Isomerization and Dissociation in Competition. The Pentene Ion Story

Liam M. Duffy, Jeffrey W. Keister, and Tomas Baer*

Chemistry Department, University of North Carolina, Chapel Hill, North Carolina 27599-3290 Received: July 5, 1995; In Final Form: September 22, 1995[®]

Various isomeric C_5H_{10} ⁺⁺ ions are prepared by photoelectron photoion coincidence (PEPICO) in selected energies above their dissociation limit. All ions dissociate by losing either C₂H₄ or CH₃. The PEPICO time of flight distributions of the product ions provide information about translational energy release as well as the dissociation rates in the range of 10^4 to 2×10^6 s⁻¹. An unusual aspect of these reactions is that a number of the isomers dissociate via two-component decay kinetics. The fast component is faster than we can measure by PEPICO. The rate constant associated with the slow component is the same for all five isomers investigated. The results are analyzed in terms of a potential energy surface in which ions can dissociate directly or isomerize to the more stable branched C_5H_{10} ⁺⁺ isomers. Once they fall into the lowest energy wells, they can dissociate only via a slow component. The potential energy surface involves two dissociation and four isomerization rates. From the measured slow dissociation rate and various branching ratios (fast to slow, loss of C_2H_4 to CH_3^{\bullet} , etc.) it is possible to extract experimental values for all six rate constants which range from 10^5 to 10^{11} s⁻¹. These rate constants as a function of the ion internal energy are then fitted with the RRKM theory. The three density of states associated with the three stable isomer wells are calculated with vibrational frequencies obtained from *ab initio* molecular orbital calculations. It is significant that the **RRKM** calculations are made with only six adjustable parameters. Since each k(E) curve requires two parameters [slope and magnitude], the ability to fit each rate constant with only one parameter is strong evidence for the validity of the proposed potential energy surface.

Introduction

The multidimensional potential energy surfaces of polyatomic hydrocarbon radical cations are extremely complex. The difficulties associated with experimentally determining the mechanisms involved in the dissociation of such ions are compounded by the fact that the kinetics are dependent on the ion internal energy. This is because isomerization and dissociation rates are governed not only by transition state barrier heights but also by the entropy associated with a given transition. For example, although 1,2-H atom transfers have higher energy barriers than those of 1,4- or 1,5-H atom shifts, they also have a lower transition entropy.¹ At high ion internal energies then, hydrogen atom transfer reactions may proceed via multiple 1,2-H atom shifts, while at low energies ring-forming 1,4- or 1,5-H atom transfers may dominate.¹

These subtleties make it difficult to compare experimental studies of radical cation dissociations. For many years it has been known that the electron impact mass spectra of pentene isomers are very similar; the only differences observed are that the branched isomers and 2-pentene ions lose predominantly methyl radicals, while cyclopentane and 1-pentene preferentially lose neutral ethene. A number of experimental studies have been performed to elucidate the mechanisms involved in pentene ion dissociations and to find ways of differentiating the various isomers.^{1–11} In an early attempt to discern the mechanisms involved in ethene loss from 1-pentene and cyclopentane, Millard and Shaw¹ performed isotopic labeling studies in a conventional electron impact mass spectrometer. They found that cyclopentane dissociation proceeds only after ring opening and that significant hydrogen scrambling occurs in both isomers before ethene is lost. Their results are difficult to interpret in light of the energetics described above and because they did not distinguish the low-energy dissociation of metastable ions from the higher energy and prompt reactions. Later studies did, however, investigate the dissociation of low-energy, metastable pentene ions.^{4,6-10} Bowen and Williams⁴ predicted and observed similar metastable product-branching ratios and dissociation rates for all pentene isomers using electron impact ionization mass spectrometry. In work carried out in this laboratory, Brand and Baer^{7,9} found that the metastable rates of all isomers as a function of absolute energy are identical. They concluded that all isomers at least partially isomerize to the lowest energy ion, 2-methyl-2-butene. In their studies, multicomponent dissociation rates were observed for all the isomers except 2-methyl-2-butene. However, no simple model could be found to explain the observed dissociation kinetics.

In this work we repeat the experiments of Brand and Baer,⁹ this time using a molecular beam to cool the isomers before ionization. Under these new conditions, multicomponent rates are well-resolved and the low internal energy kinetic mechanisms involved in the pentene ion dissociation become clear. A model potential energy surface with three wells is proposed to explain the results, and a novel analysis is employed to experimentally measure the six individual rate constants that the potential implies. A new isotopic labeling technique for determining reaction mechanisms when multicomponent rates are observed in threshold photoelectron photoion coincidence (TPEPICO) studies is proposed.

Procedure

The experiments were conducted using the TPEPICO technique. Briefly, dispersed photons from a H₂ discharge lamp $(h\nu \approx 10.8 \rightarrow 11.2 \text{ eV})$ intersect a seeded molecular beam in a constant electric field region of the spectrometer. Upon ionization zero-kinetic energy photoelectrons are selected by a line of sight energy selector and detected. The electron signal is delayed for 10.5 μ s and then used as the "start" trigger of a time to pulse height converter (TPHC). After passing through

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two acceleration regions, the ions enter a field-free region and are subsequently detected. The ion signal is used as the "stop" trigger of the TPHC. The ion time of flight (TOF) spectrum is then displayed on a multichannel pulse height analyzer (MCA). The important feature to note is that since the photon and electron energies are known, the internal energy of the ion is known. If the parent ions are metastable ($k = 10^5 - 10^6 \text{ s}^{-1}$), an asymmetric daughter TOF peak will be observed. The ion dissociation rate constant can be determined from an analysis of the ion TOF distribution.

A seeded molecular beam (14% C_5H_{10} in argon) was used to cool the parent isomers. A 70 μ m conical nozzle was used with a backing pressure of about 110 Torr of argon and with C_5H_{10} expanding into a source chamber maintained at roughly 10^{-5} Torr. Stronger expansion conditions were not used because cluster formation was observed at backing pressures above 200 Torr.

