaction as a function of the amount of energy deposited upon ionization [44]. The applicability of this procedure to alkane eliminations has been validated by comparison of breakdown patterns implied by PI results to fragmentation patterns of energized ether ions formed by isomerizations [8]. Curves that represent the first derivatives of the PIE curves for dissociations of **1** and **2** are given in Figures 2 and 3.

The first differential curves for $C_4H_8^+$ formation from **1** and **2** quickly rise to maxima at 1050–1070 kJ mol^{-1} and then decline with increasing energy. However, they do not decline to zero, at least not up to 1200 kJ mol^{-1} , which demonstrates that methane elimination occurs up to more than 145 kJ mol^{-1} above its onset. Ethane elimination from both **1** and **2** is substantial even 150–180 kJ mol^{-1} above threshold. The corresponding differential curves for the simple dissociations—formation of $C_3H_7^+$ and $C_4H_9^+$ from both **1** and **2**—rise rapidly and continuously over the energy range of the measurements, which indicates that the formations of alkyl ions all increase steadily in importance relative to the alkane eliminations over the energy range of our measurements.

Competition between H Abstraction and C—C Bond Formation in **3**: Configurations Accessed by the Partners

We addressed our goal to estimate the degree of C—C bond formation ($3 \rightarrow 2$) versus H transfer ($3 \rightarrow CH_3CH = CH_2^+ + C_2H_6$) by a comparison of the dis-

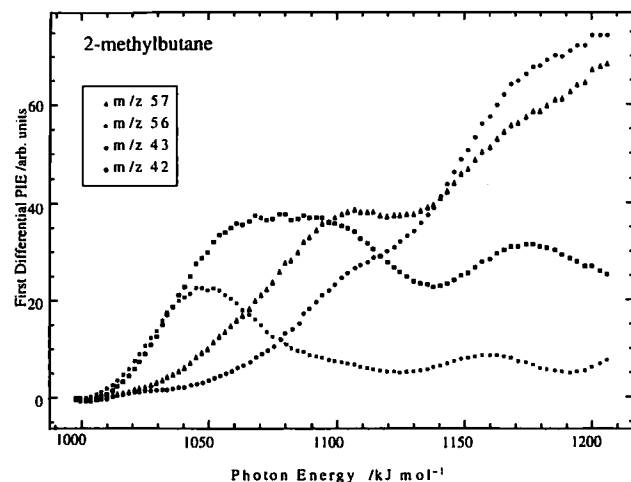


Figure 2. First differential photoionization efficiency curves for the loss of CH_3 (m/z 57), CH_4 (m/z 56), C_2H_5 (m/z 43), and C_2H_6 (m/z 42) from ionized 2-methylbutane.

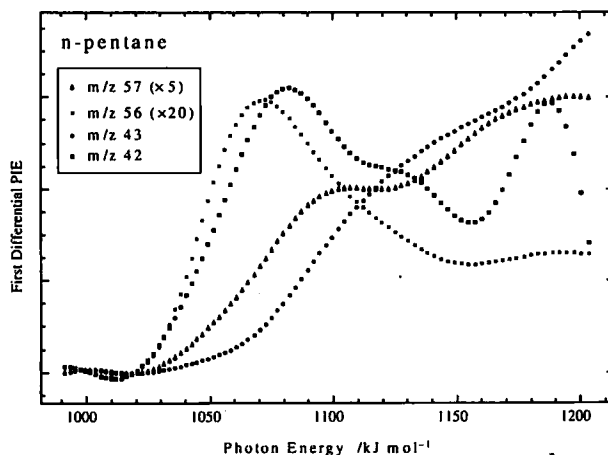


Figure 3. First differential photoionization efficiency curves for the loss of CH_3 (m/z 57), CH_4 (m/z 56), C_2H_5 (m/z 43), and C_2H_6 (m/z 42) from ionized *n*-pentane.

