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The influence of fragment size and intermediate barriers on competing near-identical simple cleavage reactions: A variational RRKM study

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Dedicated to Professor Tino Gäumann in recognition of his many early contributions to mass spectrometry.

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ABSTRACT

The fragmentation reactions of almost-symmetrical radical cations exhibit remarkable energy-dependent selectivity. The simple cleavage of the *N*-propylbutylamine radical cation and its *N*-methyl analog results in loss of ethyl or propyl radicals. The energy required to expel the ethyl radical (the smaller alkyl fragment) is lower, and ethyl loss is the preferred reaction of ions with low internal energy. The branching ratio is reversed for ions with higher energy, which can be accounted for with variational transition state theory. The competition between the two concurrent cleavage reactions is not governed by product-like orbiting transition states, but by relatively tight transition states; however, these are not equally tight. The transition state for loss of ethyl from higher energy reactant ions lies earlier on the reaction coordinate than does the transition state for loss of propyl, and the latter will in turn be slightly more product-like and hence more loose. $k(E)$ vs E for loss of propyl radicals therefore rises more steeply with increasing internal energy, and this reaction becomes the more rapid process for higher-energy reactants such as the molecular ions formed in mass spectrometers with 70 eV electron ionization. The transition states for cleavage reactions exhibit energy-dependent shifting also when moderate intermediate barriers are present.

1. Introduction

A simple cleavage is a unimolecular fragmentation reaction which proceeds directly from the reactant to the products by fission of a single bond without concurrent rearrangement. Simple cleavage reactions are frequently encountered among the unimolecular fragmentation reactions of neutral and charged aliphatic radicals such as the expulsion of alkyl radicals from alkyl and alkoxy radicals (Scheme 1). Competition between simple cleavage reactions is possible when the reactant is unsymmetrical, but examination of the outcome can be difficult when the reactant is uncharged; however, competing reactions of ions can often be studied with mass spectrometers.

Unsymmetrical aliphatic radical cations undergo competing simple cleavage reactions, and the branching ratio is governed by the internal energy of the reactant. Using the α-cleavage reactions of gas-phase amine radical cations as a prototype of the simple cleavage, we reported [1] that when the reaction involves loss of alkyl radicals which differ only in length, loss of the smaller radical is the thermochemically favored process. This is also the outcome observed experimentally when mass spectrometers are used to study the cleavage of low-energy radical cations (the metastable molecular ions); the smaller radical is lost more readily. However, the branching ratio is reversed for reactant ions with higher internal energy; these exhibit preferential loss of the larger radical. This is the behavior generally reflected in 70 eV mass spectra, and it is in turn often considered to be the expected outcome of competing simple cleavage reactions of radical cations [2,3].

The energy dependent reversal of the branching ratio demonstrates that the rate constant for loss of the larger alkyl radical increases more steeply with increasing internal energy than does the rate constant for loss of the smaller radical. The $k(E)$ curves cross. To account for this behavior with a standard RRKM model, the transition states of the two cleavage reactions should be reasonably different, but that would appear to be contrary to chemical intuition when considering reactions as closely related as the loss of homologous alkyl radicals in otherwise identical reactions (Scheme 2) [4–6]. McAdoo and coworkers [4] examined this problem and found that the properties of one of the transition states for two competing simple cleavage reactions must be arbitrarily modified (significantly lowered vibrational frequencies) for traditional RRKM-theory to reproduce the result that the branching ratio for loss of large and small radicals is reversed as a function of the reactant internal energy.

Within the framework of classical transition state theory, it is assumed that the transition state is associated with a potential energy maximum, a saddle point. However, the typical simple cleavage reaction is expected to be an endothermic process with no

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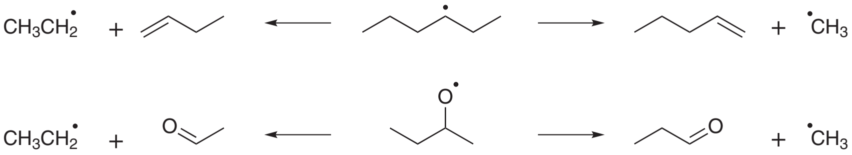


Scheme 1. Competing cleavage reactions of 3-hexyl radicals and of *sec*-butyloxy radicals.

significant energy maximum between the reactants and the products. Systems like that are often well described with microcanonical variational transition state theory (VTST) [7–12]. This theory was originally devised by Wigner [13] and Horiuti [14], and later refined by Keck [15]. The VTST transition state is located at a minimum-flux surface that separates the reactant and product regions of phase space and is orthogonal to the reaction coordinate. The position of this state on the reaction coordinate is not necessarily associated with a potential energy maximum.

