tetra-*n*-butylammonium picrate in a series of non-hydrogen-bonding solvents ranging in dielectric constant from 2.2 to 6.0.[25,26] The apparent dipole moments in this series range from 13.8 to 16.8 D and vary in a random manner with the dielectric constant. Less extensive solvent effects are known for tetra-*n*-butyl-ammonium bromide and for tetraisoamylammonium nitrate and iodide.[25,27] Here the changes in the apparent dipole moment are 1.6, 0.6, and 2.5 D, respectively. Dielectric relaxation has been studied for tetra-*n*-butylammonium perchlorate in a number of aprotic and hydrogen-bonding solvents whose dielectric constants range from 3.3 to 20.7D.[28] Measurements at the lowest fre-

quencies in this study[28] indicate that molar dielectric increments vary with the solvent, but the frequencies of the measurements were too high for dipole moments to be reported.

In conclusion, our results for AEM⁺Ts⁻ demonstrate that the average electric dipole moments of quaternary ammonium ion pairs can vary considerably with the solvent, not only because of hydrogen bonding to the anion in appropriate solvents but because of changes in the average interionic geometry. Such changes can arise, first, because the formal ion-pair species may in fact be a mixture of interionic isomers whose equilibrium ratios vary with the solvent and, second, because the interionic geometries of the individual ion-pair isomers may vary with the solvent.

(25) Gilkerson, W. R.; Srivastava, K. K. *J. Phys. Chem.* **1960**, *64*, 1485.
(26) Richardson, E. A.; Stern, K. H. *J. Am. Chem. Soc.* **1960**, *82*, 1296.
(27) Grunwald, E.; Effio, A. *J. Solution Chem.* **1973**, *2*, 373, 393.

(28) Sigvartsen, T.; Gestblom, B.; Noreland, E.; Songstad, J. *Acta Chem. Scand.* **1989**, *43*, 103.

Collisional Activation of Distonic Radical Cations and Their Conventional Isomers in Quadrupole Tandem Mass Spectrometry

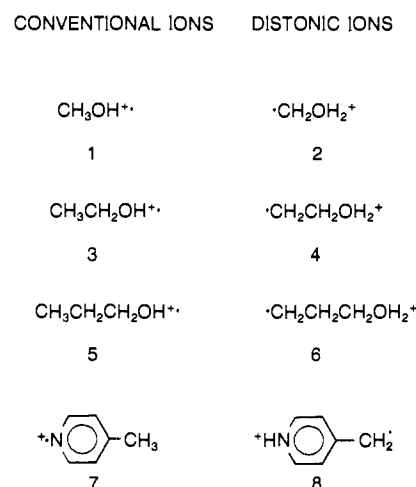## Vicki H. Wysocki*,† and Hilkka I. Kenttämaa*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-3699. Received September 18, 1989

Abstract: Competition between collision-activated isomerization and fragmentation of the distonic radical cations ${}^\bullet CH_2(CH_2)_nOH_2{}^+$ ($n = 0-2$) and their conventional counterparts $(CH_3(CH_2)_nOH^{\bullet+}$, $n = 0-2)$, was examined under different experimental conditions in a triple quadrupole mass spectrometer and in a Paul-type quadrupole ion trap. All the above pairs of isomers give structurally characteristic fragmentation products upon low-energy (eV) collisional activation under single- and multiple-collision conditions in the triple quadrupole instrument. Fast direct bond cleavages dominate the fragmentation. Thus, abundant even-electron ionic fragments are obtained for the conventional ions, while the distonic isomers yield predominantly odd-electron ionic fragments. Further, the results suggest that the barrier between the ions $CH_3CH_2CH_2OH^{\bullet+}$ and ${}^\bullet CH_2CH_2CH_2OH_2{}^+$ is significantly lower than the barriers associated with the shorter chain homologues ($n = 0$ or 1). This is consistent with findings reported recently for the nitrogen analogues. The quadrupole ion trap yielded collision-activated dissociation spectra that were indicative of distinct structures *only* for the isomers $CH_3CH_2OH^{\bullet+}$ and ${}^\bullet CH_2CH_2OH_2{}^+$. This is explained on the basis of the observation that the light helium target used for collisional activation in the ion trap makes fragmentation pathways with high internal energy requirements (>30 kcal/mol) inaccessible in this case. Other ions studied include ionized 4-methylpyridine and an isomer. Results obtained for these ions comprise evidence for the structures of odd-electron ionic products of protonated alkyl pyridines and suggest that these ions may have distonic structures.

The dependence of ionic fragmentation on the method of excitation[1] is of considerable interest in tandem mass spectrometry[2,3] since a number of different activation methods are currently used to induce decomposition of mass-selected gas-phase ions. The most commonly used method employs collisions of accelerated ions with neutral target gas (collision-activated dissociation).[2,3] The ion kinetic energies are usually either in the eV range (low-energy collisional activation) or in the keV range (high-energy collisional activation). Low-energy collisional activation is often carried out in quadrupole reaction chambers. This experiment allows optimization of a number of parameters, including the collision energy and the number of activating collisions the ions experience during the reaction time.[2,3] Moreover, comparison of the results obtained under different experimental conditions can yield information concerning the potential energy surfaces and fragmentation dynamics of gas-phase ions, assuming that the effects of the experimental variables are well understood.[2-7]

Our study has a 2-fold goal: (i) to understand better the effects of the various parameters that control collisional activation of ions
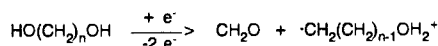
Scheme I

CONVENTIONAL IONS	DISTONIC IONS
$CH_3OH^{+\bullet}$	${}^\bullet CH_2OH_2{}^+$
1	2
$CH_3CH_2OH^{+\bullet}$	${}^\bullet CH_2CH_2OH_2{}^+$
3	4
$CH_3CH_2CH_2OH^{+\bullet}$	${}^\bullet CH_2CH_2CH_2OH_2{}^+$
5	6

in quadrupole tandem mass spectrometry, and (ii) to provide further insight into the gas-phase chemistry of some interesting

Collisional Activation of Distonic Radical Cations

J. Am. Chem. Soc., Vol. 112, No. 13, 1990 5111

Scheme II

$$HO(CH_2)_nOH \xrightarrow[-2\ e^-]{+\ e^-} CH_2O + \cdot CH_2(CH_2)_{n-1}OH_2^+$$

ionic species, namely, ions that are characterized by separate charge and radical sites (Scheme I). The properties of *distonic ions* have been the focus of intensive theoretical and experimental research[8,9] since it was discovered[10,11] that they can be kinetically as well as thermodynamically more stable than their conventional counterparts. Some researchers have reported the intriguing discovery that the stability difference between a distonic ion and its conventional counterpart often decreases when the distance between the radical site and the charge site increases.[8,12,13] It follows that a series of distonic ions with increasing chain length may provide a tool to probe the ultimate performance of different tandem mass spectrometric methods in isomer differentiation.

