1- and 2-Adamantyl Radicals and Cations in the Gas Phase: Thermochemistry and Mass Spectrometry

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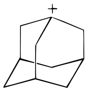
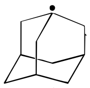
The heats of formation of the 1- and 2-adamantyl cations and of the 1-adamantyl radical have been measured directly by electron impact appearance energies. The values are $\Delta_f H°[\text{1-adamantyl}^+] = 152 \pm 3$ kcal mol^{-1}, $\Delta_f H°[\text{2-adamantyl}^+] = 171 \pm 3$ kcal mol^{-1} and $\Delta_f H°[\text{1-adamantyl}^\bullet] = 12 \pm 3$ kcal mol^{-1}. The results also lead to a value of 16 kcal mol^{-1} for the heat of formation of the 2-adamantyl radical. Collision-induced dissociation mass spectra of the 1- and 2-adamantyl cations allow low internal energy ions to be distinguished. However, it is shown that at higher internal energies the two ions share a common potential energy surface. This is supported by the statistical mixing of all hydrogen and deuterium atoms, prior to the lowest energy dissociation channel, in the 1-adamantyl-3d_1^+ isotopomer.

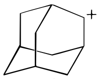
Introduction

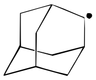
Adamantane and its derivatives possess an unusually rigid, tricyclic molecular structure and so have been the subject of much research.[1] This has resulted in these species being used in many applications including polymers, pharmaceuticals, and agrochemicals.[2]

Homolytic or heterolytic cleavage in 1- or 2-adamantyl derivatives may yield the radicals and cations identified below:


$1Ad^+$


$1Ad^\bullet$


$2Ad^+$


$2Ad^\bullet$

These species are notable examples of bridgehead cations and radicals where geometric restraints make reaction centers pyramidal.

In solution, both $1Ad^\bullet$ and $2Ad^\bullet$ have been generated and characterized by ESR.[3] The $1Ad^+$ can be prepared by treating adamantane with super acids, and the ions so produced have been well-characterized by ^1H and ^{13}C nuclear magnetic resonance spectroscopies; it is believed that the ions retain their tricyclic structure.[4] The isomerization of $1Ad^+$ to generate $2Ad^+$, by a 1,2-hydride shift, is strongly inhibited in the ionic species because the vacant orbital at the carbon center and the orbital of the migrating group are rigidly held in a conformation unfavorable for the H^- migration.[5] Thus, although this isomerization has been observed in super acidic media, it was recently shown to result from bimolecular reactions.[6]

In the gas phase, $1Ad^\bullet$ and $2Ad^\bullet$ can be generated pyrolytically[7] but also by the dissociative ionization of 1- and 2-substituted adamantyl compounds, whose fragmentation results in the charge being retained on the substituent, e.g., $1\text{-AdCH}_2\text{NH}_2 \rightarrow 1Ad^\bullet + {}^+CH_2NH_2$. This method has been widely used for the measurement of radical heats of formation[8] by determining the appearance energy (AE) of the fragment ion.

Few thermochemical data pertaining to both the radical and ionic species are available in the literature (see below). Furthermore, the structure of the two ions as well as their possible interconversion has not been investigated in any detail. The thermochemical and mass spectrometric study that follows will provide reliable heat of formation ($\Delta_f H°$) values for the $1Ad^\bullet$, $2Ad^\bullet$, $1Ad^+$, and $2Ad^+$ species as well as an investigation of the structures of the $1Ad^+$ and $2Ad^+$ ions and their interconversion.