Chesnavich et al. [16–18] have shown that when applied to polyatomic systems such as $C_4H_8^{\bullet+}$, a VTST description implies that the rate of specific fragmentation reactions can be governed by quite different transition states, 'orbiting' and 'tight', depending on the internal energy of the reacting species. This phenomenon was called 'transition state switching' and has later been examined by a number of other authors [10,19–21]. The present study attempts to demonstrate that a closely related description can account qualitatively for the energy-dependent reversal of the branching ratio for loss of nearly identical alkyl radicals observed when aliphatic amine radical cations undergo unimolecular fragmentation. By forgoing any attempt to arrive at quantitative predictions, we avoid some of the problems that would arise from possibly arbitrary choices and simplifying assumptions, while retaining a comprehensive view of the reactions. A preliminary discussion of the reversal was included in our earlier paper [1].

It has been pointed out [10,12,22,23] that the transition state for a monotonically endothermic reaction becomes progressively less product-like as the internal energy of the reactant increases, in the sense that the transition state inter-fragment distance diminishes. We examine this aspect by studying the energy-dependence of the simple cleavage of CC bonds in the radical cations of ethylamine, propylamine and butylamine, as well as their *N*-methyl- and *N*,*N*-dimethyl analogs.

The assumption that simple cleavage of CC bonds in straight-chain alkyl groups is continually exothermic and free from intermediate enthalpy barriers is examined by studying the relationship between electronic energy and the length of the CC bond under cleavage in the same simple amine radical cations as well as in the radical cations of *N*-propylbutylamine (**1**) and *N*-methyl-*N*-propylbutylamine (**2**) (Scheme 2).

We then examine whether the energy dependent changes of the transition state properties can account for the experimentally observed [1,4,24] reversal of the branching ratio for loss of different alkyl radicals, using as prototypes the competing cleavage reactions of ionized **1** and **2**.

Finally, we illustrate that moderate intermediate enthalpy barriers can be present when simple cleavage takes place at branching points; the transition states for cleavage appear not to be tied to the saddle points but exhibit some energy dependent shifting.

2. Methods

2.1. Variational transition state theory

Within the framework of classical RRKM theory, the rate constant is a function of the internal energy (E), as given by Eq. (1), where $G(E-E_0)$ is the number of states of the transition state (presumably the saddle point), $N(E)$ is the density of states of the reactant, and σ is the number of equivalent paths [25].

$$k(E) = \frac{\sigma G(E-E_0)}{hN(E)} \tag{1}$$

Variational criteria for locating the rate limiting situations are particularly useful when the reaction in question can be assumed to have negligible reverse enthalpy barriers. The VTST transition state for reactants of potential energy E corresponds to a minimum in the sum of states, G, along the reaction coordinate. If r is the reaction coordinate and $V(r)$ is the potential energy of the reacting molecule, then the variational transition state is located at the value of r that satisfies Eq. (2) when external rotations are ignored [18,22]. $G(E-V(\mathrm{r}))$ depends on the frequencies of the vibrations that are orthogonal to the reaction coordinate; these are known as the projected frequencies [26,27].

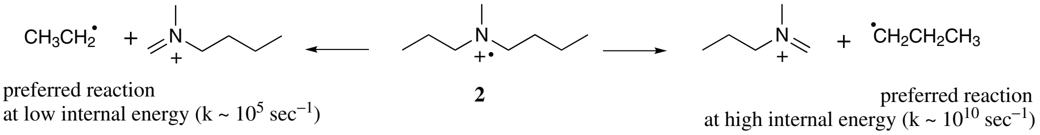
$$\frac{\mathrm{d}G(E-V(r))}{\mathrm{d}r} = 0 \tag{2}$$

To obtain the variational transition state theory rate constant, $G(E-E_0)$ is replaced in Eq. (1) by $G^*(E)$, which is the number of energy states at the variational transition state.