In the present work, competition between collision-activated fragmentation and isomerization of distonic ions with varying chain length was studied with two different quadrupole instruments, a triple quadrupole mass spectrometer[14] and a Paul-type quadrupole ion trap.[15] The triple quadrupole mass spectrometer employs a quadrupole mass filter to mass select reactant ions that are then collisionally activated in a quadrupole reaction chamber. The products are analyzed by using another quadrupole mass filter. In the quadrupole ion trap used in this work,[16] ions always reside in the same chamber, and alternating and direct current voltages are used to isolate reactant ions, to kinetically excite them, and to analyze their fragmentation products. With these two instruments, information concerning energetics of fragmentation reactions is obtained by varying the collision energy, and thereby changing the internal energy of the fragmenting ions (energy-resolved mass spectrometry).[2,3,15b] Other experimental parameters that affect the fragmentation product distributions include the reaction time, the type of collision gas used,[2,3,17] and the collision gas pressure.[2,3,6,7,17] The stability of distonic ions at high collision gas pressures, i.e., under multiple-collision conditions, is of special interest since (i) these experimental conditions are commonly used in quadrupole collision chambers[2,3,17] and (ii) multiple-step low-energy collisional activation is known to cause rapid isomerization in some ions.[2,7,18–20]
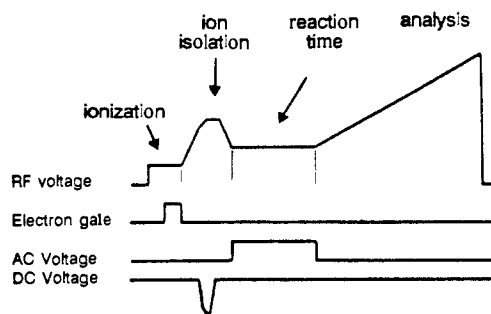

Figure 1. The sequence of radio-frequency (rf) and direct-current (dc) voltages used in the quadrupole ion trap to generate ions (ionization), mass select the ion of interest (ion isolation), accelerate the selected ion for collision-activated dissociation (reaction time) by using a supplementary alternating current voltage (ac voltage), and analyze the ionic dissociation product (analysis).

The ions investigated (Scheme I) include a series of distonic and conventional ions of the type $C_nH_{2n+2}O^{\bullet+}$ ($n = 1$–3), i.e., $\cdot CH_2(CH_2)_{n-1}OH_2^+$ (2, 4, 6) and $CH_3(CH_2)_{n-1}OH^{\bullet+}$ (1, 3, 5), as well as ionized 4-methylpyridine $CH_3C_5H_4N^{\bullet+}$ (7) and an isomer that possibly has the distonic structure $\cdot CH_2C_5H_4NH^+$ (8). The $C_nH_{2n+2}O^{\bullet+}$ ions have previously been investigated[9,21] by a number of research groups using methods such as metastable ion dissociation,[22] high-energy collision-activated dissociation,[21,22] neutralization–reionization mass spectrometry,[23] and ab initio calculations.[9,24] The body of information available for these ions makes them excellent candidates for attempts to characterize different activation methods. The pyridine isomers have not been studied previously. The distonic isomer (8, Scheme I) is of special interest as a possible representative of a series of charge-remote (remote-site) fragmentation products formed in reactions that formally involve a loss of an alkyl radical from ions of the general type $^+XCH_2(CH_2)_nCH_3$ or loss of the elements of an alkene from ions of the general type $^{+\bullet}XCH_2(CH_2)_n$.[25,26] Unimolecular dissociation reactions that appear to occur without the involvement of the charge site[25–28] are of interest not only from a fundamental but also from an analytical point of view since these reactions are very sensitive to structural details in many types of compounds.

Experimental Section

The conventional isomers were generated by 70-eV electron ionization of the corresponding neutral molecules and the distonic ions by dissociative 70-eV electron ionization of appropriate diols (Scheme II) in both of the mass spectrometers employed. The only exception was the isomer of 4-methylpyridine, an ion of m/z 93, that possibly has the structure 8. This ion was generated from 4-pentadecylpyridine (m-nitrobenzyl alcohol matrix) by dissociative ionization induced by fast-atom bombardment that mainly gives protonated 4-pentadecylpyridine. All the samples except 4-pentadecylpyridine were obtained commercially. The distonic ions generated by dissociative ionization comprise only a small part of the ion current (2–3% of the most abundant fragment ion). Therefore, tandem mass spectrometric methods that allow isolation of the ion of interest from all other ions formed at the same time is key to the examination of the properties of these distonic ions.

Collision-activated dissociation spectra (CAD) were obtained on the triple quadrupole instrument (Finnigan-MAT TSQ-70) at a number of

(1) Levsen, K. *Fundamental Aspects of Organic Mass Spectrometry*; Verlag Chemie: Weinheim, Germany, 1978.

(2) Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry*; VCH Publishers, Inc.: New York, 1988.

(3) McLafferty, F. W., Ed. *Tandem Mass Spectrometry*; Wiley and Sons: New York, 1983.

(4) Kinter, M. T.; Bursey, M. M. *J. Am. Chem. Soc.* **1986**, *108*, 1797.

(5) Kenttämaa, H. I.; Pachuta, R. R.; Rothwell, A.; Cooks, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 1654.

(6) See, for example: (a) Dawson, P. H. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *43*, 195. (b) Dawson, P. H.; French, J. B.; Buckley, J. A.; Douglas, D. J.; Simmons, D. *Org. Mass Spectrom.* **1982**, *17*, 212.

(7) Kenttämaa, H. I. *Org. Mass Spectrom.* **1985**, *20*, 703–714.

(8) Radom, L.; Bouma, W. J.; Nobes, R. H.; Yates, B. F. *Pure Appl. Chem.* **1984**, *56*, 1831–1842.

(9) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123–202.

(10) (a) Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2929–2930. (b) Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2930–2933.

(11) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgess, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 2931.

(12) Bjornholm, T.; Hammerum, S.; Kuck, D. *J. Am. Chem. Soc.* **1988**, *110*, 3862.

(13) Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron* **1986**, *42*, 6225.

(14) Slayback, J. R. B.; Story, M. S. *Ind. Res. Dev.* **1981**, 129.