Experimental Section

An AEI MS-902S mass spectrometer was used for metastable ion appearance energy, AE, measurements. AE values were determined by measuring the ion abundance versus electron energy over a small energy range (2−3 V) above the threshold. The data were treated as described in detail elsewhere, and the metastable dissociation of methyl acetate was used as the standard.[9] The apparatus sample inlet operated at room temperature. The heats of formation, $\Delta_f H°$, of the precursor molecules and neutrals cogenerated were accurately known[10] or could be estimated with confidence using Benson's additivity scheme.[11] Electron impact (EI), metastable ion (MI), and collision-induced dissociation (CID) mass spectra were recorded using a modified VG ZAB-2F mass spectrometer of BEE geometry.[12] For the CID experiments, helium was used as target gas at pressures sufficient to reduce the main ion beam intensity by ∼10%. 1-Adamantanemethylamine was originally prepared by reduction of 1-adamantanecarbonitrile with $LiAlH_4$ and recrystalized from hexane; subsequent samples were obtained from Aldrich Chemical Co. All other compounds were purchased from Aldrich Chemical Co. and used without further purification. 1-AdBr-3d_1 was prepared according to a known procedure.[13]

Results and Discussion

Thermochemistry. Several attempts to determine the $\Delta_f H°$ of $1Ad^+$ have been made in the past, and calculations have provided some information concerning the energy difference

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between the isomeric ions. These data are listed in Table 1. Beauchamp et al.[15] and Kebarle et al.[18] obtained their $\Delta_f H^\circ[1Ad^+]$ from the study of bromide, chloride and hydride transfer reactions, respectively. The values given in Table 1 are adjusted to the presently accepted value for $\Delta_f H^\circ$[t-Butyl$^+$] = 170 kcal mol^{-1}. [21] Ridge et al.[17] obtained their value by studying the reaction of Li$^+$ with 1-AdCl and 1-AdBr. In a second study concerning the adamantyl species, Beauchamp et al.[7] measured the photoelectron spectra of the radicals generated pyrolytically from 1- and 2-adamantyl methyl nitrite (by loss of NO and CH_2O), and determined the adiabatic ionization energy, IE$_a$, of the 1Ad$^\bullet$ and 2Ad$^\bullet$ radicals. By estimating the $\Delta_f H^\circ$ of the radicals ($\Delta_f H^\circ[1Ad^\bullet] = 15$ kcal mol^{-1} and $\Delta_f H^\circ[2Ad^\bullet] = 12$ kcal mol^{-1}) and combining these with the IE$_a$, they calculated $\Delta_f H^\circ$ values for the ions. It is noteworthy that the selected $\Delta_f H^\circ[1Ad^\bullet]$ was *higher* than that estimated for $\Delta_f H^\circ[2Ad^\bullet]$, bearing in mind that the established secondary and tertiary C−H bond strengths in hydrocarbons predict the reverse order of stability e.g., *D*[*s*-Butyl-H] - *D*[*t*-Butyl−H] = +4 kcal mol^{-1}.[10]

In both of their studies, Rauk et al.[19,20] used ab initio molecular orbital theory calculations, at the MP2/6-31G//6-31G level, to predict that 1Ad$^+$ is 15 kcal mol^{-1} more stable than the 2Ad$^+$.

In view of the lack of an experimental $\Delta_f H^\circ[2Ad^+]$, the disagreement between the values for $\Delta_f H^\circ[1Ad^+]$ presented in Table 1 and the ambiguity concerning the relative $\Delta_f H^\circ$ values for 1Ad$^\bullet$ and 2Ad$^\bullet$, a new series of experimental determinations of these quantities was performed using metastable peak AE measurements.

Measured Thermochemistry. The appearance energy (AE) of 1Ad$^+$ and 2Ad$^+$ ions metastably generated from the dissociation of a series of 1-adamantyl derivatives and the 2-AdBr was measured and used to obtain the corresponding $\Delta_f H^\circ$. The reactions studied were

$$1\text{-}C_{10}H_{15}Cl \xrightarrow{-e} 1\text{-}C_{10}H_{15}{}^+ + Cl^\bullet$$

$$1\text{-}C_{10}H_{15}CH_2OH \xrightarrow{-e} 1\text{-}C_{10}H_{15}{}^+ + {}^\bullet CH_2OH$$

$$1\text{-}C_{10}H_{15}COCH_3 \xrightarrow{-e} 1\text{-}C_{10}H_{15}{}^+ + {}^\bullet COCH_3$$

$$1\text{-}C_{10}H_{15}CH_2NH_2 \xrightarrow{-e} 1\text{-}C_{10}H_{15}{}^+ + {}^\bullet CH_2NH_2$$

$$2\text{-}C_{10}H_{15}Br \xrightarrow{-e} 2\text{-}C_{10}H_{15}{}^+ + Br^\bullet$$