The photoionized sample consisted of the molecular beam as well as thermal (298 K) background gas in the chamber. Because the two gas sources have very different translational energies, they are easily distinguished on the basis of their TOF distribution. The parent ion TOF distribution from the beam sample has a full width half maximum (fwhm) of ~20 ns, while the signal from the room temperature background gas is characterized by a fwhm of ~160 ns. The data were corrected for this background gas by subtracting the latter from the beam data at each photon energy investigated. The ratio of warm to beam sample (~16%) was determined by setting the photon energy below the ion dissociation limit and monitoring the parent ion TOF distribution. The TOF distribution of the pure background gas was obtained by introducing the pentene gas directly into the experimental chamber at 298 K.

Although the molecular beam was translationally cold (5 K), as determined from the narrow TOF distribution of the parent ions, the temperature associated with the internal degrees of freedom was considerably higher because the mild expansion conditions used (to prevent dimer formation) did not fully remove the vibrational energy. To find the average internal energy of the beam sample, the crossover energy in the breakdown diagram was determined for both beam and warm samples.¹² The breakdown diagram is the fractional abundance of parent and daughter ions as a function of the pentene ion internal energy. The shift toward higher energies when the thermal sample is replaced by the molecular beam is equal to the average internal energy removed by the molecular beam. This shift was measured to be 74 meV. Since the total internal energy of the pentene samples at room temperature is calculated to be 128 meV, the energy that remained in the beam sample was 54 meV, which corresponds to a vibrational temperature of 180 K. The data were corrected for this internal energy by adding the average 54 meV to the photon energy.

Energetics

Figure 1 shows the relative 0 K heats of formation of the ion and neutral C_5H_{10} isomers studied in this paper. The ordinate in this figure, labeled absolute energy, measures the energy with respect to the constituent elements of $5C + 5H_2$ in their standard states at 0 K. These 0 K heats of formation, which are needed in order to quantitatively model the observed dissociation rates, were obtained by a procedure outlined previously.^{13–15} Part of this procedure involves subtracting the average 298 K vibrational, rotational, and translational energies of an isomer from its corresponding 298 K heat of formation. Although the total average rotational and translational energy is just 3RT, the average vibrational energies at 298 K were determined using



Figure 1. Pentene neutral, ion, and product 0 K heats of formation: Unless noted otherwise, 0 K neutral heats of formation were calculated from 298 K neutral values²¹ by the standard procedure.^{13–15} The ion heats of formation were found by adding the ionization potential/ activation energies²² to the 0 K neutral heats of formation. Labels a–c are as follows: (a) $\Delta H_{f(0K)}$ of 1-propene ion (972 kJ/mol)¹² plus ethene (61 kJ/mol);²³ (b) $\Delta H_{f(0K)}$ of methylallyl ion (863 kJ/mol)²³ plus methyl radical (149 kJ/mol);²³ (c) estimated, $\Delta H_{f(288K)}$ (ion) + 30 kJ/mol.

the neutral or molecular ion frequencies. Frequencies were determined from unrestricted Hartree Fock *ab initio* calculations (scaled by 0.89), using the GAUSSIAN-92 program¹⁶ with the $3-21G^*$ basis set.

The $C_4H_7^+$ product ion was taken to be the methylallyl ion CH_2 =CHCHCH₃]⁺, which is approximately 28 kJ/mol lower in energy than the next lowest (branched) structure, CH_2 =C-(CH₃)CH₂]⁺. Likewise, the C_3H_6]⁺⁺ ion radical product is assumed to be the propene ion radical, CH_2 =CHCHA₃]⁺, since the next most stable isomer, the cyclopropane ion radical, is approximately 46 kJ/mol higher in energy.

Results

Some of the TPEPICO TOF data of various C_3H_{10} isomers are presented in Figure 2. Only the daughter fragments are shown, with the shortest TOF distributions corresponding to ethene loss and with the longer TOF distributions corresponding to methyl radical loss. The five spectra shown were taken at approximately the same absolute energy and have been corrected for thermal (298 K) background as described earlier.

All isomers studied show metastable components in methyl radical and neutral ethene loss channels. The slow metastable branching ratios and rates as a function of absolute energy are the same for all isomers. Three of the isomers, cyclopentane, 1-pentene, and *cis*-2-pentene, show fast components for one or both of these channels as well. Cyclopentane and 1-pentene have identical TOF spectra and clearly show a strong fast component in the ethene loss channel. This fast component is too fast to measure by TPEPICO. *cis*-2-Pentene also has a fast component loss of ethene, although it is smaller than that seen in cyclopentane and 1-pentene. In addition to the fast loss of ethene, *cis*-2-pentene shows a fast component loss of methyl radical. The branched isomers studied display only the slow metastable loss components.

These results differ somewhat from those of Brand and Baer.⁹ In these earlier thermal studies, all isomers except 2-methyl-2-butene were interpreted as being multicomponent. An artifact of using a thermal sample is that metastable TOF peak shapes are dominated by the most internally hot ions in the sample since these dissociate most readily. The resulting peak shapes thus appear multicomponent.



Figure 2. TPEPICO TOF spectra of pentene isomers taken at similar absolute energies of about 10.9 eV. The asymmetric TOF peaks at 14 μ s correspond to ethene loss while the TOF peaks at 16 μ s correspond to methyl radical loss. Solid lines are calculated fits. Parent ions are not shown.

The solid lines in Figure 2 are calculated TOF distributions. Ion dissociations on the microsecond time scale lead to fragmentation events during the course of acceleration and thus result in asymmetric TOF distributions. The solid lines were obtained by varying three parameters, which are the dissociation rate constant for the slow reaction, the branching ratio between CH_3^{\bullet} and C_2H_4 loss, and the branching ratio between the fast and slow dissociation channels. The TOF distribution arising from the fast dissociation was assumed to be Gaussian with a width adjusted to fit the data. This width is directly related to the translational kinetic energy released in the dissociation and was found to be approximately 30 meV.

The cutoff in the methyl loss TOF distribution at 17.2 μ s is associated with parent ions leaving the first acceleration region. Ions that dissociate after this time (e.g., within the drift region) have the same TOF as the parents but are broadened by kinetic energy release. Similarly, the small dip at 16.3 μ s in the fit of the TOF data is associated with ethene loss at the end of the first acceleration region.