(15) (a) Stafford, G. C.; Kelley, P. E.; Syka, J. E. P.; Reynolds, W. E.; Todd, J. F. J. *Int. J. Mass Spectrom. Ion Phys.* **1984**, *60*, 85. (b) Louris, J. N.; Cooks, R. G.; Syka, J. E.; Kelley, P. E.; Stafford, G. C.; Todd, J. F. J. *J. Anal. Chem.* **1987**, *59*, 1677–1685.

(16) Weber-Grabau, M.; Kelley, P.; Syka, J.; Bradshaw, S.; Brodbelt, J. Presented at the 35th Annual Conference on Mass Spectrometry and Allied Topics, Denver, Colorado, May, 1987.

(17) Schey, K. L.; Kenttämaa, H. I.; Wysocki, V. H.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Proc.* **1989**, *90*, 71–83.

(18) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

(19) Kenttämaa, H. I.; Cooks, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 1881.

(20) Brodbelt, J.; Kenttämaa, H. I.; Cooks, R. G. *Org. Mass Spectrom.* **1986**, *23*, 6.

(21) Schwarz, H. *Mass Spectrosc.* **1984**, *32*, 3 and references therein.

(22) (a) Holmes, J. L.; Mommers, A. A.; Szulejko, J. E.; Terlouw, J. K. *J. Chem. Soc., Chem. Commun.* **1984**, 165. (b) Burgers, P. C.; Holmes, J. L.; Terlouw, J. K.; Van Baar, B. *Org. Mass Spectrom.* **1985**, *20*, 202. (c) Postma, R.; Ruttink, P. J. A.; Van Baar, B.; Terlouw, J. K.; Holmes, J. L.; Burgers, P. C. *Chem. Phys. Lett.* **1986**, *123*, 409.

(23) Wesdemiotis, C.; Danis, P. O.; Feng, R.; Tso, J.; McLafferty, F. W. *J. Am. Chem. Soc.* **1985**, *107*, 8059.

(24) See, for example: (a) Bouma, W. J.; nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 1743 and references therein. (b) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805–5813.

(25) Wysocki, V. H.; Ross, M. M.; Horning, S. R.; Cooks, R. G. *Rapid Commun. Mass Spectrom.* **1988**, *2*, 214.

(26) Wysocki, V. H.; Ross, M. M. Submitted for publication.

(27) Jensen, N. J.; Tomer, K. B.; Gross, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1863.

(28) Adams, J. *Mass Spectrom. Rev.* **1990**, *9*, 141.

laboratory collision energies within the range 1–195 eV (laboratory frame). Argon was used as the collision target. Argon pressure was monitored directly in the quadrupole collision chamber with a capacitance manometer (MKS Baratron). For low-pressure conditions, 0.07 mTorr collision gas pressure was used. This pressure corresponds to single-collision conditions, as indicated by a linear increase in the fragment ion abundances of the m/z 219 ion from perfluorotributylamine as a function of argon pressure.[29] For multiple-collision conditions, 0.3–1.1 mTorr argon pressure was used. The offset voltage of the third quadrupole was ramped with mass such that all daughter ions enter the quadrupole with approximately 5–6 eV laboratory kinetic energy. This ramp is based on the assumption that the fragment ions have 90% of their expected kinetic energy (estimated on the basis of the collision energy of the precursor ion and the ratio of the masses of the precursor ion and the fragment ion in question). In this triple quadrupole instrument, the amplitude of the radio-frequency voltage applied to the second quadrupole is a variable fraction of that applied to the first quadrupole. The default value of the Mathieu parameter, q, in the second quadrupole is 0.2. Data were obtained by using the same tuning parameters for a given pair of isomers over the entire energy range examined. Energy-resolved mass spectra were plotted by normalizing each fragment ion abundance to the sum of all fragment ions of interest.

The quadrupole ion trap (a prototype Finnigan ITMS) has been described previously.[5b,16] A modified version of the commercial software was used to implement the necessary radio-frequency and direct-current voltages.[5b,16] Figure 1 illustrates the sequence of radio-frequency and direct-current voltages used for collision-activated dissociation of mass-selected ions. All the time intervals were kept as short as possible to avoid interfering ion-molecule reactions. Ions were generated by electron ionization (gated beam duration 1–2 ms). The amplitude of the radio-frequency (rf) voltage applied at 1.1 MHz to the ring electrode determines the mass range of the ions trapped (typically 10–200 daltons). Single-ion selection was carried out by raising the rf-voltage level (i.e., raising the q value) while applying an appropriate direct-current (dc) voltage to the ring electrode (time interval 3–5 ms). During the reaction time (typically 3–5 ms, q value 0.3), a supplementary alternating-current (ac) voltage (0.1–5.0 V p-p) was applied across the end caps at the fundamental frequency of the selected ions. This accelerates the ions and leads to collisional activation with the helium buffer gas. After the reaction period, the fragmentation products were ejected from the trap by using mass-selective instability induced by a rf-voltage ramp and detected with an external electron multiplier. The fragmentation products were not found to be very sensitive to variation of the voltage level of the excitation pulse (ac voltage) or to the q value during the reaction time. The samples were introduced into the ion trap through a Granville-Phillips leak valve at a nominal pressure of (1–5) × 10⁻⁶ Torr, as measured with an ionization gauge in the vacuum manifold. The nominal pressure of the helium buffer gas was 1 × 10⁻⁴ Torr.

Results

$CH_4O^{•+}$ Ions. Upon low-energy collisional activation under single- and multiple-collision conditions in the triple quadrupole instrument, the α-distonic isomer (**2**) of ionized methanol predominantly fragments by loss of H• to give $CH_2=OH^+$ (m/z 31) and by loss of H_2O to give $CH_2^{+•}$ (m/z 14). Minor signals corresponding to $H_2O^{•+}$ (m/z 18), $CH_2O^{•+}$ (m/z 30), and $CO^{•+}$ (m/z 28) from loss of CH_2, H_2, and $2H_2$, respectively, were also observed under multiple-collision conditions. Note that, excluding the ion of m/z 31, all these fragment ions are odd-electron species. Ionized methanol (**1**) yields quite different product distributions, with the even-electron ions $CH_2=OH^+$ (m/z 31) and CH_3^+ (m/z 15) from loss of H• and OH•, respectively, dominating the product distributions. In the quadrupole ion trap, *no fragments* were observed for the $CH_4O^{•+}$ ions.

