be obtained by comparing the splittings with those in another pair of compounds, HC≡CX and PhX. Table I shows data for the case where X is vinyl, derived from the UPE spectra of vinylacetylene (**7**) and styrene (**8**). In each case I_2 and I_3 are known to correspond to the π MOs of acetylene or benzene. The ratio of the splittings is 1.4, the same as for **4** and **1**.

In our studies[1] of **1** and **2**, we assumed that any field/inductive effect of a substituent in benzene will alter the energies of the benzene π MOs (a_1 and b_2) to equal extents. Support for this assumption, and for the use of PMO theory in this and the preceding[1] paper, is provided by the UPE spectrum of phenylacetylene (**9**) (Table I). Here I_3 and I_4 are known to correspond to the acetylenic π MOs. The π interaction between ethynyl and phenyl is then equal to their separation, i.e., 0.67 eV. I_1 corresponds to the perturbed (b_1) benzene π MO, the unperturbed energy of which should be greater by the π interaction i.e., equal to I_1 + 0.67 = 9.55 eV. This is essentially the same as the value for the (unperturbed) a_2 π MO (9.57 eV), showing that the field/inductive effect of ethynyl raised both by the same amount (0.35 eV).

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Supplementary Material Available: Photoelectron spectra for **3**–**6** (4 pages). Ordering information is given on any current masthead page.

Slow Multiphoton Excitation as a Probe of Bimolecular and Unimolecular Reaction Energetics. Multiphoton Dissociation of Proton Bound Alcohol Dimers

D. S. Bomse and J. L. Beauchamp*

Contribution No. 6265 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. *Received September 2, 1980*

Abstract: Many bimolecular reactions proceed through a long-lived intermediate. In some cases an alternate reaction can be used to prepare the intermediate as a stable molecule or complex. A study of the unimolecular dissociation of this species helps elucidate the energetics of the corresponding bimolecular process. Following preparation of the stable intermediate, low-power continuous-wave laser-radiation effects slow multiphoton excitation and decomposition along the lowest energy pathway. In this manner, infrared activation can be used to identify the lowest energy reaction in a complicated, bimolecular process. This technique is demonstrated in the present work. Proton bound dimers of simple aliphatic alcohols $(R_1OH)H^+(R_2OH)$ where $R_1 = R_2 = CH_3$, C_2H_5, $i\text{-}C_3H_7$, $n\text{-}C_3H_7$, $s\text{-}C_4H_9$, $t\text{-}C_4H_9$, and $t\text{-}C_5H_{11}$ are intermediates formed in gas phase reactions of the corresponding protonated alcohols with neutral alcohols. Products from the decomposition of these chemically activated species are compared with those obtained by slow multiphoton excitation. In addition, it is shown that isomeric ions are distinguished by formation of different sets of decomposition products. Also, we report the first observation of multiple sets of products arising from low-power infrared activation. This result is due to an exothermic isomerization in the transition state which makes accessible more than one reaction pathway. Use of infrared multiphoton excitation as a complementary technique to collisional activation of ions in mass spectrometric analysis of mixtures is discussed. For this study, ions are formed, stored, and detected by using techniques of ion cyclotron resonance (ICR) spectroscopy.

In complex chemical systems where multiple sets of products result from a bimolecular encounter, reaction coordinate diagrams have proven extremely useful for visualizing reaction energetics. Consider, for example, the hypothetical ion–molecule reaction between A^+ and B which has two exothermic reaction channels, reactions 1 and 2. Figure 1 depicts three possible sets of reaction coordinates for this system. Although this example is an ion–molecule reaction, the considerations are general and apply to reactions of neutral species as well. Typically, ΔH_1 and ΔH_2 are well known. AB^+ may represent a cluster or another stable species whose thermochemistry is well characterized. For most ion–molecule systems the values of activation energies E_{a1} and E_{a2} are not known. When reaction of A^+ with B yields both C^+ and F^+ all that can be inferred is that no point along paths followed on the potential energy surface from reactants to products exceeds the energy E^* available to the reactive intermediate AB^+. No information is available to distinguish among cases I, II, and III in Figure 1.

$$A^+ + B \rightarrow [AB^+]^* \rightarrow C^+ + D \qquad \Delta H_1 < 0 \qquad (1)$$

$$A^+ + B \rightarrow [AB^+]^* \rightarrow F^+ + G \qquad \Delta H_2 < 0 \qquad (2)$$