In addition, 1-$C_{10}H_{15}CH_2NH_2$ was used to generate the 1-adamantyl radical according to

$$1\text{-}C_{10}H_{15}CH_2NH_2 \xrightarrow{-e} 1\text{-}C_{10}H_{15}{}^\bullet + {}^+CH_2NH_2$$

In all cases, the 1Ad$^+$, 2Ad$^+$, and 1Ad$^\bullet$ were produced from *metastable* molecular ions, and the accompanying kinetic energy releases (KERs) were so small that kinetic shift effects could be neglected. Table 2 shows the results of the AE measurements as well as the ancillary thermochemical data used to determine the $\Delta_f H^\circ$ values, together with previous data. Our value for $\Delta_f H^\circ[1Ad^+]$ is somewhat lower than the earlier reported $\Delta_f H^\circ$ obtained from reaction equilibria measurements, but the AE values, when comparison is possible, are in excellent agreement with the photoionization measurements.[23] The $\Delta_f H^\circ[2Ad^+]$ is slightly higher than the value proposed by Beauchamp et al.,[7] and consequently, the experimentally determined $\Delta\Delta_f H^\circ$ is larger than their value and also slightly higher than the calculated value.[19,20]

TABLE 1: Available Thermochemical Data Related to the 1Ad$^+$ and 2Ad$^+$ Cations and Their Corresponding Radicals (All Values in kcal mol^{-1})

	$\Delta_f H^\circ$				$\Delta\Delta_f H^\circ$
source	1Ad$^\bullet$	2Ad$^\bullet$	1Ad$^+$	2Ad$^+$	$\Delta_f H^\circ(1Ad^+) - \Delta_f H^\circ(2Ad^+)$
Danen (1971)[14]	13				
Beauchamp (1977)[15]			159		
Houriet (1979)[16]					4
Ridge (1979)[17]			161		
Kebarle (1985)[18]			164		
Beauchamp (1986)[7]	15[a]	12[a]	158[b]	168[b]	10
Rauk (1989, 1991)[19,20]					15

[a] Estimated. [b] Calculated using estimated $\Delta_f H^\circ[R^\bullet]$ and measured IE$_a[1Ad^\bullet] = 6.21$ eV[7] and IE$_a[2Ad^\bullet] = 6.73$ eV.[7]

The measured $\Delta_f H^\circ[1Ad^\bullet]$ of 12 kcal mol^{-1} is in good agreement with the value obtained by combining $\Delta_f H^\circ[1Ad^+]$ and the IE$_a[1Ad^\bullet] = 6.21$ eV[7], which gives $\Delta_f H^\circ[1Ad^\bullet] = 9 \pm 3$ kcal mol^{-1}, thus substantiating the consistency of the present results. Our measured value is only marginally lower than the previous estimate (Table 1) and is the same as Danen's value to within the combined experimental error limits. Combination of the $\Delta_f H^\circ[1Ad^\bullet]$ with the known heat of formation[10] of AdH leads to a *D*[1Ad−H] = 96.3 kcal mol^{-1}. This is indistinguishable from *D*[*t*-Bu−H],[24] i.e., 95.9 kcal mol^{-1}, and leads to the conclusion that the thermodynamic stabilization of the 1Ad$^\bullet$ radical is close to that of t-Bu$^\bullet$, even though the bridgehead species is pyramidal and cannot benefit from conventional hyperconjugation. Of course, the equilibrium configuration of the t-Bu$^\bullet$ is also not planar. Previous competitive experiments had shown that 1Ad$^\bullet$ radicals are more easily formed and more reactive in abstraction reactions than t-Bu$^\bullet$ radicals.[25,26] As previously concluded, the higher reactivity of 1Ad$^\bullet$ is due to steric exposure of the reactive center, rather than to thermodynamic destabilization.