Described in simple terms, an approximate, classical RRKM calculation requires *inter alia* that the sum of energy states at a given internal energy is evaluated at one particular point, the transition state, based on the rovibrational frequencies of this state. A VTST calculation requires that similar calculations are carried out at several points along the reaction coordinate, each based on a different set of energy states, the projected vibrational frequencies at that particular point. The VTST transition state at a particular reactant internal energy is located at that point along the reaction coordinate where the state sum is at a minimum.

2.2. Implementing VTST

To locate the VTST transition states for simple cleavage reactions we have employed a straightforward implementation of microcanonical variational transition state theory. The vibrational energy levels that enter into the calculations of rate constants are taken to be adequately described as harmonic oscillators. For the amine radical cations studied, we define the reaction coordinate for simple cleavage as the stretching of a CC bond and describe it by a series of MP2/6-31G(d) partially optimized structures in which the CC



Scheme 2. The competing α-cleavage reactions of the *N*-methyl-*N*-propyl-butylamine radical cation.

bond length in question is increased from 1.60 Å to 3.0 Å in steps of 0.05 Å.

For each partially optimized structure of the reactant, the energy was calculated with a variant of the G3(MP2) method [28], in which the zero-point vibrational energy contributions were derived from the projected MP2/6-31G(d) frequencies scaled [29] by 0.9427. These frequencies can be employed in thermochemical estimates, even though the species in question does not correspond to a stationary point. For the reactant and product species, the G3(MP2) total energies were converted to heats of formation as described by Nicolaides et al. [30]; the required auxiliary thermochemical data were taken from the compilation by Wagman et al. [31]. The quantum chemical calculations were carried out with the Gaussian 98 and Gaussian 03 suites of programs [32].

The VTST calculations were performed in 1 cm^{-1} energy increments up to a maximum (usually 25,000 cm^{-1}). For each value of the internal energy, the rate constant was then calculated for each point on the reaction coordinate, employing the projected frequencies and a standard implementation of the Beyer–Swinehart direct-count algorithm [33].

Broadly speaking, this procedure amounts to performing conventional RRKM calculations for a substantial number of trial transition states along the reaction coordinate, rather than once, at the potential energy maximum. The results provide a set of corresponding values of the transition state CC bond length and the rate constant for alkyl radical loss, as a function of the internal energy of the reactant ion. Neglect of anharmonicity and rotations, together with the effect of treating low-frequency vibrations as harmonic oscillators, may well introduce significant error in the calculated rate constants. However, such errors notwithstanding, we believe that this procedure accounts qualitatively for the variation of the inter-fragment distance among the variational transition states. Additionally, for competing reactions it provides a qualitative description of how the ratio of rate constants varies with internal energy, leading in turn to an adequate understanding of the variation of the branching ratio of the competing simple cleavage reactions.

3. Results and discussion

Following Chesnavich et al. [16–18], we examine the simple cleavage under the initial assumption that both loose (orbiting) and tight transition states may be present, depending on the internal energy of the reactant. This assumption appears reasonable in view of the relatively low critical energy of the amine α-cleavage reactions (less than 1.2 eV, in many cases considerably less). It has been pointed out that the energy-dependent change from reaction via an orbiting transition state to reaction via a tight transition state can take place at relatively low reactant internal energy [10,16,18,34]. Our computational results concern the cleavage of CC bonds in reactants that possess sufficient energy to react via tight transition states.

3.1. Cleavage in straight-chain systems

Simple cleavage of the α CC bond in unbranched aliphatic amine radical cations proceeds as a monotonically endothermic process, as exemplified in Fig. 1. There are systematic variations with regard to how steeply the energy rises as the CC bond length increases; the more endothermic cleavage reactions, such as those in tertiary amines, exhibit the steeper initial rise. Cleavage at a branching point (e.g., loss of an ethyl radical from *sec*-butylamine radical cations, see below) may be associated with an energy barrier, but cleavage in straight-chain alkyl groups appears always to have a single-well potential surface when the amino group is situated at the terminal carbon atom.