Several experimental techniques have been developed to probe details of a reaction potential energy surface.[1] These typically involve measuring branching ratios as a function of E^*.[1] One commonly used method is to form AB^+ from different sets of reactants (such as A + B^+).[2] Varying reactant translational energy also changes the value of E^*.[3] Formation of stable (i.e., vibrationally "cold") AB^+ followed by collisional excitation provides information on activation energies and the nature of the reaction coordinate in the exit channel.[4]

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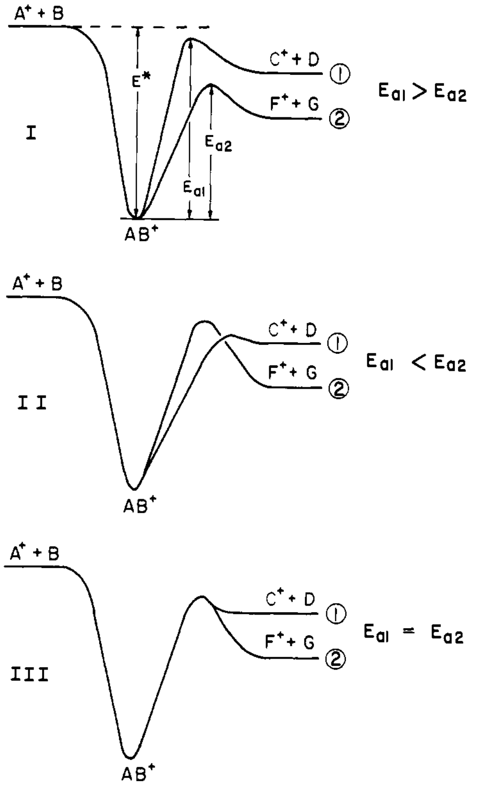

Figure 1. Three possible potential energy surfaces for the exothermic ion-molecule reaction of $A^+ + B$ leading to products $C^+ + D$ and $F^+ + G$.

We have shown that gas-phase ions irradiated by a low-power (<100 W cm^{-2}) continuous wave infrared laser undergo slow, sequential multiphoton absorption and decomposition.[5-7] Techniques of ion cyclotron resonance (ICR) spectroscopy are used to trap ions in a spatially well-defined region for periods up to 2 s. In a previous study[7] a dramatic isotope effect observed in an intramolecular competition experiment demonstrates that ions activated by continuous wave infrared laser radiation decompose at energies very close to the thermodynamic threshold. Due to the slow nature of the process, the potential energy surface available to a decomposing ion is sampled thoroughly below (but not above) the lowest energy decomposition pathway. Thus, in cases where AB^+ can be formed initially with little or no internal energy, infrared laser excitation and dissociation of AB^+ identify the lowest energy decomposition reaction.

To demonstrate the utility and scope of this methodology, we have studied the multiphoton dissociation of proton bound dimers of some simple aliphatic alcohols.[8-14] The ion-molecule reactions of the protonated alcohols[9-14] have been studied in great detail and much of the pertinent thermochemistry is available.[15] Thus they represent well-characterized bimolecular processes where the reaction intermediates can be easily prepared as stable species[8,11-15] and subjected to infrared multiphoton activation. For example, reaction of protonated isopropyl alcohol, $i\text{-}C_3H_7OH_2^+$, with the neutral alcohol $i\text{-}C_3H_7OH$ initially forms a chemically activated intermediate $(i\text{-}C_3H_7OH)_2H^+$.[12] The activated proton bound alcohol dimer can dissociate back to reactants, or eliminate H_2O to form a protonated ether $(i\text{-}C_3H_7)_2OH^+$, reaction 3, or lose propylene to yield $(i\text{-}C_3H_7OH)H^+(OH_2)$, reaction 4. Both reactions 3 and 4 are observed at room temperature.[12] Similarly for the other alcohols studied,[8-14] the proton bound dimer $(ROH)H^+(R'OH)$, where $R = R' = CH_3$, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $s\text{-}C_4H_9$, $t\text{-}C_4H_9$, and $t\text{-}C_5H_{11}$, has analogous routes to decomposition. For all of these processes except direct proton bond cleavage the activation energies for decomposition of the reaction intermeidate are unknown.[15] In the present study we utilize multiphoton dissociation of the proton bound dimer to single out and identify the lowest energy process.