Combining the $\Delta_f H^\circ[2Ad^+] = 171$ kcal mol^{-1} and IE$_a[2Ad^\bullet] = 6.73$ eV[7] gives $\Delta_f H^\circ[2Ad^\bullet] = 16$ kcal mol^{-1}, and hence *D*[2Ad−H] = 100.3 kcal mol^{-1}. This now makes the relative stability of the 1Ad$^\bullet$ and 2Ad$^\bullet$ radicals consistent with the usual order of tertiary and secondary C−H bond strengths (cf. Table 1).

These thermochemical measurements give *only* the $\Delta_f H^\circ$ values for the relevant ions and radicals and provide *no* information concerning the structure of the ionic species produced by the dissociative ionization. However, it has been shown[27] that a linear relationship for hydrocarbons exists between the heterolytic bond strength (*D*[R$^+$−H$^-$]) and the relative size of the ion as represented by the number of atoms therein. This relationship also depends on the type of carbocation formed, i.e., secondary or tertiary. Figure 1 shows a plot of the variation of the heterolytic bond strength as a function of size for secondary and tertiary carbocations, with the present values for 1Ad$^+$ and 2Ad$^+$ included for comparison. On the basis of this empirical argument, it appears that the ions formed at threshold from the dissociative ionization of 1-AdX and 2-AdBr precursor molecules are indeed tertiary and secondary carbocations, respectively. It is noteworthy that other tertiary $C_{10}H_{15}{}^+$ ions generated by loss of H$^-$ from hydrocarbons other than adamantane have estimated $\Delta_f H^\circ$ values (estimated using the tertiary *D*[R$^+$−H$^-$] for adamantane = 219 kcal mol^{-1}, $\Delta_f H^\circ[H^-] = 35$ kcal mol^{-1},[10] and the $\Delta_f H^\circ$[molecule] from additivity[11]) that are *considerably* more positive than the

TABLE 2: Experimental Determination of the $\Delta_f H°$ of $1Ad^+$, $2Ad^+$, and $1Ad^{\bullet}$ (AE in eV, KER in meV, and $\Delta_f H°$ in kcal mol^{-1})

precursor	AE ±0.1	KER	$\Delta_f H°$[molecule]^a	$\Delta_f H°$[species] cogenerated^b	$\Delta_f H°[1Ad^+]$ ±3	$\Delta_f H°[2Ad^+]$ ±3	$\Delta_f H°[1Ad^{\bullet}]$ ±3
1-$C_{10}H_{15}Cl$	9.7	4	−43^b	29	152		
1-$C_{10}H_{15}CH_2OH$	9.6	6	−75	−4^c	150		
1-$C_{10}H_{15}COCH_3$	9.4(9.51)^d	9	−70	−3^e	150		
1-$C_{10}H_{15}CH_2NH_2$	9.7(9.60)^d	17	−31	38	155		
average					152 (158)^f		
2-$C_{10}H_{15}Br$	9.9	1	−30^b	27		171 (168)^f	
1-$C_{10}H_{15}CH_2NH_2$	9.6(9.6)^d	17	−31	178			12 (15)^f

[a] Additivity, ref 11. [b] Reference 10. [c] Reference 22. [d] Photoionization, ref 23. [e] Reference 22b. [f] Reference 7.

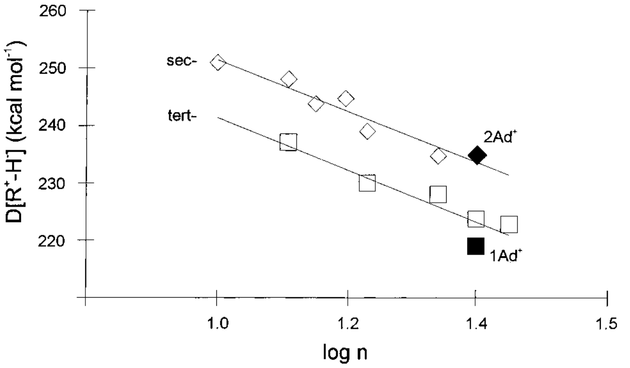


Figure 1. Effect of the number of atoms (n) on the heterolytic bond strength in secondary and tertiary carbocations.