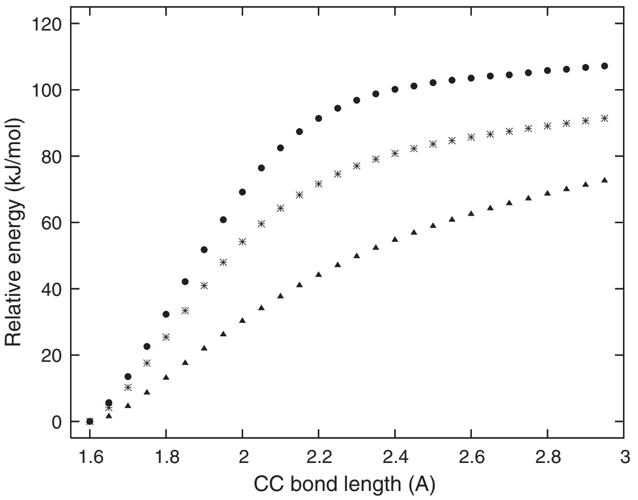


Fig. 1. Variation of the potential energy (G3MP2, kJ mol^{-1}) of the butylamine (lower trace), *N*-methylbutylamine (middle), and *N*,*N*-dimethylbutylamine (upper) radical cations as a function of the length of the CC bond under cleavage. Energies relative to the values calculated for CC bond lengths of 1.6 Å.

At a CC distance of 3 Å, the potential energy of these ions and the other straight-chain amine ions examined has come to within 15–25 kJ mol^{-1} of that required for dissociation. The interactions between the incipient fragments as the CC distance increases further are taken to be predominantly electrostatic and should not introduce energy barriers. Dissociation entails the conversion of six internal modes to external rotational and translational degrees of freedom, the so-called transitional modes [35], among which the CC-stretch becoming translational mode is taken to be the reaction coordinate. These modes will be among the lowest-energy modes as the reactant approaches the transition state, possibly the six of lowest energy [22].

Fig. 2 shows how the nine lowest projected frequencies vary when the CC bond is stretched as the *N*-methylbutylamine radical cation approaches dissociation. The vibrational frequencies of the transitional modes decrease as the CC bond is stretched, which strongly influences the calculated rate constants, because the low-energy modes make particularly significant contributions to the sums and densities of state. The change of the vibrational frequencies reflects that the transition states with longer CC distances are

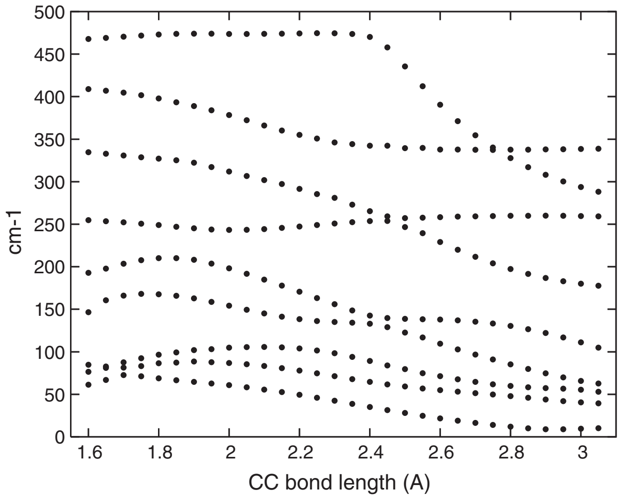


Fig. 2. Variation of the lowest vibrational frequencies (cm^{-1}) as the length of the α-CC bond of the *N*-methylbutylamine radical cation is increased from 1.6 Å to 3.05 Å (projected MP2/6-31G(d) frequencies).