$$i\text{-}C_3H_7OH_2^+ + i\text{-}C_3H_7OH \rightleftharpoons [(i\text{-}C_3H_7OH)_2H^+]^* \rightarrow (i\text{-}C_3H_7)_2OH^+ + H_2O \quad (3)$$

$$i\text{-}C_3H_7OH_2^+ + i\text{-}C_3H_7OH \rightleftharpoons [(i\text{-}C_3H_7OH)_2H^+]^* \rightarrow (i\text{-}C_3H_7OH)H^+(OH_2) + C_3H_6 \quad (4)$$

Experimental Section

The theory, techniques, and instrumentation of trapped ion ICR spectroscopy have been previously described in detail.[16,17] The spectrometer used in this study was built at Caltech and incorporates a 15-in. electromagnet capable of 23.4 kG. A flat ICR cell is utilized, in which the upper source plate is replaced with a 92% transmittance mesh to allow irradiation of trapped ions.

All ICR experiments were carried out in the range between 5×10^{-7} and 5×10^{-6} torr, corresponding to neutral particle densities between 1.5×10^{10} and 1.5×10^{11} molecules cm^{-3}. Pressure is measured with a Schulz-Phelps type ionization gauge calibrated against an MKS Instruments Baratron Model 90H1-E capacitance manometer. It is expected that absolute pressure determinations are within ±20% by using this method, with pressure ratios being somewhat more accurate. Sample mixtures are prepared directly in the instrument by using three sample inlets and the Schulz-Phelps gauge.

Proton bound methanol dimers are formed by ion-molecule reactions in a mixture of CH_3OH, H_2O, and Br_2CHCH_3.[8] Proton bound ethanol dimers are produced in a mixture of C_2H_5OH and CH_3F.[11] All other proton bound alcohol dimers form rapidly following ionization of the parent alcohol.[12-15] All reagents except H_2O were obtained from commercial suppliers. Samples were degassed by repeated freeze-pump-thaw cycles.

ICR spectrometer modifications and details of the experimental arrangement used for infrared laser photochemistry studies are published elsewhere.[7] In a typical experiment ions are formed by a 10-ms pulse of electrons (70 eV except for the ethanol system for which the electron energy is 14 eV). During the first 0.5 s of trapping time ion-molecule reactions go to completion, forming proton bound alcohol dimers. Laser irradiation occurs during the next 0.5 s and ion abundances are measured at ~1.0 s of trapping time. Laser intensity is adjusted (15-50 W cm^{-2}) so that ~60% of the dimer ions are dissociated. This insures sufficient formation of product ions for ICR double resonance[16] analysis while minimizing the extent of subsequent product ion photolysis. Double resonance refers to the selective ejection from the ICR cell of ions of a particular charge to mass ratio allowing positive identification of reaction pathways.[16] For each system the temporal variation of ion population

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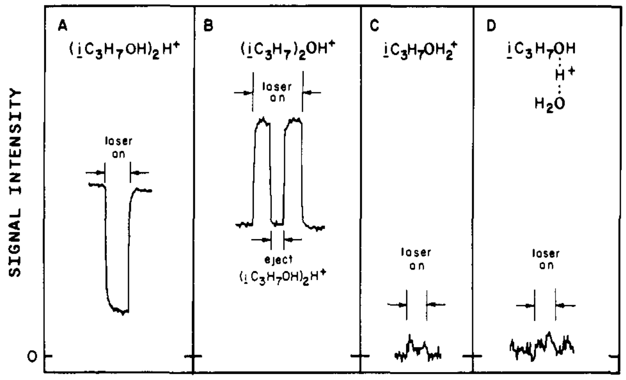

Figure 2. ICR signal intensities measured at 950 ms of trapping time of four ions generated following 70 eV electron impact ionization of 3.1 × 10^{-7} torr $i\text{-}C_3H_7OH$. Intensities should be multiplied by 1.00, 1.17, 0.13, and 0.29 for A, B, C, and D, respectively, to allow direct comparison. Laser irradiation (33 W cm^{-2}) begins at 500-ms trapping time as does double resonance ejection, where noted. Ions A, B, C, and D are identified in the figure.

during laser irradiation is also measured. In each case photodissociation is found to be first order (in ion population) and it is possible to dissociate 100% of the ions. The laser wavelength is 944 cm^{-1} (P(20) line of the 10.6-μm branch) except where noted.