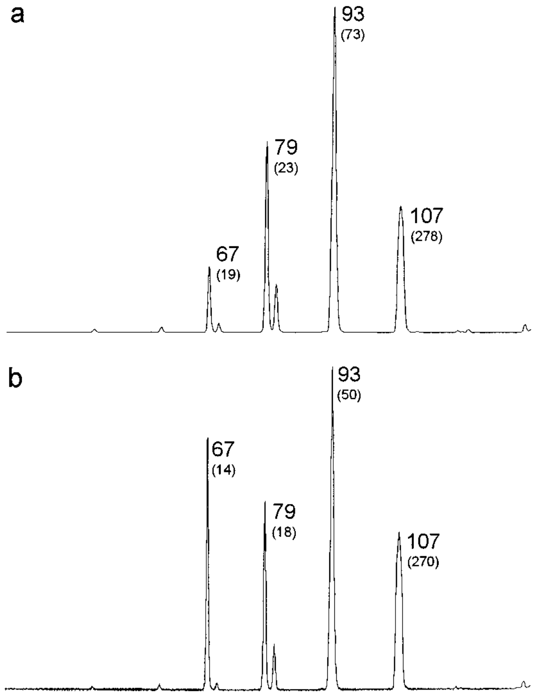
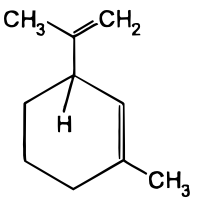


Figure 2. MI mass spectra of (a) $1Ad^+$, generated from 1-$C_{10}H_{15}CH_2NH_2^{\bullet +}$ and (b) $2Ad^+$, generated from 2-$C_{10}H_{15}Br^{\bullet +}$. KER (meV) values are given in parentheses.

$C_{10}H_{15}^+$ ions generated from adamantane and 1-AdX species. For example, heterolysis of the tertiary C−H bond in the $C_{10}H_{16}$ isomer shown below ($\Delta_f H° = 1$ kcal mol^{-1}, by additivity[11]) produces a resonance stabilized ion with $\Delta_f H°[C_{10}H_{15}^+] \cong 184$ kcal mol^{-1}, well above that for $1Ad^+$.



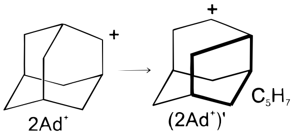
Mass Spectrometric Investigation of $1Ad^+$ and $2Ad^+$ Ions. The thermochemical data discussed above provide the relative energies of the $1Ad^+$ and $2Ad^+$ cations and furthermore indicate that the ions are distinct and retain their tricyclic structure at threshold. However, no information concerning the possible interconversion of the two ions (and hence the isomerization barrier) was obtained. A large number of mass spectrometric investigations on substituted adamantanes deal with the effect of the nature and position of the substituent on the dissociation characteristics of the molecular ions,[28] but the great majority do not address in any detail the structure of the $C_{10}H_{15}^+$ ions generated. It has, however, been shown that the species formed by loss of $Br^{\bullet}$ from ionized 2-bromoadamantane have slightly different collision-induced dissociation (CID) mass spectra than those of the ions generated from 1-bromoadamantane (loss of $Br^{\bullet}$) and adamantane itself (loss of $H^{\bullet}$);[29] it was concluded that the small differences were significant, permitting $2Ad^+$ to be distinguished from $1Ad^+$, and that both ions retained their tricyclic structures. These experiments have been repeated and extended here, and the results are presented below.

Metastable Ion (MI) Mass Spectra. For all the precursor molecules used to generate either $1Ad^+$ or $2Ad^+$, the electron impact mass spectra were dominated by the peak at m/z 135, corresponding to the $C_{10}H_{15}^+$ species. Metastable m/z 135 ions produced from all the precursor molecules exhibited four major competing dissociations corresponding to the losses of C_2H_4 (m/z 107), C_3H_6 (m/z 93), C_4H_8 (m/z 79), and C_5H_8 (m/z 67). Reducing the energy of the ionizing electrons showed that loss of C_3H_6 is the process of lowest energy requirement. Figure 2 shows the MI mass spectra of the $1Ad^+$ and $2Ad^+$ ions. For both, all the fragment ion peaks are Gaussian, except that corresponding to the loss of C_2H_4 (m/z 107). This peak is composite, a narrow component atop a broad component, showing that two reaction channels lead to C_2H_4 loss. The narrow component is only a minor feature of the peak, and the relative abundance of both components varies with the precursor molecule used to generate the m/z 135 ions. The m/z 135 ions generated from the dissociative ionization of all the 1-AdX precursor molecules were *indistinguishable*. However, the MI mass spectrum of the m/z 135 ion produced from the 2-$AdBr^{\bullet +}$ has *one* distinctive feature, relative to that of the $1Ad^+$: the relative abundance of the m/z 67 fragment peak.