$C_2H_6O^{•+}$ Ions. Low-energy collision-activated dissociation of the β-distonic isomer (**4**) of ionized ethanol is always dominated by loss of water to give $CH_2=CH_2^{•+}$ (m/z 28; Figures 2b and 3b). In contrast, ionized ethanol (**3**) preferentially loses a hydrogen radical or a methyl radical to give $CH_3CH=OH^+$ (m/z 45) and $CH_2=OH^+$ (m/z 31), respectively (Figures 2a and 3a). Ionized ethanol does not produce an abundant ion of m/z 28 under any conditions (<2% from total fragment ion current). At higher energies, loss of •CH_2OH to give CH_3^+ (m/z 15) is also observed for ionized ethanol. The fragment ions H_3O^+ (m/z 19) and

---

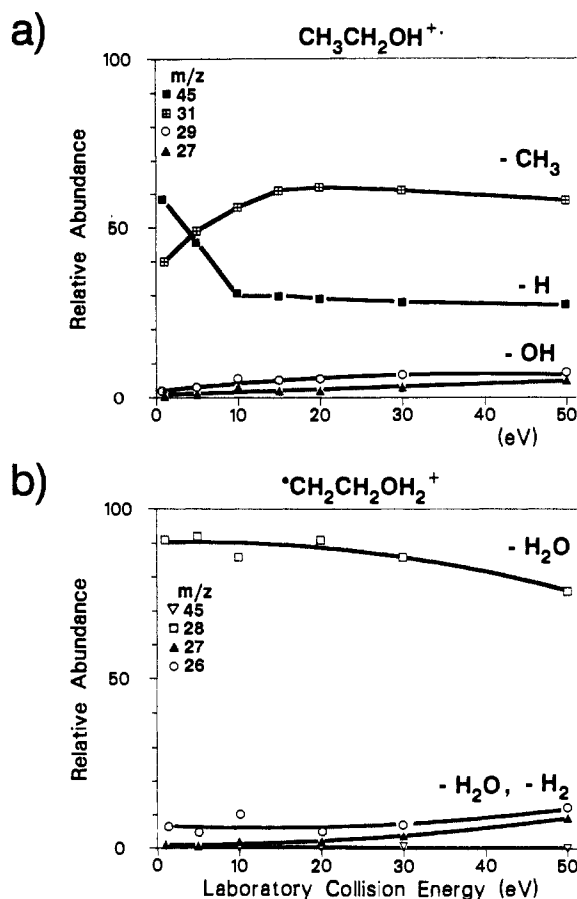(29) Nystrom, J. A.; Bursey, M. M.; Hass, J. R. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *55*, 263.

Figure 2. Collision-activated dissociation spectra plotted as a function of laboratory collision energy for (a) ionized ethanol and (b) its β-distonic isomer. These energy-resolved mass spectra were obtained by using the triple quadrupole instrument with an Ar pressure of 1 mTorr (multiple-collision conditions). The ions of each plot account for 95–99% of the total fragment ion current.
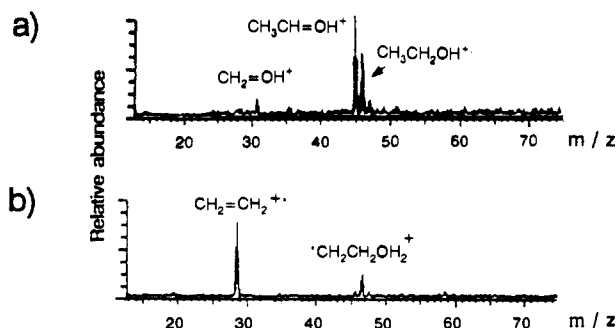

Figure 3. Collision-activated dissociation spectra obtained by using the quadrupole ion trap for (a) ionized ethanol and (b) its β-distonic isomer.

$CH_2=CH^+$ (m/z 27) were formed approximately in the ratio 1:1 *for both* $C_2H_6O^{•+}$ *isomers* at higher collision energies in the triple quadrupole instrument (laboratory collision energies >50 eV for the distonic structure **4** and >15 eV for the conventional isomer **3**). The dissociation patterns obtained with the quadrupole ion trap (Figure 3) were similar to those obtained in the triple quadrupole at low collision energies. For the triple quadrupole instrument, the product distributions obtained under single-collision conditions at higher collision energies were similar to those obtained under multiple-collision conditions at low collision energies.

$C_3H_8O^{•+}$ Ions. Low-energy collisional activation of the γ-distonic isomer (**6**) of ionized propanol always yields only one major product, an ion of m/z 42 due to loss of H_2O (Scheme III; Figure 4b). In the triple-quadrupole mass spectrometer, minor fragments were also observed at the following m/z values 45 (–CH_3), 41 (–H, –H_2O), 31 (–C_2H_5), and 27 (–CH_3, –H_2O). For ionized propanol (**5**), fragments formed by α-cleavages of $CH_3CH_2^•$ (m/z

Collisional Activation of Distonic Radical Cations
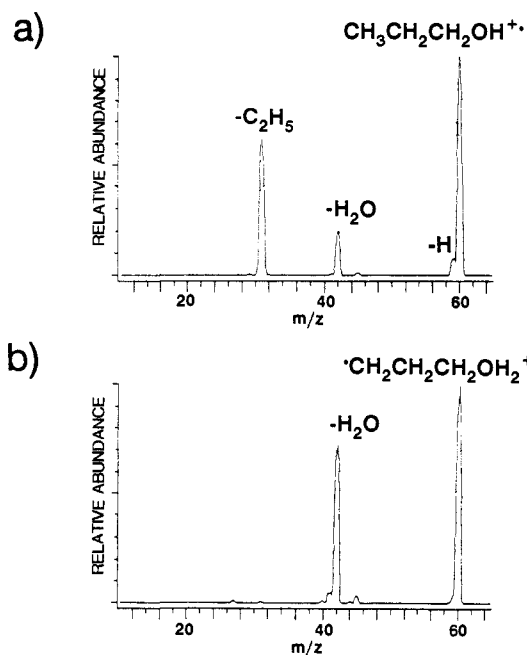
J. Am. Chem. Soc., Vol. 112, No. 13, 1990 5113