Results and Discussion

For aliphatic alcohols the ion-molecule reactions of the protonated alcohol ROH_2^+ with neutral alcohol ROH, shown specifically for isopropyl alcohol by eq 3 and 4, can be generalized by the processes indicated in eq 5 and 6.[9-14] In these reactions

$$ROH_2^+ + ROH \rightleftharpoons [(ROH)_2H^+]^* \rightarrow R_2OH^+ + H_2O \quad (5)$$

$$ROH_2^+ + ROH \rightleftharpoons [(ROH)_2H^+]^* \rightarrow (ROH)H^+(H_2O) + \text{olefin} \quad (6)$$

the proton bound alcohol dimer $(ROH)_2H^+$ is equivalent to the hypothetical intermediate AB^+ shown in Figure 1. Reaction 5 is observed for all the alcohols used in this study, whereas ionic dehydration, eq 6, occurs only for R = $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $s\text{-}C_4H_9$, $t\text{-}C_4H_9$, and $t\text{-}C_5H_{11}$. At the pressures (<5 × 10^{-6} torr) used in these experiments, formation of proton bound dimer by *direct* bimolecular clustering of ROH_2^+ and ROH occurs only for the *n*-propyl alcohol case. Full details of alcohol ion-molecule chemistry including reaction sequences leading to $(ROH)_2H^+$ formation[8-14] and pertinent thermochemistry are published elsewhere.[15]

Infrared laser irradiation leads to multiphoton dissociation of each proton bound alcohol dimer investigated. By analogy to the general case shown in Figure 1 and eq 5 and 6, there are three plausible routes to decomposition of $(ROH)_2H^+$, eq 7-9.

$$(ROH)_2H^+ \rightarrow ROH_2^+ + ROH \quad (7)$$

$$(ROH)_2H^+ \rightarrow R_2OH^+ + H_2O \quad (8)$$

$$(ROH)_2H^+ \rightarrow (ROH)H^+(H_2O) + \text{olefin} \quad (9)$$

Typical experimental results for R = $i\text{-}C_3H_7$ are shown in Figure 2. Data indicate ICR signal intensities of four ions measured at 950 ms of trapping time. Intensities of different ions are not directly comparable[16] but should be multiplied by 1.00, 1.17, 0.13, and 0.29, respectively (reading left to right). Scan A, at the far left in Figure 2, shows the decrease in proton bound alcohol dimer, $(i\text{-}C_3H_7OH)_2H^+$, caused by infrared laser irradiation (33 W cm^{-2} beginning at 500 ms of trapping time). Part B shows the increase in $(i\text{-}C_3H_7)_2OH^+$ due to laser radiation. When corrected for variations in ICR sensitivity the increase in $(i\text{-}C_3H_7)_2OH^+$ accounts for 99% of the decrease in $(i\text{-}C_3H_7OH)_2H^+$. All of the laser-induced signal enhancement in B is eliminated by double resonance ejection (also beginning at 500 ms) of $(i\text{-}C_3H_7OH)_2H^+$. This identifies reaction 8 (R = $i\text{-}C_3H_7$) as a multiphoton dissociation pathway. In Figure 2, part C shows a very slight increase in protonated alcohol resulting from laser irradiation. Double resonance (not shown) establishes this increase results from dissociation of $(i\text{-}C_3H_7)_2OH^+$. Finally, part D shows no measurable change in $(i\text{-}C_3H_7OH)H^+(OH_2)$ intensity with laser irradiation. Consideration of ICR detection limits indicates *no more than* 2% of $(i\text{-}C_3H_7OH)_2H^+$ dissociates to give a product ion *other than* $(i\text{-}C_3H_7)_2OH^+$. Experimental results for the other proton bound dimers show comparable uncertainties in determining "null" reaction pathways. Thus we conclude that neither reaction 7 nor reaction 9 occurs for R = $i\text{-}C_3H_7$ and process 8 is the decomposition pathway with minimum activation energy.

Table I. Unimolecular Decomposition Reactions of Proton Bound Alcohol Dimers[a]

dimer ion $(R_1OH)H^+(R_2OH)$	ΔH reaction 7	ΔH reaction 8	ΔH reaction 9	$\Delta H'$[b] reaction 9
1, $R_1 = R_2 = CH_3$[c]	31	$\underline{18}$	89	
2, $R_1 = R_2 = C_2H_5$	32	$\underline{15}$	19	
3, $R_1 = R_2 = n\text{-}C_3H_7$	$\underline{33}$ (71%)	$\underline{17}$ (17%)	$\underline{19}$ (12%)	
4, $R_1 = R_2 = i\text{-}C_3H_7$	31	$\underline{19}$	22	
5, $R_1 = R_2 = s\text{-}C_4H_9$	32	$\underline{15}$ (38%)	$\underline{20}$ (62%)	
6, $R_1 = i\text{-}C_3H_7$; $R_2 = s\text{-}C_4H_9$	33^d	$\underline{19}$ (37%)	$\underline{18}^e$ (63%)	24^f
7, $R_1 = R_2 = t\text{-}C_4H_9$	31	$\underline{20}$	23	
8, $R_1 = R_2 = t\text{-}C_5H_{11}$	31	19	$\underline{22}$	
9, $R_1 = i\text{-}C_3H_7$; $R_2 = t\text{-}C_4H_9$	30^d	$\underline{13}$	22^g	23^h