The metastable rates of parent depletion, extracted from the above TOF fits, have been plotted in Figure 3 for all the isomers as a function of absolute energy. It is evident that even though the various ionic isomers investigated have very different heats of formation, and therefore very different activation energies, they dissociate with the same slow rate constant.

The low-energy k vs E data of Figure 3 do not follow the predicted solid curve. The dashed line in Figure 3 is a calculated correction to the solid line found by taking into account the effects of the initial energy distribution of the ion ($E_{ave} = 54$ meV) in combination with the kinetic shift. As the photon energy is reduced, a fraction of the ions dissociate in the 6.28 μ s that the parent ions spend in the acceleration region. For instance, at a rate of 10^5 s^{-1} , only 20% of the ions dissociate in the drift region where they show up as a slightly broadened peak at the TOF characteristic of the parent ion. Hence, ions near



Figure 3. Total slow dissociation rate constant for all isomers as a function of absolute energy. Isomer symbol shapes are the same as in Figure 2. The solid line is fit based on the proposed potential energy surface, and the dashed curve accounts for the effects of kinetic shift and the internal energy distribution of the ions.



Figure 4. Slow production rate constants of methyl radical (solid symbols) and ethene neutral (open symbols) calculated from the rates in Figure 3 and the product branching ratios. Symbol meanings are the same as in Figure 2. The solid lines were found from the solid line in Figure 3 and the product branching ratios as determined by the solid line in Figure 6. Dashed and dotted lines are attempts to fit the data using RRKM theory and a conventional one-well, two-product channel potential energy surface.

the low-energy region of the thermal distribution are discriminated relative to those at the high end. The net effect of lowering the photon energy is that the signal gets weaker, but the range of ion internal energies samples remains nearly the same. As a result, the rate constant appears to level off. This is only a problem near the dissociation threshold since at higher energies all ions have enough energy to dissociate in the acceleration region. Treating the ions in terms of an average internal energy accounts adequately for this 54 meV of thermal energy. This also explains why the slow component of the ethene loss TOF peak in Figure 2 (which is one of the lowest energies investigated) suggests a slightly higher parent dissociation rate than the methyl loss TOF peak. That is, the calculated TOF distribution slightly underestimates the rate constant for the ethene loss TOF peak because its dissociation threshold is higher than that of the methyl loss channel.

In Figure 4 the rates for the slow production of methyl radical (solid symbols) and ethene neutral (open symbols) have been found and plotted as a function of absolute energy. This was done by dividing the observed slow parent depletion rate



Figure 5. Ratio *f* for cyclopentane (squares) and 1-pentene (circles). The solid line is an empirical fit.



Figure 6. Ratios $R_{\text{eth/tot}}$ for all isomers (solid symbols) and $R_{\text{ETH/TOT}}$ for *cis*-2-pentene (open symbols). Symbols are the same as in Figure 2. The solid line is given by the ratio of rate constants in Figures 12 and 13; $k_3 f/(k_3 f + k_6)$.

between the two product channels in accordance with their slow component-branching ratios. The same slow componentbranching ratios for CH_3^* and C_2H_4 loss are found for all isomers. These data demonstrate that all of the ions isomerize to the lowest energy isomer (2-methyl-2-butene ion) and dissociate from that structure with the same slow rate. The origin of the narrow peaks in the case of the cyclopentane and straight chain pentene ions will be discussed in the following section.

The dissociations of the C_5H_{10} ion radicals are evidently coupled by isomerization reactions, which in some cases compete effectively with direct dissociation. A similar competition has recently been proposed for the toluene ion dissociation by Lifshitz and co-workers.^{17,18} Although only one dissociation rate is measured, additional information is derived from various branching ratios. These are plotted as a function of absolute energy in Figures 5–7. Figure 5 shows the ratio, *f*, between the fast component loss of ethene from cyclopentane and 1-pentene to the total of all areas. The dashed line is an empirical fit in which the onset at 10.71 eV is the 0 K ethene product dissociation limit $[\Delta H^{\circ}_{f0}(C_2H_4) + \Delta H^{\circ}_{f0}(C_3H_3^{\bullet+})]$.

Figure 6 shows the ratio, $R_{eth/tot}$, between the slow ethene loss area to the total slow ethene and methyl loss areas for all the isomers. The three empty downward pointing triangles in this figure represent the same ratio but with the fast component areas of *cis*-2-pentene instead; we call this ratio $R_{ETH/TOT}$. The similarity between $R_{eth/tot}$ and $R_{ETH/TOT}$ is an important finding and will serve to support the potential energy surface to be proposed. The significance of the solid line will be discussed later.



Figure 7. Ratio R_{Bfvs} for *cis*-2-pentene. The dashed line is an empirical fit while the solid line is the ratio of rate constants in Figure 12 and 13: $(k_3f + k_6)/k_4$.

Finally, Figure 7 shows the ratio, R_{Bfvs} , between the fast methyl and ethene loss components to the total slow and undissociated components of *cis*-2-pentene. The onset at 10.49 eV for this quickly rising function has been set to the 0 K methyl loss product dissociation onset $[\Delta H^{\circ}_{f0}(CH_3^{\bullet}) + \Delta H^{\circ}_{f0}(C_4H_7^{+})]$.

Rate Analysis

The data in Figure 2 suggest that the C_5H_{10} ⁺⁺ isomers fall into three different classes. The branched isomers, which have identical product ion TOF distributions, are connected via low isomerization barriers so that they dissociate by a common pathway. Because these isomers are in complete equilibrium with 2-methyl-2-butene, the lowest energy isomer, they dissociate only via the slow rate. The straight chain pentenes and the cyclopentane isomers all dissociate via two-component dissociation rates for ethene loss. However, the 2-pentene isomer is different from the other two in that it also has a substantial fast component for the methyl loss channel.