Introduction of a small amount of collision gas does *not* affect the process leading to m/z 107, whereas the other processes are all *weakly* collision sensitive. The fragment ions produced from metastable $1Ad^+$ and $2Ad^+$ were characterized by transmitting them into the third field-free region of the instrument, where they were activated by collisions with helium. The CID mass spectra of the ions at *m/z* 107, 93, 79, and 67 exhibited *identical* dissociation characteristics, indicating that the fragment ions formed by the dissociations of metastable $1Ad^+$ and $2Ad^+$ have the same structures. These observations show that rearrangement can take place in both $1Ad^+$ and $2Ad^+$ to common dissociating configurations at some energy between the bottom of the $2Ad^+$ well and the dissociation limit for C_3H_6 loss (refer to Figure 4, which is discussed later).

Collision-Induced Dissociation (CID) Mass Spectra. CID mass spectra of ions selected from the mass spectrometer's ion source are a combination of metastable and collision-induced dissociations. Furthermore, source-generated ions generally have internal energies from their ground state to their dissociation limit. To eliminate the MI contribution and to study ions having internal energies close to the bottom of their potential energy wells, the CID mass spectra of *metastably generated m/z* 135 ions were obtained. Figure 3 shows the CID of metastably generated *m/z* 135 from $1\text{-}AdCH_2NH_2^{\bullet+}$ and $2\text{-}AdBr^{\bullet+}$. (Although not shown in the figure, the CID mass spectra of *m/z* 135 ions generated from the other metastable, ionized 1-adamantyl derivatives were the same as the CID mass spectrum from metastable $1\text{-}AdCH_2NH_2^{\bullet+}$.)

As in the MI mass spectra, the distinction between the CID mass spectra of the metastably generated $1Ad^+$ and $2Ad^+$ ions lies only in differences of relative intensities, the most obvious being the intensities of the *m/z* 93 and 67 ions relative to *m/z* 79 ions. The ratios *m/z* 93:79 and *m/z* 67:79 are 0.72 and 0.29 for the $1Ad^+$ and 1.26 and 0.87 for the $2Ad^+$. The origin of these intensity differences may be rationalized *only* in the $2Ad^+$ species. The flanking bridgeheads to the 2-position allow the potential formation of five- and six-membered rings; this is illustrated below. Note that this ion $((2Ad^+)')$ can formally be represented by four equivalent forms.



This alternative secondary carbocation, $(2Ad^+)'$, formally contains an intact C_5H_7 unit, and this may account for the greater ease with which the $2Ad^+$ generates *m/z* 67 fragment ions. In addition, it is also formally easier to expel a C_3H_6 unit from $(2Ad^+)'$ (scission of the mobile bond) to produce the *m/z* 93 fragment ions. For the $1Ad^+$, no such simple effect yields another isomeric tertiary cation; the tertiary cation contains only intact C_6H_8 units.

This simple view is supported by the calculations by Rauk et al.[19,20] The ground state structure for $2Ad^+$ was found to be significantly distorted from the symmetrical $2Ad^+$ form.[19] The $C_\alpha{-}C^+{-}C_\alpha$ bridge is bent toward one face of the cation, the $C^+{-}H$ bond becomes more pyramidal, and the $C_\alpha{-}C_\beta$ bonds become very unequal. These effects were rationalized in terms of enhanced C−C hyperconjugation rather than the formation of a nonclassical "bridged" cation. $(2Ad^+)'$ is therefore a discrete species and was also investigated by the same authors.[20] Two minima were found on the potential energy surface, one of which is ca. 2 kcal mol^{-1} above $2Ad^+$, with only a small energy barrier between them.