Figure 4. Collision-activated dissociation spectra of (a) ionized propanol and (b) its γ-distonic isomer. The spectra were obtained on the triple-quadrupole instrument at a laboratory collision energy of 10 eV with 0.3 mTorr Ar (multiple-collision conditions).
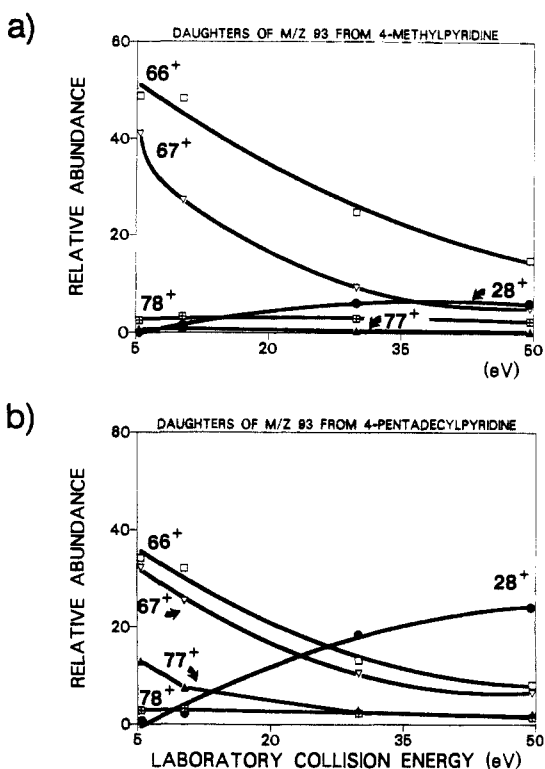

Figure 5. Collision-activated dissociation spectra plotted as a function of laboratory collision energy for (a) ionized 4-methylpyridine (m/z 93) and (b) the m/z 93 ion produced by fast-atom bombardment of 4-pentadecylpyridine. The data were obtained on the triple-quadrupole instrument with 0.5 mTorr Ar (multiple-collision conditions).

Figure 6. Collision-activated dissociation spectra of (a, c) ionized 4-methylpyridine (m/z 93) and (b, d) the ion of m/z 93 produced by fast-atom bombardment of 4-pentadecylpyridine. The data were obtained on the triple-quadrupole instrument at laboratory collision energies of (a, b) 5 eV and (c, d) 50 eV with 0.5 mTorr Ar (multiple-collision conditions).

Scheme III

31) and H⁺ (m/z 59), and by a rearrangement reaction leading to loss of H_2O (m/z 42), dominate the spectra obtained in the triple quadrupole (Figure 4a). Other minor fragments observed include the ions of m/z 45 (-CH_3), 29 (-CH_2OH), and 19 (H_3O^+). The product distributions obtained in the triple-quadrupole instrument for the $C_3H_8O^{•+}$ isomers under single-collision conditions were similar to those obtained under multiple-collision conditions at low collision energies. In the quadrupole ion trap, ionized *n*-propanol and its γ-distonic isomer give only one colli-
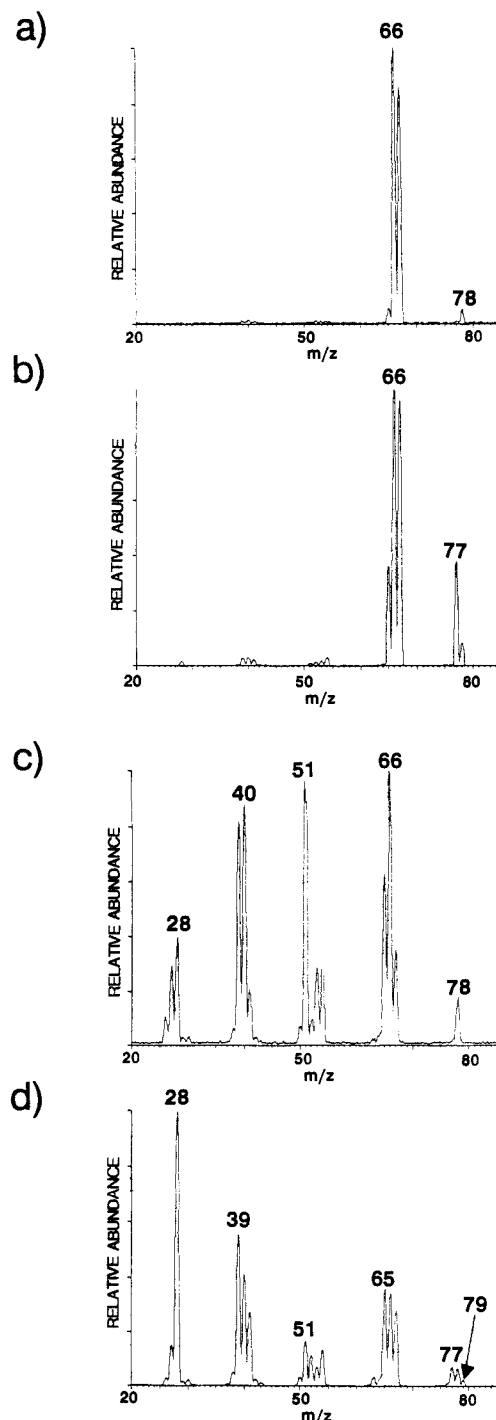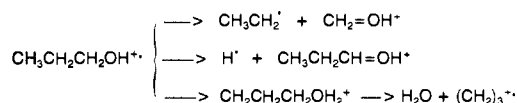
sion-activated dissociation product, the ion of m/z 42 (-H_2O).

$C_6H_7N^{•+}$ Ions. An ion of m/z 93 that may have the structure 8 (Scheme I) was generated by fast-atom bombardment of 4-

Table I. Literature Data Used To Construct the Potential Energy Surfaces of Figures 7-9[a]