Because all the isomers dissociate with the same slow rate as the lowest energy isomer, it should be possible with RRKM theory to model the dissociation rate using only the 2-methyl-2-butene ion density of states and the ethene and methyl loss sum of states. The predicted rates for ethene (dashed line) and methyl loss (dotted line) are plotted in Figure 4. Although the calculated methyl loss rate may arguably fit the data, the calculated ethene loss rates clearly rise too sharply with energy. In order to match the slope of the ethene loss data, the dissociative transition state frequencies need to be tightened. This, however, leads to expected rates that are orders of magnitude lower than those observed. In other words, the observed rates are too high for such a low slope so close to the dissociation threshold. Thus, without lowering the accepted ethene loss dissociation threshold energy, a more complicated mechanism must be used to account for the slope of the ethene loss metastable k(E) vs E rate data.

Before the proposal of a mechanism, the conditions that give rise to single and two-component dissociation rates, as well as a smaller slope than expected, will be discussed.

(a) One- and Two-Component Dissociation Rates. Consider the case of a single well, single product channel, potential energy surface ($A^* \rightarrow \text{products}$). According to the statistical RRKM theory, the rate constant for product formation is given by

$$k_{\rm obs}(E) = \frac{N^{\dagger}(E - E_{\rm o})}{h\rho(E)} \tag{1}$$



Figure 8. Two-well one-product channel potential energy surface. If isomer A is initially prepared and $k_1 \approx k_2$, two rate components will be observed. The fast rate $(k_{\text{fast}} \approx k_1 + k_2)$ is just the rate of isomer A depletion, while the slow rate is the same as the rate observed if we start with isomer B.

where $N^{\ddagger}(E - E_{o})$ is the sum of states in the transition state, *h* is Planck's constant, $\rho(E)$ is the density of states of the parent molecular ion, *E* is the ion internal energy, and E_{o} is the activation energy.

The simple addition of one more well on the way to products leads to two-component dissociation rates, the analytical forms of which are much more complex than eq 1. Figure 8 shows a model potential with two isomerization wells and one product channel. Not only are the observed rates now a function of three individual rate constants, but they also depend upon which isomeric well is initially prepared.

The kinetic equations for $P_1 \leftarrow A \rightleftharpoons B \rightarrow P_2$ have been worked out previously.⁷ We will briefly outline the salient features of the kinetics for the potential in Figure 8 ($P_1 \leftarrow A \rightleftharpoons$ B) since they will prove to be useful in illustrating several steps in the more complex C_5H_{10} ⁺⁺ ion radical potential surface to be proposed.

In Figure 8 the rate of parent depletion, our experimental observable, depends upon which isomer is initially prepared. The changes in concentration of these isomers with time are given by the following coupled, linear, homogeneous differential equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{A}] = -(k_1 + k_2)[\mathbf{A}] + k_3[\mathbf{B}]$$
$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{B}] = k_2[\mathbf{A}] - k_3[\mathbf{B}]$$

The solutions to these equations are of the form

$$[A] = c_1 \alpha_{\text{fast}} e^{-k_{\text{fast}}t} + c_2 \alpha_{\text{slow}} e^{-k_{\text{slow}}t}$$
(2)

$$[\mathbf{B}] = c_1 \beta_{\text{fast}} \mathbf{e}^{-k_{\text{fast}}t} + c_2 \beta_{\text{slow}} \mathbf{e}^{-k_{\text{slow}}t}$$
(3)

When β_{fast} and β_{slow} are set equal to 1 (only the ratio between β and α is important), $\alpha_{\text{fast}} = (-2k_3 + k_{\text{fast}})/(-2k_2 - k_1 + k_{\text{fast}})$ and $\alpha_{\text{slow}} = (-2k_3 + k_{\text{slow}})/(-2k_2 - k_1 + k_{\text{slow}})$. The coefficients c_1 and c_2 are determined by the initial conditions, and since [B] (t = 0) must equal zero when only isomer A is initially prepared, $c_2 = -c_1$. When this occurs eqs 2 and 3 reduce to

$$[A] = \alpha_{slow} e^{-k_{slow}t} - \alpha_{fast} e^{-k_{fast}t}$$
(4)
$$[B] = e^{-k_{slow}t} - e^{-k_{fast}t}$$

From these equations it is clear that the concentration of parent isomer A is the sum of two exponential terms. The observed rate of parent depletion will then be two-component, with rates k_{fast} and k_{slow} . The ratio $\alpha_{\text{fast}}/\alpha_{\text{slow}}$ determines the relative magnitude of the components.

It is possible to express the fast and slow observed rates in terms of the individual rate constants in Figure 8. For a molecule initially prepared in well A, the exact analytical solution for the observed parent depletion rate is given by

$$k_{\text{slow}} = \frac{1}{2}(k_1 + k_2 + k_3) - \frac{1}{2}\sqrt{(k_1 + k_2 + k_3)^2 - 4k_1k_3}$$
(5)

and

$$k_{\text{fast}} = \frac{1}{2}(k_1 + k_2 + k_3) + \frac{1}{2}\sqrt{(k_1 + k_2 + k_3)^2 - 4k_1k_3}$$
(6)

It can be shown that if k_1 and k_2 are much greater than k_3 , and isomer B is initially prepared, only the slow rate will be observed.

The form of eqs 5 and 6 makes it difficult to gain physical insight into the competing factors affecting isomerization and dissociation. With certain reasonable approximations it will be easier to understand the interplay between isomerization and dissociation.

Two approximations that account for the vast majority of isomerization interactions lead to trivial reductions of eqs 5 and 6 and occur when the isomerization barrier relative to product formation is very high $(k_1 \gg k_2, k_3)$ or very low $(k_1 \ll k_2, k_3)$. The former case is equivalent to isolating isomers A and B in phase space such that A dissociates with a rate k_1 while B dissociates with a rate k_3 . In the second limiting case, the observed rate will only be slow with the rate given by

$$k_{\rm obs} = \frac{N_1^{\,\pm}}{h(\rho_{\rm A} + \rho_{\rm B})}$$

where ρ_A and ρ_B are the densities of states of isomers A and B and N_1^{\dagger} is the sum of states for the dissociative transition state. If the energy of B is significantly less than that of A, then ρ_A $+ \rho_B \approx \rho_B$. Although the densities and sums of states remain functions of the energy, for the sake of brevity we drop the explicit energy variable in these expressions for the remainder of the paper.