The CID mass spectra of the metastably generated $1Ad^+$ and $2Ad^+$ ions (ions which are sampled *near* the bottom of the potential energy well) are *distinct* and thus indicate that these two ions occupy *independent* potential energy wells, *separated* by a barrier to interconversion high enough to prevent the ions from interconverting at low internal energies. However, the similarity of the dissociation characteristics confirms that these $C_{10}H_{15}^+$ ions are capable of interconverting at energies below the lowest dissociation limit, C_3H_6 loss (see above). The depth of the potential energy wells of the $1Ad^+$ and $2Ad^+$ (approximately the difference between the sum of the product $\Delta_f H^\circ$ values for the lowest energy dissociation channel and the $\Delta_f H^\circ$ of the ions) are on the order of 41 and 23 kcal mol^{-1}, respectively, so that near the dissociation threshold the density of states will be large. At these energies, both the $1Ad^+$ and $2Ad^+$ may interconvert and must also access the large number of different structures that give rise to the four major fragment ions. This is supported by the isotopic labeling experiment, described below. In keeping with this is the total lack of sensitivity to collision gas of the *m/z* 107 peak in the MI mass spectra of both isomers, which shows that the reacting configuration for the C_2H_4 loss is only (just) accessed by $C_{10}H_{15}^+$ ions, very close to the dissociation limit. The weak sensitivity of the other MI peaks shows that the reacting configurations for these dissociations are also reached only at high internal energies.

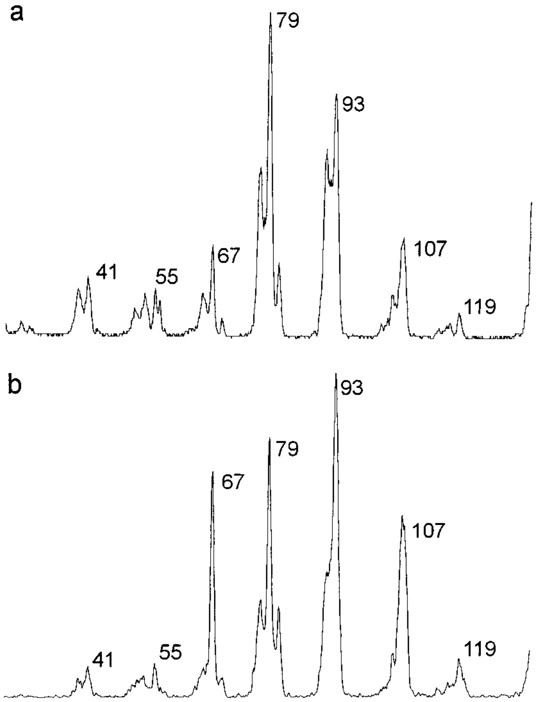


Figure 3. CID(He) of metastably generated (a)$1Ad^+$, from $1\text{-}C_{10}H_{15}\text{-}CH_2NH_2^{\bullet+}$ and (b) $2Ad^+$, generated from $2\text{-}C_{10}H_{15}Br^{\bullet+}$.

Figure 4 shows a potential energy diagram for the two ions. It is not possible experimentally to determine the height of the barrier to interconversion, but it is clear from these experiments that it is high enough to prevent isomerization at low internal energies. For comparison, the barrier to the isomerization of *sec*-butyl and *tert*-butyl ions (from the tertiary to the secondary cation) has been calculated to be 19.6 kcal mol^{-1}.[30] The corresponding *relative* energies are $t\text{-}C_4H_9^+ = 0$ kcal mol^{-1} ($\Delta_f H^\circ[t\text{-}C_4H_9^+] = 170$ kcal mol^{-1} [21]), $s\text{-}C_4H_9^+ = 14$ kcal mol^{-1} ($\Delta_f H^\circ[s\text{-}C_4H_9^+] = 184$ kcal mol^{-1} [10]), and the dissociation limit (to $C_3H_5^+$ and CH_4) is 38 kcal mol^{-1} [10], all remarkably similar to the adamantyl system.