[a] Thermochemical data, in kcal/mol, taken from ref 15. Numbers in parentheses are product distributions for laser-driven reactions where more than one product is observed. Underlined numbers denote observed IR laser-driven reactions. [b] $\Delta H'$ refers to enthalpy change for the alternate reaction 9 pathway available when R_1 and R_2 are not identical. [c] Reference 30. [d] Assumes more basic alcohol is protonated. [e] Products are $(i\text{-}C_3H_7OH)H^+(OH_2)$ + *trans*-2-butene. [f] Products are $(s\text{-}C_4H_9OH)H^+(OH_2)$ + propene. [g] Products are $(t\text{-}C_4H_9OH)H^+(OH_2)$ + propene. [h] Products are $(i\text{-}C_3H_7OH)H^+(OH_2)$ + isobutylene.

Table I lists the alcohol proton bound dimers, enthalpy changes for reactions corresponding to processes 7–9, and observed multiphoton dissociation pathways. Infrared activation of dimers **1**, **2**, **4**, **7**, and **9** leads to formation of the lowest enthalpy products as would be expected for type I potential energy surfaces (Figure 1). $(t\text{-}C_5H_{11}OH)_2H^+$, **8**, is the one example which is described by a type II potential energy surface.[18] The remaining proton bound alcohol dimers listed in Table I (**3**, **5**, and **6**) dissociate yielding two or more sets of products. Significantly, these are also the first examples of slow multiphoton dissociation following more than one reaction pathway.

Low-power infrared laser activation does not open up any additional reaction channels available to $(ROH)_2H^+$. Products of multiphoton dissociation of $(ROH)_2H^+$, eq 5 and 6, are the same products generated by exothermic reaction of ROH_2^+ and ROH, eq 8 and 9. The only difference is that laser activation is more selective. For example, multiphoton dissociation of $(C_2H_5OH)_2H^+$ yields exclusively $(C_2H_5)_2OH^+$ and H_2O (Table I) which is also the only set of products formed at pressures <10^{-5} torr by exothermic ion-molecule reaction of $C_2H_5OH_2^+$ and C_2H_5OH.[9,11] This result can be understood as follows. Although the exact energy requirements for reactions 8 and 9 are unknown, the energy required for reaction 7 is well defined because simple hydrogen bond cleavage does not have an activation energy in excess of reaction endothermicity. Thus the enthalpy change (E^* in Figure 1) for dissociation of $(ROH)_2H^+$ to ROH_2^+ and ROH, reaction 7, determines an upper bound to the level of infrared excitation in $(ROH)_2H^+$ since decomposition is faster than continued excitation at energies above reaction threshold. No process which is more endothermic than formation of ROH_2^+ and ROH can be achieved by slow multiphoton dissociation of $(ROH)_2H^+$.

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(18) For dimer **8** the difference in reaction enthalpies for reactions 6 and 9 is comparable to the uncertainty in the reported enthalpies.[15]

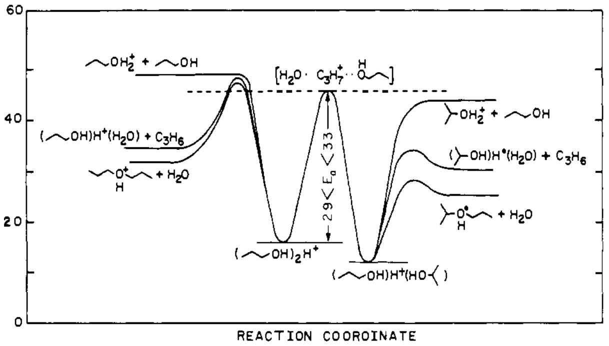
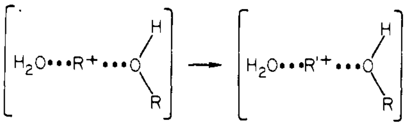


Figure 3. Reaction coordinate diagram for isomerization and decomposition of the proton bound dimer of 1-propanol. Thermochemical data from reference 15.