Although the limiting cases above account for most isomerization reactions, they cannot account for multicomponent rates. This will only be possible when isomerization and dissociation rates become comparable.

(b) Steady State Approximation. The steady state approximation for the concentration of isomer A with time in Figure 8 leads to a reduction of the complexity of eq 5. Consider the case where ion B is initially produced and where the well associated with isomer A is very shallow so that $k_1, k_2 \gg k_3$. Then a solution to the coupled differential equations leads to the following observed dissociation rate constant:

$$k_{\rm obs} = \frac{k_1 k_3}{k_1 + k_2} = \frac{N_{\rm iso}^* N_1^*}{h \rho_{\rm B} (N_1^* + N_{\rm iso}^*)} \tag{7}$$

where N_{iso}^{\dagger} is the sum of states in the isomerization transition state and N_1^{\dagger} is the sum of states for the dissociative transition state.

A commonly expected situation especially for ions, will be the following. The isomerization from $B \rightarrow A$ will involve a tight transition state so that the sum of states associated with this reaction, N_{iso}^{\ddagger} , increases rather slowly with energy. On the other hand, isomer A has a structure that "looks like" the



Figure 9. Proposed pentene ion potential energy surface. Cyclopentane is part of the A well, and 2- 3-methyl-1-butenes are part of well C. All ethene loss occurs via well A while all methyl radical loss occurs via well B.

products so that the dissociation step is characterized by a loose transition state and N_1^* rises rapidly with the energy. Thus, at the energy of the dissociation limit, N_{iso}^* will be greater than $N_1 = 1$, while at higher energies, N_1 will become greater than N_{iso}^* . At low energies then, eq 7 reduces to $k_{obs} = N_1^*/h\rho_B$ while at high energies $k_{obs} = N_{iso}^*/h\rho_B$. These two asymptotic limits of eq 7 then lead to a k_{obs} rate vs energy curve that rises quickly at dissociation onset, as eq 1, but then crosses to the slower rising k_3 rate curve at higher energies.

(c) Potential Energy Surface. In order to model the data, a common potential energy surface is proposed (see Figure 9). In this potential, cyclopentane and 1-pentene have been placed in a common well, labeled A. This is justified by the fact that the TOF spectra of these two isomers are identical. As with all the other isomers, the slow components are the same. In addition, these two isomers have the same ratios between fast and slow components (see Figure 5).

It is possible that two different reaction channels, one fast and one slow, exist for the loss of ethene. However, in the interest of simplicity, the proposed potential assumes that the fast and slow ethene loss channels are one and the same. The only difference is that the slow channel involves isomerization to a much lower energy structure before coming back. The energy and density of states of the A well have been chosen to correspond to those of the 1-pentene ion radical isomer, the lower of the two isomers. For this approximation to be valid, isomerization between 1-pentene and cyclopentane ion radicals must be rapid.

As discussed earlier, the TOF spectrum of the cis-2-pentene isomer is unique in that it clearly has fast component mechanisms for both methyl and ethene loss channels. If only one ethene and one methyl loss channel exists for all the isomers at the energies studied, then the cis-2-pentene ion radical must lie between the branched and linear isomers, as represented in Figure 9 by well B.

Well C in Figure 9 is assumed to have the energy and density of states of the 2-methyl-2-butene ion radical. The 3-methyl-1-butene and the 2-methyl-1-butene branched ion radical isomers show TOF spectra identical to those of the more stable 2-methyl-2-butene ion radical and have this been grouped into the same well. Again, the assumption is that isomerization between the branched isomers is much faster than dissociation. No direct dissociation pathway between the C well and either product has been drawn. Instead all isomers "entering" the C well must first undergo isomerization to the B well before dissociating.



Figure 10. Pentene ion pathways of possible ion radical isomerization and dissociation paths. Heats of formation are 0 K values in kJ/mol (see Figure 1) Superscript a in the figure indicates values that are estimates from ref 4.

The potential represented in Figure 9 should then be viewed as a two-dimensional projection of a multidimensional surface where well C is a phase space dead end.

It is important to reiterate that the potential in Figure 9 is a gross simplification of the true isomerization pathways. The barriers should be viewed as phase space bottlenecks and not as single step isomerizations.

(d) Reaction Mechanism. The three-well potential energy surface in Figure 9, which is consistent with the experimentally observed decay rate data, is also consistent with reasonable mechanistic features of the pentene ion dissociation. The mechanisms in Figure 10 consist of individual hydrogen and methyl transfer steps. In fact, multiple steps may occur in a concerted fashion, as with ring opening/hydrogen transfer between cyclopentane and 1-pentene ion radicals.⁴ What is essential for the mechanism's validity is that dissociation can only occur from structures that can produce the lowest energy products [i.e., $CH_3^{\bullet} + CH_2 = CHCH^+CH_3$ or $C_2H_4 + CH_3$ - $CH=CH_2^{+}$ via simple cleavages with no reverse activation barrier.⁴ According to this criterion, the 2-pentene ion alone is capable of directly losing CH₃. On the other hand, none of the isomers investigated can lose C₂H₄ without prior rearrangement. However, the 1-pentene ion radical can produce an ion radical •CH₂CH₂CH₂CH⁺CH₃ via a simple 1,5-H atom transfer step, and this ion radical is capable of losing the ethene unit without further rearrangement. Similarly, the cyclopentane ion radical can form the same precursor for ethene loss by a concerted mechanism involving ring opening and a 1,2-H atom shift. The similar decay behavior of the 1-pentene and cyclopentane ions means that these two ions are in rapid equilibrium with the ethene loss precursor and each other.

It should be mentioned that although H loss is actually favored energetically by ~ 4 kJ/mol over the methyl loss channel, it has not been observed in this or previous studies.^{4.9} Apparently, this dissociation channel is blocked by a potential energy barrier.