sociation pattern of **1** at a photon energy of 1055 kJ mol^{-1} to that of **2** at a photon energy of 1060 kJ mol^{-1} . Patterns at the different photon energies are compared because for **1** a given ion internal energy is at a photon energy that is 4.6 kJ mol^{-1} lower than **2** due to the difference between the heats of formation of the neutral alkane precursors (Table 2). The pattern of **2** was used to subtract the contribution of the portion of **1** that dissociates after $1 \rightarrow 2$ from the breakdown pattern for **1**. This is justified by the prediction of Rice–Ramsperger–Kassel–Marcus theory that at a particular energy, formation of **2** by $1 \rightarrow 2$ and by ionization of 2-methylbutane will be followed by the same relative rates of $C_3H_6^+$ and $C_4H_8^+$ formation. At the chosen energy, **2** eliminates ethane 1.8 times as often as it loses methane (Figure 2). $C_4H_8^+$ formation from **1** occurs only following $1 \rightarrow 3 \rightarrow 2$ (see preceding and following text), so at a photon energy of 1055 kJ mol^{-1} , all $C_4H_8^+$ formation and 1.8 times as much $C_3H_6^+$ formation as $C_4H_8^+$ formation should follow $1 \rightarrow 3 \rightarrow 2$. This constitutes 12% of the methane plus ethane elimination from **1** (Figure 3), which leaves 88% loss of ethane directly from **3**. Thus, at this near threshold energy **3** eliminates ethane about seven times as often as it produces **2** by formation of a C—C bond. Therefore **2** is largely by-passed in the elimination of ethane from **1**, which demonstrates that *the system usually does not pass through 2 on the way from the transition state for isomerization to the transition state for hydrogen transfer*. Therefore, the partners move fairly freely relative to each other rather than follow the minimum energy pathway from one point to the other, and those varied trajectories contribute more to the product distribution than does the minimum energy pathway. A similar conclusion was arrived at in an ab initio study of methane elimination from the *n*-butane ion [23].

PIE Studies of 1-3,3- D_2 and 1-1,1,1,5,5,5- D_6

To isolate for study the different dissociation pathways of **1**, we determined PIE curves and their first differ-

entials for dissociations of isotopically labeled species. We did this to determine how reactions between the fragments depend on energy made available by the isomerizations of the propyl and butyl groups of 1. AEs for dissociations of 1-1,1,1,5,5,5-D₆ and 1-3,3-D₂ are given in Table 3.

The PIE curves for the losses of CD₄, CHD₃, CH₃D, and CH₄ (products at *m/z* 58, 59, 61, and 62, respectively) from 1-1,1,1,5,5,5-D₆ rise rapidly from threshold and then more slowly (Figure 4a for losses of CH₄ and CHD₃). If H/D reshuffling preceded the dissociations, *m/z* 61 and 62, respectively could contain contributions from [•]CHD₂ and [•]CH₂D losses. However, there cannot be such interference at *m/z* 59 (loss of [•]CD₃ gives a product at *m/z* 60), so the similar amplitudes and shapes for the PIE curves for *m/z* 62 and 59 and their first differential curves (Figure 4) imply that [•]CH₂D loss does not influence the curve for *m/z* 62. The closeness of the PIE curves for losses of CH₄ and CHD₃ also demonstrates that there is nearly equal formation of [CD₃CH₂CH⁺CD₃ [•]CH₃] and [CD₃CH₂CH⁺CH₃ [•]CD₃] from 1-1,1,1,5,5,5-d₆, because those complexes are intermediates in the respective methane eliminations. Because the second complex can form only following 1 → 3 → 2 (because there is no loss from 1 of methyl radical that contains C₂), the near equality of the rates of elimination of CH₄ and CHD₃ also demonstrates that both complexes are formed exclusively following 1 → 3 → 2 over the energy range of the measurements. (The essentially equal rates of CH₃D and CHD₃ elimination also indicate that there are no appreciable secondary isotope effects on methane eliminations that start from 1. This is surprising in light of the large secondary isotope effects on methane eliminations that start from metastable 2. The difference in isotope effects is attributable [12] to differences in the energy content at which the dissociations of 1 and 2 occur.) This extends to higher energies

Table 3. Photoionization appearance energies (kilojoule per mole) for dissociations of deuterium-labeled *n*-pentane ions^a

<i>m/z</i>	CD ₃ CH ₂ CH ₂ CH ₂ CD ₃	CH ₃ CH ₂ CD ₂ CH ₂ CH ₃
78	998 (C ₅ H ₆ D ⁺)	
74		999 (C ₅ H ₁₂ D ₂ ⁺)
63	1071 (C ₄ H ₃ D ₆ ⁺)	
62	1066 (C ₄ H ₂ D ₆ ⁺)	
61	1058 (C ₄ H ₃ D ₅ ⁺)	
60	1076 (C ₄ H ₆ D ₃ ⁺)	
59	1066 (C ₄ H ₅ D ₃ ⁺)	1071 (C ₄ H ₇ D ₂ ⁺)
58	1058 (C ₄ H ₆ D ₂ ⁺)	1066 (C ₄ H ₆ D ₂ ⁺)
57		1066 (C ₄ H ₇ D ⁺)
56		
46	1077 (C ₃ H ₄ D ₃ ⁺)	
45	1069 (C ₃ H ₃ D ₃ ⁺)	1072 (C ₃ H ₅ D ₂ ⁺)
44	1069 (C ₃ H ₄ D ₂ ⁺)	1063 (C ₃ H ₄ D ₂ ⁺)
43		1063 (C ₃ H ₅ D ⁺)

^a Values are corrected to 0 K (see Experimental section).