Furthermore, any exothermic reaction of ROH_2^+ and ROH (eq 5 and 6) must follow a pathway that is *always* lower in energy than the reactants. Such a pathway is a low-energy route to decomposition of $(ROH)_2H^+$ whether the activated proton bound dimer is prepared by collision of ROH_2^+ and ROH or by infrared laser excitation.

Proton bound alcohol dimers **3**, **5**, and **6** each yield more than one set of products from slow multiphoton dissociation (Table I). The measured branching ratios are invariant to changes in laser wavelength (942–1079 cm^{-1}) or laser power (27 to 63 W cm^{-2}). Dimers **3**, **5**, and **6** contain 1-propanol or 2-butanol. Of the alcohols used in this study, only these two can isomerize to more stable alcohols. We infer that more than one set of dissociation products is formed because an isomerization occurs in the transition state which releases sufficient energy to make accessible two or three reaction channels. This corresponds to case III in Figure 1. Results of a previous study indicate slow multiphoton dissociation is extremely sensitive to small differences in activation energies. More than one set of products can arise from different transition states only if the corresponding activation energies are almost identical.[7] It is highly unlikely that an accidental degeneracy exists in three different proton bound dimers.

A candidate for a transition state which allows for alkyl isomerization comprises an alkyl cation R^+, water, and alcohol ROH, in which R^+ isomerizes to R'^+ (**10** → **10′**). Loss of H_2O results



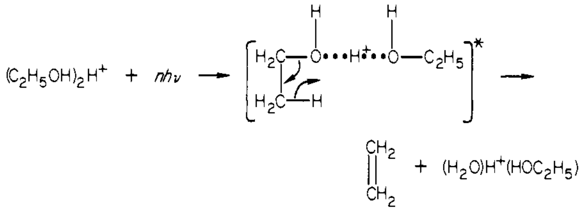
$$\left[H_2O\cdots R^+\cdots O{<}^{H}_{R}\right] \longrightarrow \left[H_2O\cdots R'^+\cdots O{<}^{H}_{R}\right] \qquad (10)$$

10 10′

in formation of protonated ether $RR'OH^+$. The other products result from deprotonation of R'^+ to yield $(R'OH)H^+(OH_2)$ plus an olefin or recombination of R'^+ and H_2O to form $R'OH_2^+$ and ROH. Ion–molecule complexes have been invoked in related studies to explain isotopic exchange processes[19] and isomer distributions among neutral products[20] of several ion–molecule reaction systems. In these intermediates bonding between the ion and neutral components is predominantly electrostatic rather than covalent.[19,20]

Thermochemical constraints imposed on the isomerization and decomposition of $(n\text{-}C_3H_7OH)_2H^+$, **3**, are shown in Figure 3. ΔH_f for the transition state must be <49 kcal/mol; otherwise direct dissociation to $n\text{-}C_3H_7OH_2^+$ and $n\text{-}C_3H_7OH$ (reaction 7) would occur. Assuming only one alkyl group isomerizes,[21] the transition state heat of formation must be >44.5 kcal/mol to allow formation of $i\text{-}C_3H_7OH_2^+$ and C_3H_7OH. The activation barrier for reaction is determined to be $29 < E_a < 33$ kcal/mol. Furthermore, as seen at the left side of Figure 3, enthalpies of transition states leading directly to $(n\text{-}C_3H_7)_2OH^+$ and H_2O (reaction 5) as well as $(n\text{-}C_3H_7OH)H^+(OH_2)$ and C_3H_6 (reaction 6) must both be above ΔH_f of the isomerization transition state. This places the former two values very close in energy to $n\text{-}C_3H_7OH_2^+$ and $n\text{-}C_3H_7OH$. Such a requriement is consistent with the observation that for R = $n\text{-}C_3H_7$ the bimolecular rates for reactions 5 and 6 as well as the direct clustering processes are all comparable. Analysis similar to that shown in Figure 3 for the isomerization reaction of dimer **5** brackets the activation energy between 13 and 26 kcal/mol.[22]