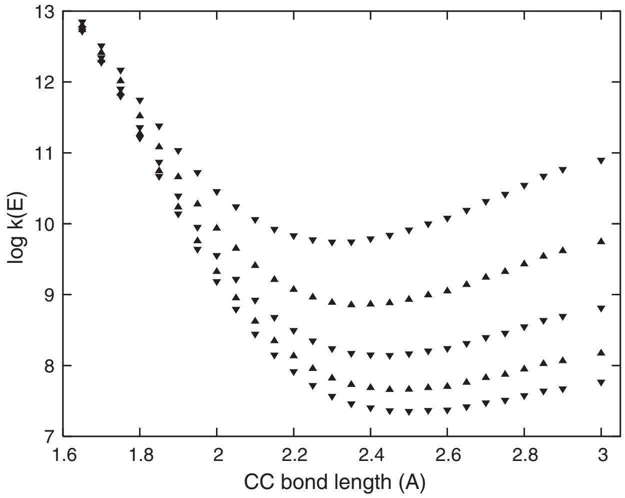


Fig. 3. Log $k(E)$ for loss of propyl radicals from *N*-methylbutylamine radical cations as a function of the CC bond length, shown for five different values of the internal energy (500, 1000, 2000, 4000, 8000 cm^{-1} above threshold). 2.95 Å values omitted owing to computational problems.

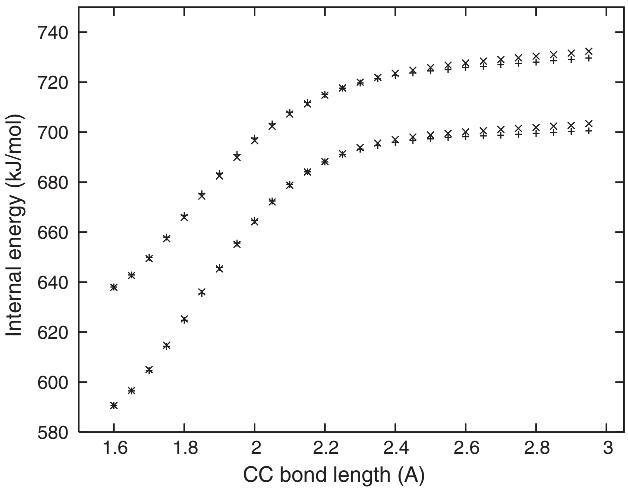


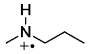
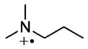
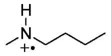
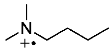
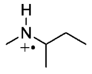
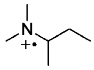
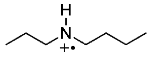
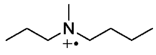
Fig. 4. Variation of the potential energy (G3MP2, kJ mol^{-1}) of the radical cations of **1** and **2** as the CC bonds are stretched en route to loss of ethyl and propyl radicals.

more loose. The conserved mode frequencies are largely unaffected by the change of the CC distance.

The bond length in the tight transition state varies with the reactant internal energy, becoming shorter as the energy increases (see Fig. 3 and Table 1). At our level of approximation, the variation amounts to 0.2–0.3 Å for excess energies of up to some 2 eV, with a typical CC distance around 2.3 Å when straight-chain alkyl groups undergo α-cleavage. This is not very different from the CC distances encountered when neutral systems undergo fragmentation [9], or from the fragment separation in the traditional energy-barrier transition states that govern CC cleavage in amine radical cations with branched alkyl groups (see below).

The calculated rate constant varies with the transition state looseness which is reflected in the length of the CC bond under cleavage. Fig. 3 illustrates this relationship for five values of the internal energy of the reactant. Each minimum indicates the location of the tight transition state for cleavage of ions of that particular internal energy. These results confirm that the transition state CC bond length decreases when the reactant energy increases. The variations exemplified in Fig. 3 are typical of the results obtained for the straight-chain amines examined for internal energies of up to more than 1 eV in excess of the dissociation threshold.

Table 1
CC Bond lengths of the variational transition states for amine α-cleavage[a].

	Ethyl loss		Propyl loss	
	500[b]	5000[b]	500[b]	5000[b]
	2.42	2.32		
	2.42	2.31		
			2.53	2.34
			2.47	2.33
	2.26	2.21		
	2.26	2.21		
	2.44	2.32	2.53	2.35
	2.41	2.29	2.48	2.32

[a] Values in Å.
[b] Energy above dissociation threshold, in cm^{-1}.

Over-all, these results justify the expectation that CC cleavage in straight-chain aliphatic amine radical cations takes place on a single-well potential surface, that a tight transition state exists for reactants of moderate internal energy, and that cleavage in higher-energy reactants involve increasingly tight transition states and hence shorter CC distances.