Although there is one predominant precursor for ethene loss via simple bond cleavage ($^{C}CH_2CH_2CH_2CH^+CH_3$), there are two possibilities for the production of methyl radical. The first one, already mentioned, is the 2-pentene ion radical, while the second is from the distonic ion, $^{C}CH_2CH(CH_3)CH^+CH_3$, shown in Figure 11a. The choice of the 2-pentene ion radical, as the precursor to the methyl radical, is based on the fact that the *cis*-2-pentene ion radical shows a fast component loss of methyl radical.

Many possible isomerization pathways exist between the various C_5H_{10} ion radical isomers. In the proposed reaction scheme of Figure 10, the 2-pentene ion radical has been placed at the center between the branched and linear chained isomers. This is justified by the fact that fast component losses of ethene

Figure 11. Some alternative pentene ion reaction pathways and products. Heats of formation are 298 K values in kJ/mol.²² Superscript a indicates values from ref 21.

and methyl radicals are observed from the *cis*-2-pentene ion radical. This placement is also consistent with expected facile isomerization mechanisms. Isomerization between 1- and 2-pentene ion radicals involves simple hydrogen transfers, and isomerization between 2-pentene and 2-methyl-2-butene ion radicals involves methyl group migration along the conjugated 2-pentene backbone. This latter isomerization mechanism is the only possible pathway between the linear and branched structure that does not involve a cyclization step. Three possible cyclization steps are presented in parts d-f of Figure 11. Energetically, however, these cyclic intermediates are not as stable as the 2-pentene ion radical. They are also expected to have tight transition state frequencies and correspondingly slower isomerization rates.

In addition to alternative pathways for isomerization, higher energy product channels are expected to open up at higher energies (see parts a and b of Figure 11.) The formation of cyclopropane ions from cyclopentane, pathway IV-11(b), is most likely responsible for the preferential ethene loss from cyclopentane compared to 1-pentene seen in the breakdown data of Brand et al.⁹ and Li et al.⁵ The onsets for these channels, however, are at energies above the range of energies where metastable dissociation rates can be measured by our experiment. Over the energies employed by this current study the product branching ratios of cyclopentane and 1-pentene are indistinguishable.

(e) Fitting Data with a Three-Well, Two-Product Channel Model Potential. Equation 1 is the observed parent depletion rate constant for a simple one-well/one-product channel potential. The complexity of the observed parent depletion rate jumps dramatically with the simple addition of one more well on the way to products, yielding two observed rate components given by eqs 5 and 6. It follows that the exact analytical form for a three-well system with two product channels is correspondingly much more cumbersome and has three observed rate components. Although no simple exact analytic solution may be obtainable, it is possible to arrive at a numerical solution to the coupled differential equations for the concentrations of the various isomers with time.

The methodology for determining the applicability of the model potential in Figure 9 to C_5H_{10} ion radicals involves the following steps. First, the steady state approximation for isomer A is used to find an analytical solution for the observed slow dissociation rate. Next, the various ratios discussed earlier in the "Results" section are found and fit. From these ratios and the observed slow dissociation rate, the six rate constants in



Figure 12. Steady state approximation of the potential in Figure 9.

Figure 9 are found. These six rate constants are then individually fit by RRKM theory so that the isomerization barrier heights and transition state entropies are determined. Finally, the six rate constants used in the full coupled differential equations for the full potential and numerical predictions for the observed dissociation rates are found and compared to those predicted by the steady state approximate potential.

The steady state approximation to the full potential in Figure 9 can be seen in Figure 12. If we view B to A isomerization in isolation from the rest of the potential, as in Figure 8, then the rate of fast ethene production from isomer B is given by eq 7, or $k_{\text{Eth}} = k_3 f$, where $f = k_1/(k_1 + k_2)$. In Figure 5, f is plotted for cyclopentane and 1-pentene and is the ratio between the fast ethene loss area and the total of all areas, including parent.

An analytical solution may be found for the simplified potential with two wells. If isomer B is initially prepared in this new potential, the expected parent depletion rate constant will be two-component and given by

$$k_{\text{slow}} = \frac{1}{2}(k_3f + k_4 + k_5 + k_6) - \frac{1}{2}\sqrt{(k_3f + k_4 + k_5 + k_6)^2 - 4k_5k_6 - 4k_5k_3f}$$
(8)

and

$$k_{\rm med} = \frac{1}{2}(k_3 f + k_4 + k_5 + k_6) + \frac{1}{2}\sqrt{(k_3 f + k_4 + k_5 + k_6)^2 - 4k_5 k_6 - 4k_5 k_3 f}$$
(9)

In eq 9, k_{med} denotes the fast rate component seen when isomer B is initially prepared. The term "med" has been used so as not to confuse this component with the faster component seen when isomer A is initially prepared. Although eq 9 reduces to $k_{med} = k_3 f + k_4 + k_6$ for $k_5 \ll k_3 f$, k_4 , k_6 , no such simplification can be made to eq 8.

The next task on the way to determining the six k's in Figure 9 involves finding enough experimental observables to identify uniquely each individual rate constant. Fortunately, only four observables are needed since only four of the rate constants are truly unique. This is because two pairs of rate constants differ only by their respective microcanonical equilibrium constants, i.e., the ratio between their isomeric densities of state:

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$$k_2 = k_3 \frac{\rho_{\rm B}}{\rho_{\rm A}} \tag{10}$$

$$k_5 = k_4 \frac{\rho_{\rm B}}{\rho_{\rm C}} \tag{11}$$

These density of states ratios as a function of internal energy were calculated by inversion of the partition function using the method of steepest descents, discussed elsehwere.^{19,20} The molecular ion vibrational frequencies used in these calculations were those of 1-pentene, *cis*-2-pentene, and 2-methyl-2-butene (isomers A, B, and C, respectively). The method for finding these frequencies is discussed earlier. The important point is that there are no adjustable parameters in calculating the isomeric equilibrium constants.