Of the three plausible dimer decomposition reactions, eq 7–9, process 8 entails the most extensive rearrangement yet is the most prevalent reaction. There is no obvious direct mechanism for protonated ether formation, reaction 8. Most likely the dissociation proceeds through an ion–molecule complex such as **10**. In contrast, one can imagine a simple four-center intermediate[23] available to all dimers (except **1**) leading directly to olefin elimination, reaction 9. This intermediate is shown in eq 11 for the ethanol proton



$$(C_2H_5OH)_2H^+ + nh\nu \longrightarrow \left[\begin{array}{l} H_2C{-}\overset{H}{O}\cdots H^+\cdots\overset{H}{O}{-}C_2H_5 \\ H_2C{-}H \end{array}\right]^* \longrightarrow CH_2{=}CH_2 + (H_2O)H^+(HOC_2H_5) \qquad (11)$$

bound dimer. However, only ion **8** dissociates exclusively via pathway 9. The slight difference in structure between *tert*-butyl alcohol and *tert*-amyl alcohol does not seem sufficient to explain a preference for the four-center intermediate in decomposition of **8** compared to reaction of $(t\text{-}C_4H_9OH)_2H^+$, **7**. In fact, reactions proceeding through four-center intermediates such as shown in eq 11, while not formally "forbidden"[23] by orbital symmetry consideration, usually show sizable activation barriers.[24] Thus, it appears that all ions $(ROH)_2H^+$ dissociate through an ion–molecule intermediate[25] **10** and the selectivity demonstrated by **1**, **2**, **4**, and **7**–**9** reflects differences in activation energies for the various pathways to decomposition of **10**.

Figure 4 shows the variation in photodissociation yield with laser wavelength (925–1080 cm^{-1}) for isomeric ions $(n\text{-}C_3H_7OH)_2H^+$, **3**, and $(i\text{-}C_3H_7OH)_2H^+$, **4**. Photodissociation yield, P_D, is defined as the fraction of ions decomposed by 500-ms laser irradiation at a laser power of 34 W cm^{-2} for $(n\text{-}C_3H_7OH)_2H^+$, upper spectrum, and 17 W cm^{-2} for $(i\text{-}C_3H_7OH)_2H^+$, lower spectrum. Neither photodissociation spectrum has any distinct, readily identified features. Instead, both are characterized by a continuous band showing a slight increase in P_D with increasing photon energy. At lower laser powers, where P_D values are not as close to "saturation" (i.e., P_D = 1.00), a check of several laser wavelengths indicates no change in the overall appearance of the photodissociation spectra of **3** and **4**. Although both spectra in Figure 4 show similar P_D values at each wavelength, the laser powers used differ by a factor of 2. Previous studies indicate apparent multiphoton

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(19) Bowen, R. D.; Williams, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 2752.

(20) Morton, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 1596.

(21) For the free alkyl cation, rearrangement of $n\text{-}C_3H_7^+$ to $i\text{-}C_3H_7^+$ occurs on a time scale of $\sim 10^{-10}$ s, indicating no additional activation energy is required: Ausloos, P.; Lias, S. G. In "Ion-Molecule Reactions"; Franklin, J. L., Ed.; Plenum: New York, 1979; Vol. 2.

(22) There is an activation barrier for the isomerization of uncomplexed $s\text{-}C_4H_9^+$ to $t\text{-}C_4H_9^+$. However, the isomerization remains the lowest energy process. Dymerski, P. P.; McLafferty, F. W. *J. Am. Chem. Soc.* **1976**, *98*, 3734. Ausloos, P. A.; Shold, D. M. *Ibid.* **1976**, *100*, 7915.

(23) The presence of a lone-pair orbital on oxygen makes this process differ from a 2 + 2 symmetry-forbidden reaction.[19]

(24) Huntress, W. T., Jr.; Sen Sharma, D. K.; Jennings, K. R.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *24*, 25.

(25) In comparison, multiphoton dissociation of proton bound diethyl ether dimer yields only hydrogen bond cleavage products[5,7] although a reaction analogous to reaction 9 is of lower enthalpy.[7] Differences in reactivities between $[(C_2H_5)_2O]_2H^+$ and proton bound alcohol dimers reflect different energy requirements in formation of a ion–molecule complex, **10**. For example, energy required to form a free $C_2H_5^+ + H_2O$ from $C_2H_5OH_2^+$ is 37 kcal/mol[15] whereas the corresponding process in $(C_2H_5)_2OH^+$, $(C_2H_5)_2OH^+ \rightarrow C_2H_5^+ + C_2H_5OH$ (ΔH = 53 kcal/mol[15]) is much more endothermic. Using these numbers as estimates of the *relative* endothermicities of ion–molecule complex formation is consistent with observed differences in reactivities.