3.2. Competing cleavage reactions

The CC cleavage reactions in the *N*-propylbutylamines, **1** and **2**, exhibit the same properties as cleavage in the smaller amines. In particular, there are no intermediate energy barriers as the CC bond length increases when ethyl radicals are lost, nor when propyl radicals are lost (Fig. 4).

As expected, the calculated VTST rate constants for the CC cleavage reactions of **1** and **2** increase with increasing internal energy of the reacting ions, but it turns out that they do not rise equally steeply. The $k(E)$ vs E curves for loss of ethyl and propyl from **1** and from **2** cross (Fig. 5). This provides a convincing rationale for the experimental results [1], that loss of ethyl radicals is favored for lower-energy reactants, loss of propyl radicals for higher-energy reactants.

The reason for the reversal of the alkyl radical loss branching ratio is related to the change in transition state CC bond length as the internal energy of the reactant increases. It is perhaps more easily understood by first considering the properties of reactants with internal energy just above that required for loss of propyl radicals (which is slightly higher than that required for ethyl loss [1]). The properties of the propyl loss transition state have not yet changed much from those at threshold, whereas the transition state for ethyl loss has become more tight (the excess energy is higher). This difference will persist as the internal energy increases, loss of ethyl will retain the advantage, and the transition state will continue to be (slightly) more tight than that for loss of propyl, as indicated by the CC bond length differences (Table 1). The competition between the two reaction channels will depend on whether it is more important for the sum of energy states that the excess energy is higher (which would favor loss of ethyl), or that there are more low energy states (more loose transition state, which would favor loss of propyl). With increasing internal energy, the difference between the excess energies of the two transition states is

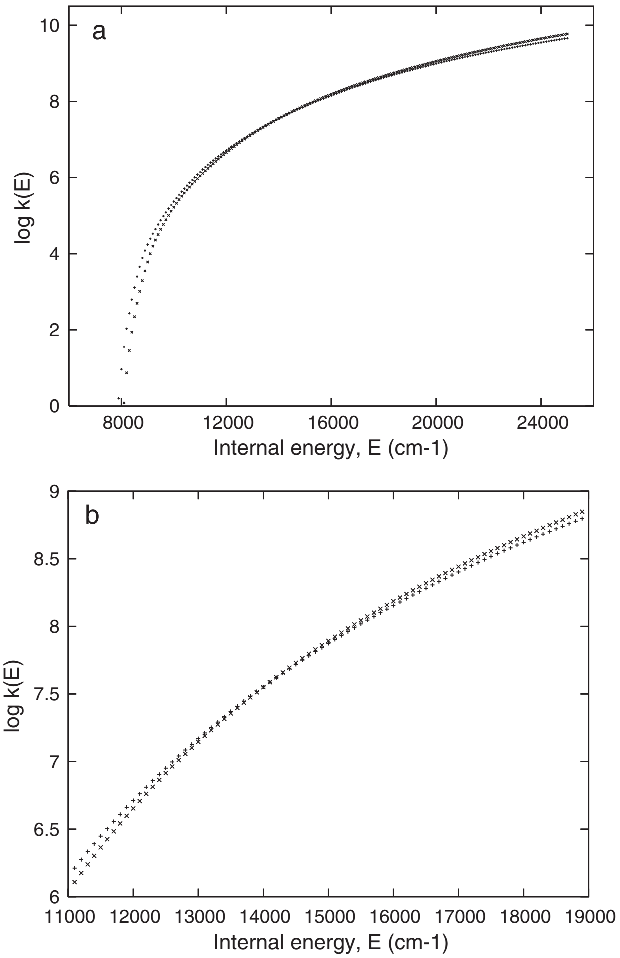


Fig. 5. (a) Variation of log $k(E)$ with E (cm^{-1}) for loss of ethyl and propyl radicals from *N*-propylbutylamine radical cations (**1**). (b) Excerpt to emphasize the reversal of the ratio of rate constants, ethyl loss initially more rapid than propyl loss.

reduced (relatively speaking), whereas the low-lying energy states assume increased importance, and it is in turn reasonable to find these factors reflected in the branching ratio, so that the $k(E)$ vs E curves cross.