Experimentally, it is possible to find various ratios between product TOF areas and their fast and slow components. Ratios of areas that are also exact ratios between rate constants are chosen. As an example of how TOF areas relate to the individual rate constants, it is useful to take the case of ethene production when isomer A is initially prepared. In this case, the rate of ethene production is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}[\text{ethene}] = k_1[\mathrm{A}] = k_1([\mathrm{A}_{\text{fast}}] + [\mathrm{A}_{\text{med}}] + [\mathrm{A}_{\text{slow}}])$$

where the concentration of A has been broken into exponential terms like those of eq 4. In this model, however, three components are expected.

To find the total area associated with the ethene product channel TOF peak, the equation above must be integrated over the time the parent isomer takes to traverse the acceleration region of the experiment. If only the area of the fast component of the TOF peak is of interest, then only the first exponential term in the above equation is used in the integration.

fast ethene area =
$$k_1 \int_0^{t_1} [A_{\text{fast}}] dt$$

where t_1 is the time for the parent ion to traverse the acceleration region. Since the exact form of $[A_{fast}]$ is very complicated, ratios that cancel these integrals are chosen. This can be seen for the f ratio already mentioned above where

$$f = \frac{\text{fast ethene area}}{\text{total of all areas}} = k_{1} \int [A_{c_{1}}] dt$$

$$\frac{k_1 \int [\mathbf{A}_{\text{fast}}] \, \mathrm{d}t}{k_1 \int [\mathbf{A}_{\text{fast}}] \, \mathrm{d}t + k_2 \int [\mathbf{A}_{\text{fast}}] \, \mathrm{d}t} = \frac{k_1}{k_1 + k_2}$$

Note that the k_2 term in the denominator of the above equation accounts for all portions of the TOF spectrum, including undissociated parents, but does not account for the fastest ethene loss component. Also note that this *f* ratio can only be found for isomers in rapid equilibrium with the A well of Figure 9 (cyclopentane and 1-pentene).

By use of the same method above, additional ratios have been found. For all isomers, the following ratio is measured and plotted in Figure 6.

$$R_{\text{eth/tot}} = \frac{\text{slow ethene loss area}}{\text{slow ethene + slow methyl loss areas}} = \frac{k_3 f}{k_3 f + k_6}$$
(12)

One last ratio must be observed in order to find four unique k's. This ratio is found from the fast vs slow components of



Absolute Energy (eV)

Figure 13. Individual rate constants of the potential in Figure 9. Points were determined from eqs 17-20. Symbol meanings are the same as in Figure 2. The lowest two energy points have been removed. Solid lines through the data points are RRKM fits of the individual rate constants k_2-k_6 . For k_1 the dashed line is an attempted RRKM fit, while the solid line is derived from eq 13 and the solid line fit of f in Figure 5.

the cis-2-pentene TOF data and is as follows:

$$R_{\rm Bfvs} = \frac{\text{medium (ethene + methyl) areas}}{\text{total slow + parent areas}} = \frac{k_3 f + k_6}{k_4}$$

With this ratio we now have relationships between all six rate constants. Plugging these ratios into eq 8, the observed parent depletion rate, we can solve for k_3 , which yields

$$k_{3} = 2 \frac{k_{\text{slow}}}{f} \frac{R_{\text{eth/tot}} R_{\text{Bfvs}}}{1 + R_{\text{Bfvs}} + \frac{\rho_{\text{B}}}{\rho_{\text{C}}} - \sqrt{\left(1 + R_{\text{Bfvs}} + \frac{\rho_{\text{B}}}{\rho_{\text{C}}}\right)^{2} - 4R_{\text{Bfvs}} \frac{\rho_{\text{B}}}{\rho_{\text{C}}}}$$

Note that every variable on the right side of the above equation is a measured value except for the ratio $\rho_{\rm B}/\rho_{\rm C}$, which is calculated with no adjustable parameters.

In terms of k_3 , all the other variables may now be calculated from the relations in eqs 10 and 11 and the following:

$$k_{1} = k_{3} \frac{f}{(1-f)} \frac{\rho_{\rm B}}{\rho_{\rm A}}$$

$$k_{4} = k_{3} f \frac{1}{R_{\rm eth/tot}} R_{\rm Bfvs}$$

$$k_{6} = k_{3} f \left(\frac{1}{R_{\rm eth/tot}} - 1 \right)$$
(13)

The symbols in Figure 13 are these experimentally determined rate constants as a function of absolute energy. It was necessary to use the fits in Figures 5 and 7 to interpolate values for f and R_{Bfvs} since these ratios cannot be measured for all isomers. Again, it is important to reiterate that the six rates in Figure 13

are experimentally determined and are not the result of any adjustable parameters. Even if the fits to the various ratios are poor, the relative magnitude of the six rate constants will only be slightly affected.

(f) RRKM Calculations. Now that the experimental rate constants in Figure 13 have been determined, it is possible to fit each rate constant individually using RRKM theory. To fit uniquely any one of the six individual rate constants both in magnitude and slope, four things need to be known. These are the heat of formation of the parent, the density of states of the parent, the heat of formation of the transition state, and the entropy change from parent to transition state. Of these, only the last two are adjustable parameters. Equations 10 and 11 show that not all the rate constants are independent. Of the 12 adjustable parameters needed only 6 are truly independent. These are the 2 isomerization barrier heights and the entropy changes associated with the 4 transition states in the proposed potential.