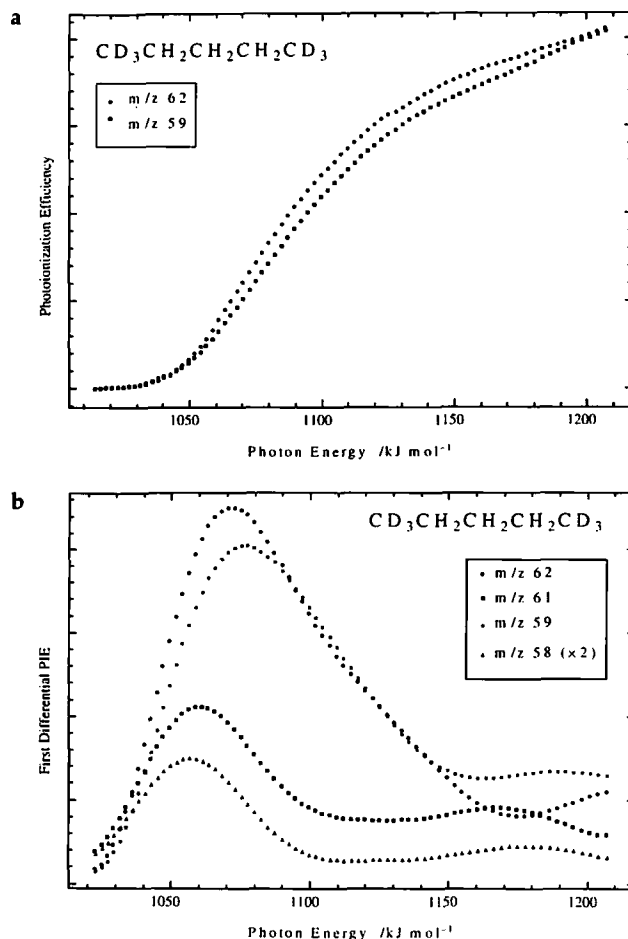


Figure 4. (a) Photoionization efficiency curves for the loss of CH₄ (*m/z* 62) and CHD₃ (*m/z* 59) and (b) first differential photoionization efficiency curves for the loss of CH₄ (*m/z* 62), CH₃D (*m/z* 61), CHD₃ (*m/z* 59), and CD₄ (*m/z* 58), all from ionized *n*-pentane-1,1,1,5,5,5-D₆.

the preceding conclusion that methane elimination from metastable 1 occurs only following 1 → 3 → 2 and confirms that methane is not eliminated directly following partial simple cleavage of a C1—C2 bond.

The products with masses of 58 and 61 are formed by elimination of CD₄ and CH₃D, respectively. Previous workers demonstrated that methane elimination that starts from both 1 and 2 forms ionized 1-butene as well as ionized 2-butene [11], which explains these processes. The production of both butene ions is not surprising, because both are accessible from 3 (Figure 1). The formation of these additional products does not alter our interpretations. However, it is interesting that the derivatives of the PIE curves for these reactions are shifted to lower energies than those for the other methane eliminations, which implies that the higher energy processes occur at slightly lower energies. We have no certain explanation for this curious observation.

CD₃CH₃ was eliminated about 30% more often than was CD₃CH₂D by 1-1,1,1,5,5,5-D₆ at all energies (Figure 5). Elimination of CH₃CH₃ from 1-3,3-D₂ was favored similarly relative to elimination of CH₃CH₂D

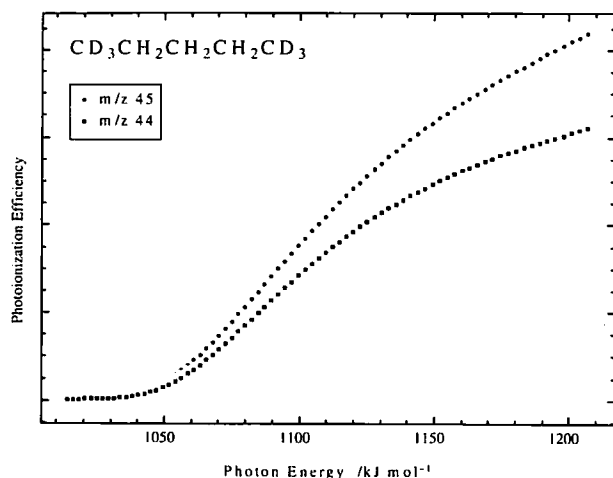


Figure 5. Photoionization efficiency curves for the loss of CD_3CH_3 (m/z 45) and $\text{CD}_3\text{CH}_2\text{D}$ (m/z 44) from ionized *n*-pentane-1,1,1,5,5,5- D_6 .