reaction	IE/AE, eV	ΔHf[e] kcal/mol		
		reactant	ionic product	neutral product
$CH_3OH \rightarrow CH_3OH^{\bullet+}$	10.85[b]	-48.2	202.0	
$CH_3OH^{\bullet+} \rightarrow CH_2OH^{\bullet+} + H$	11.66[a]	202.0	168	52.10
$CH_3OH^{\bullet+} \rightarrow CH_2O^{\bullet+} + H_2$	12.45[a]	202.0	224.8	0
$CH_3OH^{\bullet+} \rightarrow CH_3^+ + OH$	13.5[a]	202.0	261.3	9.3
$CH_3OH^{\bullet+} \rightarrow CH_2^{\bullet+} + H_2O$	15.3[a]	202.0	331	-57.80
$^\bullet CH_2OH_2^+ \rightarrow CH_3OH^{\bullet+}$		195	202.0	
$^\bullet CH_2OH_2^+ \rightarrow CH_2{=}OH^+ + H$		195	168	52.10
$^\bullet CH_2OH_2^+ \rightarrow CH_2^{\bullet+} + H_2O$		195	331	-57.80
$CH_3CH_2OH \rightarrow CH_3CH_2OH^{\bullet+}$	10.47[b]	-56.1	185.3	
$CH_3CH_2OH^{\bullet+} \rightarrow CH_3CH{=}OH^+ + H$	10.78[a]	185.3	139	52.10
$CH_3CH_2OH^{\bullet+} \rightarrow CH_2{=}OH^+ + CH_3$	11.25[a]	185.3	168	34.8
$CH_3CH_2OH^{\bullet+} \rightarrow CH_2{=}CH_2^{\bullet+} + H_2O$	12.0[a]	185.3	254.8	-57.80
$^\bullet CH_2CH_2OH_2^+ \rightarrow CH_3CH_2OH^{\bullet+}$		175	185.3	
$^\bullet CH_2CH_2OH_2^+ \rightarrow {}^+H_2OCH_2CH_2^\bullet$		175	175	(Barrier 2-3 kcal/mol)[f]
$^\bullet CH_2CH_2OH_2^+ \rightarrow CH_2{=}CH\,H{-}OH_2^+$		175	186[e]	
$^\bullet CH_2CH_2OH_2^+ \rightarrow CH_2{=}CH_2^{\bullet+} + H_2O$		175	254.8	-57.80
$CH_3CH_2CH_2OH \rightarrow CH_3CH_2CH_2OH^{\bullet+}$	10.22[b]	-60.9	175	
$CH_3CH_2CH_2OH^{\bullet+} \rightarrow CH_3CH_2CH{=}OH^+ + H$	10.71[b]	175	131	52.10
$CH_3CH_2CH_2OH^{\bullet+} \rightarrow CH_2{=}OH^+ + C_2H_5$	11.16[c]	175	168	28
$CH_3CH_2CH_2OH^{\bullet+} \rightarrow$ [protonated oxirane, ^+OH/$CH_2{-}CH_2$] $+ CH_3$	11.35[c]	175	165	34.8
$CH_3CH_2CH_2OH^{\bullet+} \rightarrow$ [cyclopropane radical cation, $CH_2^{+\bullet}$/$CH_2{-}CH_2$] $+ H_2O$	10.56[d]	175	240	-57.80
$HO(CH_2)_4OH \rightarrow {}^\bullet CH_2CH_2CH_2OH_2^+ + CH_2O$	10.7[d]			
$^\bullet CH_2CH_2CH_2OH_2^+ \rightarrow CH_3CH_2CH_2OH^{\bullet+}$		171	175	
$^\bullet CH_2CH_2CH_2OH_2^+ \rightarrow$ [cyclopropane radical cation, $CH_2^{+\bullet}$/$CH_2{-}CH_2$] $+ H_2O$	11.1[d]	171	240	-57.80

[a-d] Values for ionization energies (IE) and appearance energies (AE) are from (a) ref 30, (b) ref 31, (c) ref 32, and (d) ref 22a. The value (AE - IE) was used for fragmentation thresholds for the conventional isomers. For each group of reactions, the neutral molecule for which the appearance energies were determined is presented in the first entry. Plausible structures were assumed for all fragment ions and relative enthalpies were calculated based on these structures, although the structures have not been experimentally proven in all cases.

[e] Values for enthalpies of formation (298 K) are from ref 31.
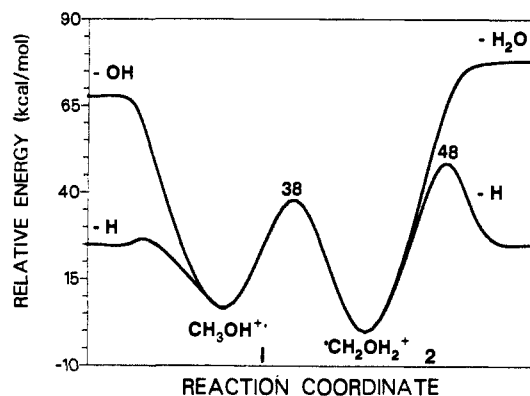
[f] From ref 22c.

Figure 7. The potential energy profile of ionized methanol and its α-distonic isomer. All values are relative to the heat of formation of the distonic ion which has been set to zero. The isomerization barrier of 38 kcal/mol and the dissociation barrier of 48 kcal/mol are from ref 9.
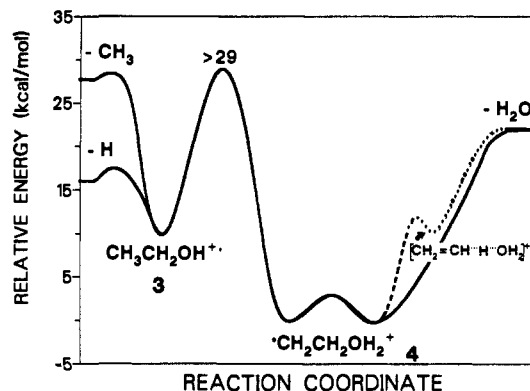

Figure 8. The potential energy profile for ionized ethanol and its β-distonic isomer. All values are relative to the heat of formation of the distonic ion which has been set to zero.

pentadecylpyridine. This ion fragments upon collisional activation to give a spectrum that is distinct from that obtained for ionized 4-methylpyridine (7) (Figures 5 and 6). The most significant differences include the relative abundances of the fragment ions of m/z 77 and 78. The ion generated from 4-pentadecylpyridine produces, at low energies, an abundant ion of m/z 77 (loss of CH₄ or NH₂; Figure 6b) and a smaller amount of an ion of m/z 78 (-CH₃), whereas ionized 4-methylpyridine produces only a small amount of the ion of m/z 77 (Figure 6a). At higher energies (Figure 6d), the ion of m/z 93 generated from 4-pentadecylpyridine fragments by loss of 14 amu (-CH₂) to produce a fragment ion of m/z 79 that is never observed for ionized 4-

methylpyridine. The pyridine isomers were not examined in the ion trap.

Discussion

Isomerization and Fragmentation Reactions. The data obtained for the $C_nH_{2n+2}O^{\bullet+}$ isomers are discussed by reference to potential energy surfaces associated with each system (Figures 7-9). These surfaces are based on literature data and results presented here. The literature data used are summarized in Table I.