The solid lines in Figure 13 are the resulting fits for all six rate constants, having varied six adjustable parameters. The entropy changes were accomplished by arbitrarily increasing (tightening) or decreasing (loosening) the lowest five frequencies of the four transition states. For ethene production the transition state frequencies are taken as those of 1-pentene while for the three other transition states cis-2-pentene frequencies are used. For each of the two dissociative transition states one of the vibrational modes between 800 and 900 cm⁻⁺ was removed to account for the loss of the dissociating carbon-carbon bond. In this manner the cis-2-pentene frequencies were loosened until a satisfactory fit to k_6 was obtained with a corresponding entropy of dissociation of $\Delta S_6^{\dagger}(600 \text{ K}) = 12.2 \text{ cal/K}$. Such a loose transition state is consistent with simple bond cleavage. Tight transition states are expected for isomerization transition states. Although this was found to be true for B to C isomerization, $\Delta S_{isoBC}^{\dagger}(600 \text{ K}) = -5.1 \text{ cal/K}$, it was not found to be true of B to A isomerization, $\Delta S_{isoBA}^{\dagger}(600 \text{ K}) = 5.5 \text{ eu}$. A possible explanation for this is discussed later. On an absolute energy scale the A to B isomerization barrier height is found to be 10.19 eV, while the B to C barrier is 9.75 eV. The dashed line fit to the k_1 data is too steep and required a large entropy change of $\Delta S_1^{\dagger}(600 \text{ K}) = 22.7 \text{ cal/K}$. This poor fit underscores the problem of modeling the 1-pentene dissociation as a single step dissociation mechanism and will be discussed later. The solid line fit that does go through the k_1 data is derived from f and the RRKM fit of k_3 and eq 13.

To check the consistency between the RRKM-calculated rates and the observed parent depletion rate, the RRKM rates were input into eq 8. The solid line in Figure 3 is the result. Similar checks were made with the various ratios of TOF areas and the RRKM-calculated rate constants (the solid lines in Figures 6 and 7).

Finally, the individual rate constants found from the RRKM fits and k_1 from eq 13 were used as input into the coupled differential equations for the full potential in Figure 9, and the numerical solutions for the concentrations with time are found. The rate of the slowest component in this concentration profile is compared to that predicted by the steady state rate, eq 8. These rates were found to be identical over the energy range of our experiments. The strong agreement between the data and the numerical solution suggests that the steady state approximation to the full potential is valid.

(g) Further Tests of the Model Potential. By use of the steady state approximation drawn in Figure 12, an additional ratio of product areas is found to be of interest. This ratio, found for isomer B, is given by

$$R_{\text{ETH/TOT}} = \frac{\text{fast ethene loss area}}{\text{fast ethene + fast methyl loss areas}} = \frac{k_3 f}{k_3 f + k_6}$$

This is equivalent to the ratio $R_{\text{eth/tot}}$ given in eq 12 and is an important test of the proposed potential surface. The fact that this ratio, open triangles in Figure 6, is similar to $R_{\text{eth/tot}}$ of all the other isomers is very strong evidence in support of the proposed potential in Figure 9 because it indicates that the slow reaction must pass through the 2-pentene well.

Two observations that are not fully consistent with the proposed potential need to be explained. The first is the poor RRKM fit of k_1 (dashed line in Figure 13). This most likely reflects the fact that ethene loss from isomer A is not a simple bond dissociation. The expected mechanism, as displayed in Figure 10, involves the 1,4 distonic ion intermediate structure. This calls for modeling the k_1 step with the two-well one-product channel mechanism already outlined in part a of the rate analysis section of this paper. Such an analysis, with the introduction of two new parameters, could certainly be made to fit the $k_1(E)$ data. However, in view of the many experimental constaints on the two new parameters, adding this step to the potential curve in Figure 9 seems unwarranted.

The second inconsistency with the proposed potential is that the entropy change aassociated with B to A isomerization is positive (i.e., the transition state frequencies are looser than those of *cis*-2-pentene). Isomerization transition states typically involve some restricted geometry and should have correspondingly higher frequencies. Just as the ethene loss channel is not a simple bond cleavage, B to A isomerization involves more than a single hydrogen transfer.

The two inconsistencies described above illustrate that the features of the proposed model potential cannot be viewed as simple single step isomerizations and dissociations. Instead, the gross features reflect "bottlenecks" in the phase space that may involve several individual steps.

There is an experimental test that could further validate the proposed potential energy surface. A very interesting aspect of cold multicomponent TPEPICO TOF spectra is that they offer a direct way of determining reaction mechanisms through isotopic labeling studies. Since the fast and slow components are so clearly resolved in the cold TOF spectra, it should be possible to see different isotopic TOF shifts for the prompt components (no isomerization) and metastable components (multiple isomerizations which result in H/D scrambling). For example, the fast ethene loss component of CD₂:CH·CH₂·CH₂·- CH_3 ⁺ \rightarrow CHD_2 $CH:CH_2$ ⁺ + $CH_2:CH_2$ should be narrow and centered at m/z = 44, unlike the slow component which should be distributed over masses 42-44. Likewise, the medium methyl loss rate component of CH₃·CH:CH·CH₂·CD₃ $|^{+} \rightarrow$ $CH_3 \cdot CH^+ \cdot CH: CH_2 + CD_3 \cdot should be narrow and centered at$ m/z = 55 while the slow rate component should be weighted toward the higher masses between m/z = 55 and 58. These shift differences should be clearly distinguishable in our **TPEPICO** experiment and may be attempted in the future.

Conclusions

Six isomers of C_5H_{10} ⁺⁺ are studied in these experiments and are found to be in rapid equilibrium with one another. For some isomers, however, direct dissociation is found to compete with isomerization. For all isomers, the slowest metastable rates of parent depletion, as a function of absolute energy, are identical. The linear isomers have additional fast dissociation rate components. Three distinct types of TOF spectra are observed, suggesting that three isomeric structures are dominating the dissociation kinetics.

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A model potential energy surface with three wells, corresponding to 1-pentene, cis-2-pentene, and 2-methyl-2-butene ion radicals, is proposed. In this potential, ethene loss proceeds from the 1-pentene structure, while methyl radical loss results directly from cis-2-pentene bond cleavage. cis-2-Pentene is placed at the center of the potential, the intermediate structure between linear and branched species. Cyclopentane is in rapid equilibrium with 1-pentene, as are the branch isomers with 2-methyl-2-butene.

Remarkably, enough information exists in the TOF spectra that the six individual rate constants associated with the proposed potential can be extracted. RRKM theory is used to determine the isomerization transition state barrier heights and entropies. A steady state approximation to the full potential energy surface is made and an analytical solution for the observed metastable dissociation rate is found to agree well with the data. In addition, a numerical solution to the full potential is also found to agree well with the data. A novel way to test the potential energy surface through cold TPEPICO isotropic labeling studies is proposed.

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