(not shown). The differences are attributable largely to isotope effects, because in both instances H abstraction was favored relative to D transfer. Thus in 3, H abstraction occurs to essentially the same extent from both ends of $i\text{-C}_3\text{H}_7^+$ over a substantial energy range. This demonstrates that the partners are sufficiently separated from each other to reorient [45] to the point that their reactions are not influenced by their initial configuration. This and the preference for H abstraction over formation of a C—C bond ($3 \rightarrow 2$) substantiates the picture of 3 as an $i\text{-C}_3\text{H}_7^+ - \text{CH}_3\text{CH}_2$ pair that move fairly freely relative to each other. The energy dependencies of the losses of $\text{C}_2\text{H}_3\text{O}_3$, $\text{C}_2\text{H}_2\text{O}_2$, and CH_3 , all processes that follow formation of 3, are similar (Figure 6).

A Simple Dissociation Directly Driven by the Energy Made Available by Isomerization

Our third goal was to explore whether the potential energy made available by isomerization can specifi-

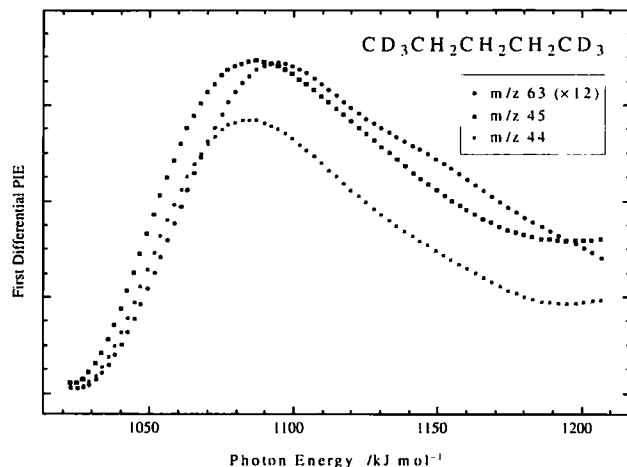


Figure 6. First differential photoionization efficiency curves for the loss of CH_3 (m/z 63), CD_3CH_3 (m/z 45), and $\text{CD}_3\text{CH}_2\text{D}$ (m/z 44) from ionized *n*-pentane-1,1,1,5,5,5- D_6 .

cally affect the rate of associated dissociation. To determine the energy dependence of the methyl loss directly from 1, that is, without going through 2, we derived a PIE curve for direct $1 \rightarrow \text{C}_4\text{H}_9^+ + \text{CH}_3$ by subtracting the PIE curve for loss of CH_3 by 1-1,1,1,5,5,5- D_6 from the corresponding curve for loss of CD_3 (Figure 7). This procedure assumes that all of the first process and an equal amount of the second follow $1 \rightarrow 3 \rightarrow 2$, an assumption supported by the close similarity of the ion abundances in the PIE curves for eliminations of CH_4 and CHD_3 from 1-1,1,1,5,5,5- D_6 (Figure 4). The onset derived for the direct loss of a methyl radical is about 29 kJ mol^{-1} higher than that for methyl radical loss following $1 \rightarrow 2$, but still below the minimum energy that would be needed to form $n\text{-C}_4\text{H}_9^+$.

We previously demonstrated that neither $1 \rightarrow 4 \rightarrow 2$ nor $1 \rightarrow 4 \rightarrow \text{C}_4\text{H}_8^+ + \text{CH}_4$ occurs. We believe that both missing reactions are prevented by energy made available in the isomerization associated with cleavage of the C1—C2 bond that drives the partners apart faster than they can react with each other. Similar effects undoubtedly account for no observation of the loss of methyl radical-containing C2 [13, 14] from higher ionized alkanes. The excess energy present following $1 \rightarrow \text{C}_4\text{H}_9^+ + \text{CH}_3$ simply may cause dissociation to be fast enough to prevent subsequent reactions between the partners [6–8] or concentration of that energy during the synchronous H transfer and C—C bond cleavage may propel the fragments apart.