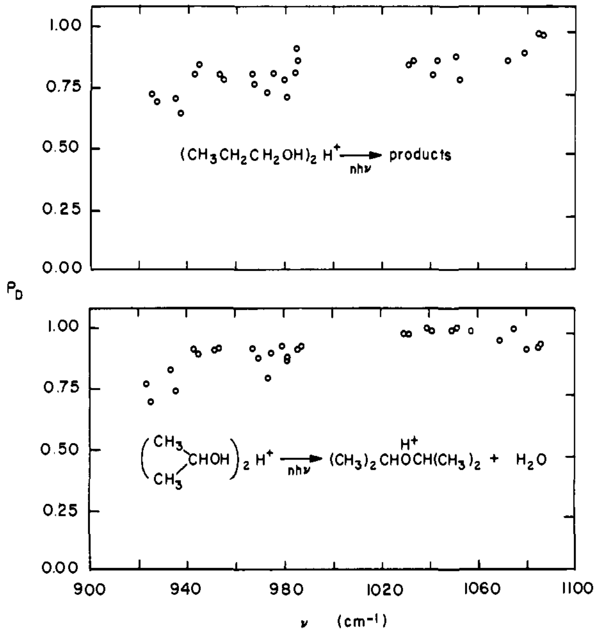

Figure 4. Infrared photodissociation spectra of isomeric ions ($(n\text{-}C_3H_7OH)_2H^+$ (top) and $(i\text{-}C_3H_7OH)_2H^+$ (bottom). For upper spectrum, laser power is 34 W cm^{-2} and n-C_3H_7OH pressure is 4.1×10^{-7} torr. In lower spectrum, laser power is 17 W cm^{-2} and i-C_3H_7OH pressure is 4.4×10^{-7} torr. In both spectra ions are formed by a 70-eV 10-ms pulse of electrons, laser irradiation begins at 500-ms trapping time, and ions are detected at 1.0-s trapping time.

photodissociation cross sections to be a very sensitive function of the ion–molecule collision rate.[6,7] Data for both spectra in Figure 4 were obtained at nearly identical pressure (4.1×10^{-7} torr of n-C_3H_7OH for the upper spectrum compared with 4.4×10^{-7} torr of i-C_3H_7OH for the lower spectrum). Thus, these results indicate $(i\text{-}C_3H_7OH)_2H^+$ has a much larger photodissociation cross section at each wavelength studied than does $(n\text{-}C_3H_7OH)_2H^+$.[5-7]

Conclusions

Slow multiphoton dissociation represents a sensitive probe of reaction potential energy surfaces. Products of multiphoton dissociation of proton bound dimer $(ROH)_2H^+$ are also products of an exothermic reaction of ROH_2^+ and ROH. All observed alcohol dimer decompositions, including those giving multiple sets of products, are consistent with the formation of a "solvated" alkyl cation as an electrostatically bound intermediate.

Multiphoton dissociation reactions can be used to distinguish structural isomers of ions. Proton bound dimers **3** and **4** have identical charge-to-mass ratios, and even identical infrared photodissociation spectra. However, the isomers yield different characteristic sets of products from multiphoton dissociation. Similarly isomers **5** and **7** form distinguishable sets of products following infrared laser excitation. Although the sample of photodissociation spectra shown in Figure 4 represents a negative result, other systems should demonstrate greater wavelength selectivity.

To date most detailed information about reaction coordinate profiles in ion–molecule reactions has been obtained from studies of metastable ion fragmentations.[1b,19,26] In those experiments the decomposing species are ions initially formed with internal energy at, or slightly above, threshold for unimolecular decomposition. Infrared activation is an additional and complementary technique for the study of unimolecular decomposition of gas-phase ions with internal energy slightly in excess of dissociation thresholds.

In light of current interest in mass spectrometric techniques[27] used to analyze complicated mixtures and to "fingerprint" ions by their secondary fragmentation patterns, infrared multiphoton excitation represents a novel method for ion decomposition. Although low-power (<100 W cm^{-2}) infrared radiation leads to decomposition exclusively by the lowest energy pathway,[5-7] pulsed laser irradiation at high peak powers ($\geq$ 1 MW cm^{-2}) is known to make multiple reaction channels energetically accessible.[28,29] The only requirement is that infrared absorption rates exceed unimolecular decomposition rates of the irradiated molecule.

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(29) Reported results of high-power pulsed infrared laser photolyses of trapped ions all indicate only one set of products formed. However, only a few systems have been studied to date: Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3999. Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *J. Chem. Phys.* **1979**, *71*, 1030.

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