Earlier work[8,9,22] has demonstrated convincingly that a significant barrier separates ionized methanol (1) and its distonic form (2) (Figure 7). As expected, low-energy collisional activation of these ions in the triple-quadrupole instrument results in quite
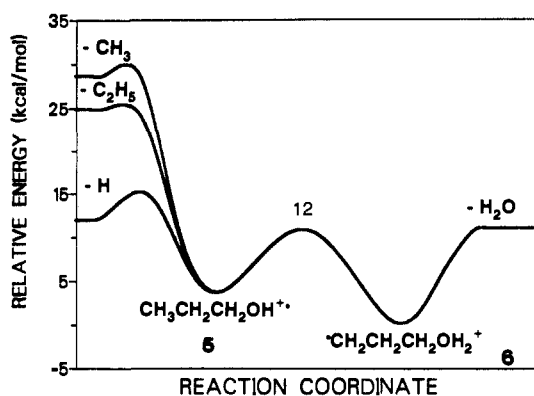
Collisional Activation of Distonic Radical Cations

J. Am. Chem. Soc., Vol. 112, No. 13, 1990 5115

Figure 9. The potential energy profile for ionized 1-propanol and its γ-distonic isomer. All values are relative to the heat of formation of the distonic ion which has been set to zero.

different fragmentation products. However, no dissociation reactions were observed in the quadrupole ion trap. This finding will be discussed later in this paper.

Low-energy collisional activation of ionized ethanol (3) and its β-distonic isomer (4) was found to produce qualitatively different dissociation products under all experimental conditions employed (Figures 2 and 3). We conclude that the barrier for isomerization of ionized ethanol to the β-distonic structure must be above the dissociation threshold to the abundant fragment $CH_2=OH^+$ (29 kcal/mol; Figure 8). It should be noted here that a degenerate 1,2-shift of water in the β-distonic ion has earlier been estimated[22c] to require only 2–3 kcal/mol. Moreover, above 10.8 kcal/mol, the distonic ion changes its structure to a hydrogen-bridged ethene–water complex, $CH_2=CH\cdots H\cdots OH_2^{\bullet+}$, in which the H_2O dipole can move around the ethene ion.[22c] This structure is probably the origin of the fragments H_3O^+ (m/z 19) and $CH_2=CH^+$ (m/z 27) formed approximately in the ratio 1:1 at higher excitation energies. It is possible that ionized ethanol, when highly excited, also can fragment via the hydrogen-bridged ethene–water structure since it produces the fragment ions of m/z 19 and 27 in a ratio 1:1 under certain conditions. According to appearance energy measurements,[30] formation of $CH_2=CH^+$ requires more than 98 kcal/mol for ionized ethanol. Accordingly, the ions 27$^+$ and 19$^+$ appear at relatively high collision energies (>15 eV, laboratory frame) where internal energies over 98 kcal/mol can be deposited in the ions;[33] upon a 15-eV collision (laboratory frame) of ionized ethanol with argon, the maximum available ion internal energy (i.e., center-of-mass collision energy, E_{com}) is about 160 kcal/mol.[2,3] It is conceivable that loss of H_2O from ionized ethanol also occurs from a hydrogen-bridged ethene–water complex.

The lowest energy reaction for both isomeric $C_3H_8O^{\bullet+}$ ions is loss of H_2O. Fragmentation of ionized propanol by loss of H_2O apparently occurs[22a] by a specific 1,3-elimination via the more stable γ-distonic structure and requires about 8 kcal/mol (Figure 9).[22a,30] Thus, isomerization of the stable γ-distonic ion to ionized propanol does not require more than 12 kcal/mol.

Our results support the earlier suggestion[22b] that isomerization of the γ-distonic ion to ionized propanol does not take place to a significant extent: only negligible amounts of $C_2H_5^{\bullet}$ loss and $H^{\bullet}$ loss were observed from the distonic ion under any conditions, while these reactions occur readily for ionized propanol (Figure 4). Energetic considerations alone would not explain why the distonic ion strongly favors fragmentation over isomerization (Figure 9). This preference may be explained on the basis of the relative rates of the reactions. Fragmentation of the γ-distonic

ion by loss of H_2O has been earlier suggested[22a] to lead to ionized cyclopropane. This reaction would be entropically more favorable than isomerization, which involves a five-membered transition state.[34] Furthermore, it is conceivable that some of the distonic ions lose H_2O in a fast direct bond cleavage. This reaction would initially lead to a distonic ion $^{\bullet}CH_2CH_2CH_2^+$ that would rapidly isomerize to the more stable $CH_3CH=CH_2^{\bullet+}$. These two isomeric ions, if generated from the γ-distonic ion of propanol, may not be in equilibrium with ionized cyclopropane because a high barrier separates ionized propene and ionized cyclopropane: an activation energy of 30–37 kcal/mol is needed[35] to isomerize ionized cyclopropane to ionized propene which is 11 kcal/mol more stable.[31] When energized, however, the $C_3H_6^{\bullet+}$ isomers are likely to interconvert rapidly prior to dissociation.[1,35] Thus, the observation[22b] that ionized cyclopropane and the dehydration product of the γ-distonic ion of ionized propanol give similar dissociation products does not necessarily mean that the structure of these ions *prior to* excitation was the same.

Collision-activated fragmentation of the $C_6H_7N^{\bullet+}$ ions indicates that at least two different stable isomeric structures exist: the ion of m/z 93, generated by loss of the elements of an alkene from 4-pentadecylpyridine during fast-atom bombardment, does not have the structure of ionized 4-methylpyridine. Low-energy collisional activation yields a very abundant fragment ion of m/z 28 (presumably protonated HCN; Figure 6d) for the ion generated from 4-pentadecylpyridine, which suggests that the fragmenting ion carries a proton on nitrogen. Further, the observation of loss of CH_2 from the ion generated from 4-pentadecylpyridine, but not from ionized 4-methylpyridine (Figure 6c,d), strongly supports the possibility that the unknown isomer has the distonic structure 8. The energy-resolved mass spectra (Figure 5) demonstrate that the differences in the fragmentation behavior are not the result of internal energy effects.

Collisional Activation under Different Experimental Conditions. Both the instruments employed in this study utilize rf-only quadrupoles as reaction chambers. These devices were operated with similar electric fields and under similar pressures. The differences expected for ionic decomposition reactions occurring in these instruments will arise from three major sources: (i) The instruments utilize different means to excite ions translationally. In a triple-quadrupole mass spectrometer, the ions are accelerated *before* they enter the reaction chamber (the center quadrupole). The collision energy is determined by the potential energy difference between the ion source and the reaction chamber.[2,3,14] However, in a quadrupole ion trap, the ions always remain in the same chamber, and they are continuously accelerated between collisions.[15,20] This experiment is characterized by an unknown distribution of collision energies. (ii) The collision gas commonly used in triple quadrupole mass spectrometers is argon,[2,3,17] while quadrupole ion traps typically utilize helium,[15] which is always present in the trap to improve the overall performance. (iii) The reaction time in the two instruments is somewhat different, being less than 100 μs for the triple quadrupole and several milliseconds for the ion trap in the experiments discussed here. Thus, ions will experience more collisions in the ion trap.[20]

The fact that the decomposition products obtained under multiple-collision conditions in the triple-quadrupole instrument were similar to those obtained under single-collision conditions, and that limited isomerization was indicated under either set of conditions, is quite remarkable. In fact, the product distributions obtained under multiple-collision conditions for the propanol ion and its γ-distonic isomer showed *more significant differences* than the products obtained under single-collision conditions. The most likely explanation for this observation is a larger amount of energy deposited in ions under multiple-collision conditions.[33] At higher excitation energies, slow rearrangement reactions cannot compete[1-3] efficiently with the fast direct bond cleavages that are structurally characteristic for the $C_3H_6O^{\bullet+}$ ions studied.