Deuterium Labeling in $1Ad^+$. Dissociative ionization of $1\text{-}AdBr\text{-}3d_1$ generated $1\text{-}C_{10}H_{14}D^+$ ions (*m/z* 136). The MI mass spectrum of this ion showed extensive H/D mixing for *all* dissociation channels. From the relative abundance of each peak, experimental ratios describing the loss or retention of the

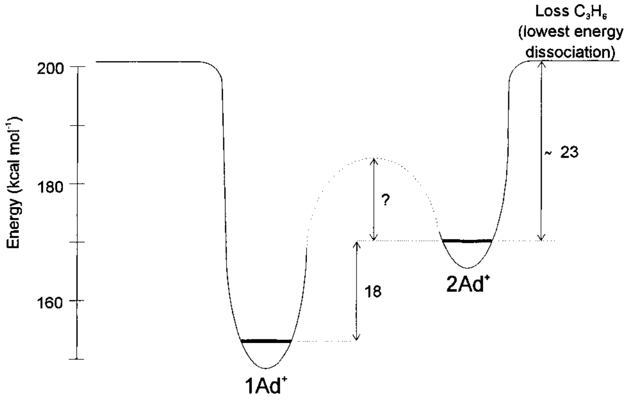


Figure 4. Potential energy surface for the 1Ad$^+$ and 2Ad$^+$ isomers.

TABLE 3: Statistical and Experimental H/D Mixing Ratios in $C_{10}H_{14}D^+$ Ions

fragmentation	statistical (14H, 1D)	experimental
loss of C_2H_4/C_2H_3D	2.75:1	~2.5:1[a]
loss of C_3H_6/C_3H_5D	1.5:1	1.4:1
loss of C_4H_8/C_4H_7D	1:1.1	1.05:1
loss of C_5H_8/C_5H_7D	1:1.1	1.05:1

[a] Because of the large KER associated with the loss of C_2H_4, the peaks were not well-resolved, and consequently, only an approximate ratio was obtained.

deuterium atom were calculated. These were compared with the expected random distribution of the hydrogen and deuterium atoms for each dissociation, assuming that different numbers of hydrogen and deuterium atoms are involved in the H/D mixing. Table 3 lists the calculated and experimentally determined ratios for the four most intense metastable processes, assuming that all the hydrogen (14H) and the deuterium (1D) atoms participate in the mixing. Clearly, the experimental and statistical distributions are almost identical, showing that the H/D mixing is essentially *complete* before the *m*/*z* 136 ions dissociate by any of the dissociation channels. This observation is consistent with the conclusion that the 1Ad$^+$ ions have access to a wide range of structures near the dissociation limit, allowing very extensive H/D mixing to occur. The behavior of these ions is similar to that of the 2-norbornyl cation, which also displays complete positional loss of identity for H (and C) atoms prior to C_2H_4 loss.[31]

Conclusions

The $\Delta_f H°$ of the 1Ad$^+$, 2Ad$^+$, and 1Ad$^\bullet$ have been measured to be 152 ± 3, 171 ± 3, and 12 ± 3 kcal mol^{-1}, respectively, and $\Delta_f H°$[2Ad$^\bullet$] was calculated to be 16 kcal mol^{-1}. It was shown that the 1Ad$^+$ and 2Ad$^+$ occupy independent potential energy wells, separated by an energy barrier that is high enough to prevent their facile interconversion. On the basis of the thermochemical measurements and the mass spectrometric data, it appears that 1Ad$^+$ and 2Ad$^+$ produced at threshold are indeed tertiary and secondary carbocations that retain their tricyclic structure. However, it is proposed that at higher energies the two isomers share a common potential energy surface, accounting for their similar dissociation characteristics. At these elevated energies, the ions must access many structures, because of the high density of states, so that the structure of the dissociating ions may no longer be the closed tricyclic structure. The complete statistical mixing of H/D atoms in the 1-$C_{10}H_{14}D^+$ ions before dissociation by any of the accessible channels on the microsecond time scale also shows that the ions must access many structures near the dissociation limit.

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