3.3. Cleavage reactions with an enthalpy barrier

Simple cleavage reactions are not always single-well processes. It is known from experiment that CC bond cleavage at branching points in amine radical cations can proceed via appreciable enthalpy barriers [36,37]. However, the presence of intermediate barriers that are lower than the endothermicity of the reaction is not easily discovered by experiment. The loss of ethyl radicals from *N*,*N*-dimethyl-*sec*-butylamine radical cations provides an illustrative example (Fig. 6).

The variational transition state for cleavage in the presence of a moderate intermediate enthalpy barrier is for low-energy reactants located at the same CC bond length as that at the barrier, but the transition state exhibits a somewhat shortened CC bond when higher internal energy reactants are considered (Table 1 and Fig. 7). In our view, the strong association between energy barrier and variational transition state assumed by other authors [8,12,18] requires that the barriers are substantial, possibly that they exceed the reaction endothermicity.

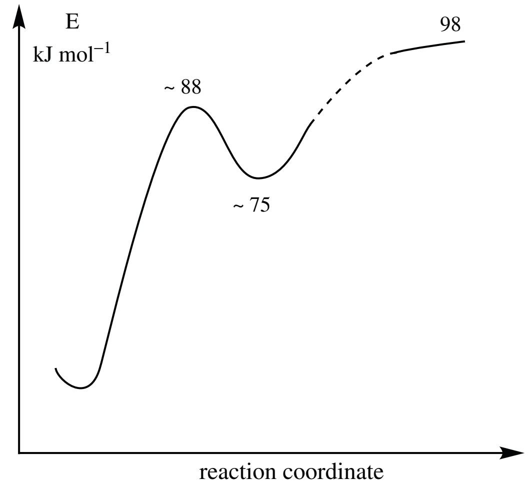


Fig. 6. Potential energy profile of the loss of an ethyl radical from the *N*,*N*-dimethyl-*sec*-butylamine radical cation.

Examination of the competing cleavage reactions of ionized 3-hexyl-amine and its *N*-methyl substituted analogs indicates that the presence of moderate barriers do not fundamentally change the situation with regard to competing α-cleavage reactions. Loss of the smaller alkyl group is only favored for lower-energy reactants. However, computational examination of cleavage reactions at branching points in amine radical cations is often complicated by conformational issues. The reactants may be present in *trans*/*gauche* conformations as well as in conformations influenced by interactions between the singly-occupied nitrogen orbital and the neighboring CC bond [38,39]. One consequence of these differences is that two competing α-cleavage reactions will rarely proceed from the same conformer of the reactant. Additional complications arise because cleavage reactions that follow the minimum energy reaction pathway often do not lead to the more stable conformer of the immonium ion products [40].

When the intermediate enthalpy barriers to cleavage become more substantial, such as when cleavage takes place at completely substituted carbon atoms, the competition can come to be determined by the barrier thermochemistry, even for higher internal energy ions, One example is the fragmentation of the *N*,*N*-dimethyl-3-methyl-3-hexylamine radical cation, **3**, which is preferably by loss of ethyl radicals at all internal energies examined. The report by

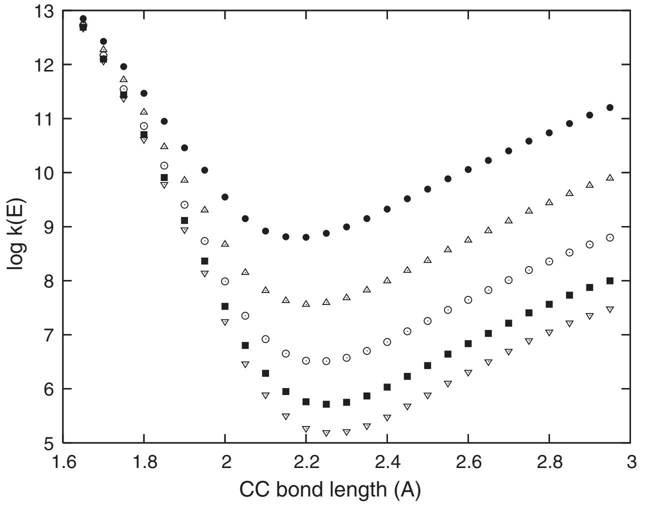
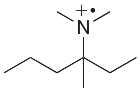


Fig. 7. Log $k(E)$ for loss of ethyl radicals from *N*,*N*-dimethyl-*sec*-butylamine radical cations as a function of the CC bond length, shown for five different values of the internal energy (500, 1000, 2000, 4000, 8000 cm^{-1} above threshold).