(30) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* 1977, *6*, Suppl. 1.

(31) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* 1988, *17*, Suppl. 1.

(32) Levin, R. D.; Lias, S. G. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.)* 1982, 71.

(33) Wysocki, V. H.; Kenttämaa, H. I.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Proc.* 1987, *75*, 181.

(34) See, for example: Winnik, M. A. *Chem. Rev.* 1981, *81*, 491.

(35) Lias, S. G.; Buckley, T. J. *Int. J. Mass Spectrom. Ion Proc.* 1984, *56*, 123.

Upon consideration of the results discussed above, it is perhaps surprising to note that ionized propanol and its γ-distonic isomer give identical fragmentation products in the quadrupole ion trap. Knowing that the ions do *not* isomerize extensively under multiple-collision conditions in the triple-quadrupole instrument, we conclude that the reason for the similar fragmentation patterns obtained in the quadrupole ion trap is the inability to excite the ions well above the fragmentation threshold (loss of H_2O). This conclusion is supported by the fact that *only the lowest energy products* were obtained in the quadrupole ion trap for all the ions studied. For example, the reactions leading to the most abundant collision-activated dissociation products for ionized ethanol, i.e., formation of $CH_3CH=OH^+$ and $CH_2=OH^+$, are known to be the lowest energy pathways for the ethanol ion (Figure 8).[30] The observation of no collision-activated dissociation for ionized methanol and its distonic form in the quadrupole ion trap indicates that 40 kcal/mol cannot be deposited in these ions in the experiment. In fact, only reactions requiring 30 kcal/mol or less were observed in the ion trap.

The limited amount of internal energy that can be deposited in the ions studied in the quadrupole ion trap may be explained by the fact that a very light collision target (helium) was used in these experiments, and each activating collision was therefore relatively inefficient.[17] Under these conditions, the ions are activated in a stepwise fashion wherein a small amount of energy is deposited in each successive collision.[7] The collisions occur in about 100-μs intervals. Thus, it is likely that an ion that has accumulated internal energy over the threshold for fragmentation will not survive until another activating collision before fragmentation. It follows that fragmentation reactions with higher energy requirements cannot compete with the lowest energy reactions, independent of the relative rates of these reactions.[36] Further, if the lowest energy reactions occur via the same intermediates for two isomeric ions, as is the case for ionized propanol and its γ-distonic isomer, the spectra obtained in the quadrupole ion trap will be identical.[37-39]

Conclusions

Ionized methanol, ethanol, and *n*-propanol fragment by loss of hydrogen and alkyl radicals yielding dominant *even-electron*

fragment ions upon low-energy collisional activation, while their α-, β-, and γ-distonic isomers, respectively, tend to lose even-electron species to give *odd-electron* ionic products. Note that a direct bond cleavage in a distonic ion results in an odd-electron fragment ion while for the conventional isomers, an even-electron ionic fragment is obtained. These results indicate that low-energy collision-activated dissociation under single- or multiple-collision conditions in a triple-quadrupole instrument can be used to distinguish ionized methanol, ethanol, and *n*-propanol from their α-, β-, and γ-distonic isomers, respectively. In fact, this approach seems to be superior to most earlier methods used to distinguish these isomer pairs since qualitatively different fragmentation products are obtained for each isomer.

In contrast to the triple-quadrupole instrument, data obtained with the quadrupole ion trap were not indicative of distinct structures in all cases. These results suggest that distinction of isomeric ions may be difficult with use of low-energy collisional activation with helium as the collision target as is often the case for quadrupole ion traps. Since the lowest energy fragmentations (activation energies below 30 kcal/mol for the ions studied here) dominate under the conditions employed here, rearrangement reactions may be preferred by ions with relatively long and flexible skeletons.

Comparison of the fragmentation product distributions obtained under different experimental conditions yielded information concerning the potential energy surfaces associated with isomerization and fragmentation of the $C_nH_{2n+2}O^{\bullet+}$ distonic ions and their conventional isomers. The isomerization barrier between ionized propanol and its γ-distonic isomer was found to be significantly lower than the barriers associated with the shorter chain analogues, which is consistent with theoretical[40] and experimental[23] results obtained recently for the nitrogen analogues.

This work provides the first direct evidence for the structure of a radical cation that may be a representative of a series of charge-remote fragmentation products formed by loss of alkyl radicals from even-electron ions.[26] It was demonstrated that an ion formed by loss of the elements of an alkene from 4-pentadecylpyridine during fast-atom bombardment is distinct from ionized 4-methylpyridine and shows fragmentation behavior characteristic of a distonic ion. Further work on structures of charge-remote fragmentation products is in progress.

(36) For a related experiment, see, for example: Thorne, L. R.; Beauchamp, J. L. In *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. 3, and references therein.

(37) There has been discussion for several years concerning the importance of the development of a standardized instrument independent collisional activation spectral library. An experimental protocol has recently been published that provides for the selection of key parameters to obviate mass discrimination effects against product ions in instruments of the type XQQ, where X is either a sector or a quadrupole mass analyzer, and QQ is a combined quadrupole collision chamber and quadrupole mass analyzer (see ref 38). The difference between the fragment ion spectra reported here, triple quadrupole vs quadrupole ion trap, suggest that a standardized collisional activation spectral library developed for a triple quadrupole instrument may not be useful for identifying unknowns from ion trap data.

(38) (a) Martinez, R. I. *Rapid Commun. Mass Spectrom.* **1988**, *2*, 8. (b) Martinez, R. I. *Res. Natl. Inst. Stand. Tech. (U.S.)* **1989**, *94*, 281.

(39) For discussion concerning the "effective temperatures" of ions in a quadrupole ion trap, see: Nourse, B. D.; Kenttämaa, H. I. *J. Phys. Chem.* In press.

(40) Yates, B. F.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 2910.

(41) Hardy, D. R.; Mushrush, G. W.; Stalick, W. M.; Beal, E. J.; Hazlett, R. N. *Rapid Commun. Mass Spectrom.* **1988**, *2*, 16.