If it is the amount of excess energy only that determines whether methane elimination from 1 and 2 occurs at the same energy, methane elimination following $1 \rightarrow 2 \rightarrow 4$ and that which would follow C1—C2 bond cleavage in 1 to form 4 while avoiding 2 should take place at the same rate. If this were so, the absence of methane elimination following direct C1—C2 bond cleavage in 1 would be due simply to

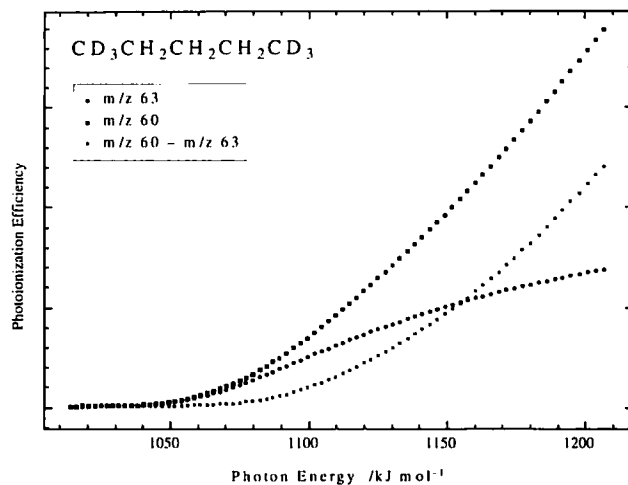


Figure 7. Photoionization efficiency curves for the loss of CH_3 (m/z 63) and CD_3 (m/z 60) from ionized *n*-pentane-1,1,1,5,5,5- D_6 . The difference curve (m/z 60 – m/z 63) represents the direct loss of CD_3 without prior isomerization to 2.

the higher energy required to cleave the C1—C2 bond. However, the first differential of the PIE curve for CH₄ elimination from 1-1,1,5,5,5-D₆ is nonzero to beyond 1210 kJ mol⁻¹ (Figure 4b). This demonstrates that that process, which follows 1 → 3 → 2, is appreciable up to more than 100 kJ mol⁻¹ above the onset for the loss of the internal methyl (about 1050 kJ mol⁻¹; Figure 7). Therefore methane elimination following 1 → 3 → 2 occurs into the energy range in which 1 → *sec*-C₄H₉⁺ + ·CH₃ takes place by direct C1—C2 cleavage. However methane elimination and methyl migration (1 → 4 → 2) do not accompany the latter cleavage. Methane also is eliminated from 2 up into this energy range (Figure 2), so the amount of energy in the system alone does not prevent methane elimination following scission of the C1—C2 bond in 1. Therefore the energy made available by the 1,2-H shift that accompanies the loss of methyl radical from 1 may be localized so as to drive dissociation before that energy becomes dispersed throughout the system. Perhaps the H shift and C—C bond cleavage are sufficiently synchronized that the fragments simply are propelled apart before they can react with each other. We know of no previous example of excess energy being concentrated in a coordinate for dissociation when the system passes through a configuration that, when accessed at the same energy by another pathway, undergoes a different reaction. However, another possible explanation is that 1 and 2 dissociate to complexes that contain different C₄H₉⁺ isomers, that is, H-bridged 2-butene and methyl-bridged butene (Scheme II), and therefore react differently. There is no obvious reason why a methyl would migrate in preference to H in 1 or 2, and the H-bridged isomer is the main experimentally observed isomer [12]. Thus we think it unlikely that the methyl-bridged butene ions would be formed from 1 almost exclusively, as would be required to prevent 1 → 4 → 2 from production of detectable decompositions. However, we cannot rule out the two isomer explanation for our observations.

The complete absence of 1 → 2 by a 1,2-methyl shift is very surprising because the related ethyl shift (1 → 3 → 2) is appreciable. One possible reason that 1 → 2 does not occur by a methyl shift is that attractive forces between partners decrease with increasing ion size and decreasing radical size [17]. Alternatively, it could be that the lighter methyl simply is propelled away from its partner more rapidly than the ethyl is. These factors also could combine to prevent the missing methane elimination. Whatever the causes, they are sufficient to allow synchronization of H shift and C—C bond scission to differently affect the rates of departure of methyl and ethyl from 1.

Summary

Results presented here reveal that (1) isomerization of incipient *n*-alkyl ions to more stable products is synchronized with the C—C bond dissociation that gener-

ates them, (2) H transfer is about seven times more frequent in a *sec*-propyl ion-ethyl radical complex than is C—C bond formation, and any influence of the initial location of the transferred hydrogen is lost, which demonstrates that the partners in 3 move fairly freely relative to each other, and (3) potential energy made available by the isomerization that accompanies cleavage of a terminal C—C bond in 1 drives the fragments apart so they cannot react with each other.

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