Mandeville et al. [24] provides additional examples that the competing α-cleavage reactions of high-energy, branched amine radical cations do not always exhibit a particular preference for loss of the larger alkyl radical.



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4. Conclusions

Using the α-cleavage reaction of aliphatic amine radical cations as the prototypical simple cleavage, we have found that the behavior of competing reactions in reactants with relatively low internal energy (the metastable ions in a mass spectrometry experiment) is unexceptional; the thermochemically favored reaction is also the more rapid. However, the situation can be reversed when higher internal energy ions react. It is an apparent violation of Stevenson's rule (or the Audier-Stevenson rule [2]) that the competition between two closely related reactions with slightly different energy requirements does not favor the process that yields the lower-enthalpy products. Nonetheless, that is the situation encountered in 70 eV electron ionization mass spectrometry, competing simple cleavage reactions in radical cations with sufficient internal energy to react rapidly in the mass spectrometer ion source take place in violation of the rule.

This situation arises because Stevenson's rule is concerned with enthalpies, not with kinetics, and it is resolved with variational transition state theory, which takes order (entropy) into account. As the reactant internal energy increases, the variational transition states for loss of ethyl and propyl from nearly symmetrical reactants such as **1** and **2** become sufficiently different to allow $k(E)$ for loss of propyl radicals to rise more steeply with E, since loss of propyl radicals will have the more loose transition state, and, in turn, a more rapidly increasing number of energy states and a larger $k(E)$ for cleavage, as the reactant internal energy increases beyond the crossing point.

Conventional sector mass spectrometers provide two windows through which to observe the dissociation of ionized molecules, the mass spectrum proper, which summarizes the reactions of ions with sufficient internal energy to react on nanosecond timescales, and the MIKE spectrum (or an equivalent account of the reactions of the metastable ions), which reflects the microsecond reactions. The internal energy of the ions that react within each of these two windows will vary considerably from system to system, but the metastable ions will in every case be the lower-energy reactants. The reversal of the branching ratio when competition is observed through the two windows can be satisfactorily rationalized under the assumption that bond cleavage takes place via transition states that are considerably more tight than those at the centrifugal barriers (the orbiting transition states). The observation of energy-dependent reversal of the branching ratio is not necessarily evidence that there is a switch from loose to tight transition states between the two windows, only that they provide access to reactions before and after the $k(E)$ vs E curves cross.

The branching ratio for the lower-energy reactants could be governed by competition between relatively tight transition states as well as by competition between loose (orbiting) transition states. In the latter case, the reactions considered here would provide additional examples of transition state switching [16], as the high and low energy transition states would be very different. However, neither the experiment nor the qualitative theory employed here allow us to determine when the internal energy is sufficiently high to allow control to pass from the orbiting to the tight transition state. In either case, the energy-dependent incremental modification of the properties of reasonably tight transition states is perhaps better described as transition state shifting. It is likely that examination of these systems with more exacting theoretical methods would in a manner of speaking shift the coordinate systems and scale the axes, modifying but not fundamentally changing the over-all picture.

The finding that transition states determined in a variational manner are located progressively later on the reaction coordinate when the internal energy of the reactant is lower, that is, closer to the conventional RRKM transition state, is not specific to the systems examined here. When closely related reactions compete, the transition state that more resembles the products is also the transition state with lower-energy frequencies, since the conversion of translational modes to external degrees of freedom will be more complete. The present results should apply equally to competing cleavage reactions of neutral aminyl- and oxyradicals and possibly to the pyrolytic cleavage of hydrocarbons, but we are not aware of any studies of energy-dependent fragmentation reactions of e.g., alkoxy radicals.

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