

nanosecond. The recombination coefficient between trapped electrons and free holes was determined as  $3.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . At very low occupancy of the semiconductor particles by electron-hole pairs, their recombination becomes first order, the mean lifetime of a single electron-hole pair being 30 ns. Under these conditions hole trapping can compete with charge carrier recombination. In the trapped state, the hole is relatively unreactive toward electrons which survive in the particles for many microseconds.

These results elucidate earlier findings obtained from the study of interfacial electron transfer from colloidal  $\text{TiO}_2$  particles to acceptors such as methylviologen. In acid solution, the charge transfer occurred in the  $10^{-6}$  to  $10^{-3}$  s domain indicating the presence of long-lived electrons in the semiconductor particles, even in the absence of hole scavengers. Hole trapping by hydroxide groups at the particle surface (eq 13) leading to a product whose reaction with electrons is relatively slow provides a rationale for these observations.

With regard to the use of colloidal  $\text{TiO}_2$  as a photocatalyst for the light-induced cleavage of water, the fact that recombination of electrons with free holes is about 10 times faster than hole trapping is disadvantageous. This explains why highly active catalysts are required to accelerate the charge carrier reactions with water. We agree with the conclusion of Brown and Darwent that fast removal of holes from the  $\text{TiO}_2$  particle is particularly important to avoid recombination.<sup>28</sup> Catalysts such as  $\text{RuO}_2$  deposited onto the particle surface can serve this purpose since they act as hole transfer catalysts.<sup>1c,d</sup> Enhancement of hole transfer to water is likely to be the reason for the beneficial effect  $\text{RuO}_2$  exerts on the quantum yield of water decomposition.<sup>1a,24,25</sup>

Work is presently in progress to assess in which way the rate of charge carrier recombination and trapping is affected by external parameters such as pH and temperature as well as the internal structure and composition of the semiconductor particles. Preliminary studies show that the rate of electron-hole recombination can be drastically accelerated or retarded by doping the colloidal particles with suitable transition-metal ions. A report on these results is forthcoming.

#### Appendix

The generation term  $G_{x,y}(t)$  is the rate at which the probability  $P_{x,y}(t)$  changes as a result of the creation of electron-hole pairs

(24) Kawai, T.; Sakata, T. *Nature (London)* **1980**, *286*, 474.

(25) Blondeel, G.; Harriman, A.; Williams, D. *Solar Energy Mater.* **1983**, *9*, 217.

by the laser pulse.  $G_{x,y}(t)$  was calculated in the following way: suppose that at time  $t$  we have the probability distribution  $P_{x,y}(t)$ . During a time interval  $\Delta t$ , the laser pulse creates on the average  $\Delta n(t, \Delta t)$  pairs per particle, with

$$\frac{\Delta n(t, \Delta t)}{\Delta t} = \frac{\langle x \rangle_0}{(2\pi)^{1/2} \sigma} e^{-(t-t_0)^2/2\sigma^2} \quad (\text{A1})$$

Here, we have assumed that the temporal profile of the laser pulse is a Gaussian. The parameter  $\sigma$  is determined by recording the scatter of the laser pulse with a transient digitizer;  $\langle x \rangle_0$ , an adjustable parameter, is the average number of electron-hole pairs per particle that the laser pulse creates. The parameter  $t_0$  has to be chosen large enough so that an integration starting from time  $t = 0$  includes more than 99.9% of the area under the Gaussian.

According to eq 8, these  $\Delta n(t, \Delta t)$  pairs will be distributed over the particles according to a Poisson distribution

$$Q_{x,y}(t, \Delta t) = \delta_{x,y} \frac{(\Delta n(t, \Delta t))^x}{x!} e^{-\Delta n(t, \Delta t)} \quad (\text{A2})$$

where  $\delta_{x,y}$  implies that an equal number of electrons and holes are created.

The electron-hole distribution at time  $t + \Delta t$  will be the combination of the distribution  $P_{x,y}(t)$  describing the system at time  $t$  and of  $Q_{x,y}(t, \Delta t)$  which is the distribution of the pairs added to the system between  $t$  and  $t + \Delta t$ .

$$P_{x,y}(t + \Delta t) = \sum_{a=0}^x \sum_{b=0}^y P_{a,b}(t) Q_{x-a,y-b}(t, \Delta t) \quad (\text{A3})$$

Finally,  $G_{x,y}(t)$  is calculated by using the definition of a derivative:

$$G_{x,y}(t) = \lim_{\Delta t \rightarrow 0} \frac{P_{x,y}(t + \Delta t) - P_{x,y}(t)}{\Delta t} \quad (\text{A4})$$

In practice,  $\Delta t$  was chosen small enough so as to ensure a good accuracy on the numerical determination of  $G_{x,y}(t)$ .

**Acknowledgment.** This work was supported by the Swiss National Science Foundation and the Gas Research Institute, Chicago, IL (subcontract with the Solar Energy Research Institute, Golden, Colorado). N.S. thanks the Natural Sciences and Engineering Research Council of Canada for support. We enjoyed helpful discussions with Dr. P. P. Infelta during the course of this work.

## Distonic Oxonium and Ammonium Radical Cations. A Neutralization–Reionization and Collisional Activation Study

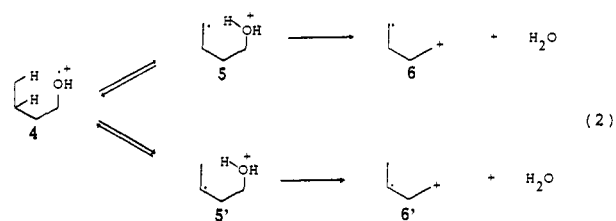
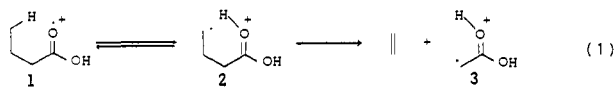
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**Abstract:** The distonic radical ions  $\cdot\text{CH}_2\text{CH}_2\text{X}^+\text{H}$ ,  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{X}^+\text{H}$ ,  $\cdot\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{X}^+\text{H}$ , and  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{X}^+\text{H}$ , where  $\text{X} = \text{OH}$  or  $\text{NH}_2$ , and their molecular ion counterparts  $\text{HRX}^+$  have been studied with isotopic labeling and mass spectra produced by neutralization–reionization (NR) and collisionally activated dissociation (CAD). The isomerization  $\text{HRX}^+ \rightarrow \cdot\text{RX}^+\text{H}$  is more exothermic for  $\text{X} = \text{OH}$ , but has a lower activation energy for  $\text{X} = \text{NH}_2$ . For this reaction a 1,5-hydrogen rearrangement is favored over 1,4-H, and the 1,3-H and 1,2-H rearrangements were not observed. NR spectra are particularly valuable for characterizing the distonic  $\cdot\text{RX}^+\text{H}$  ions, as neutralization produces an unstable hypervalent species. CAD spectra of larger  $\cdot\text{RX}^+\text{H}$  and  $\text{HRX}^+$  ions are very similar; activation of  $\cdot\text{RN}^+\text{H}_3$  mainly causes isomerization to  $\text{HRNH}_2^+$  which dissociates by  $\alpha$ -cleavage, the lowest energy pathway.

Removal of an electron from a gaseous molecule yields an odd-electron molecular ion whose charge and radical centers are

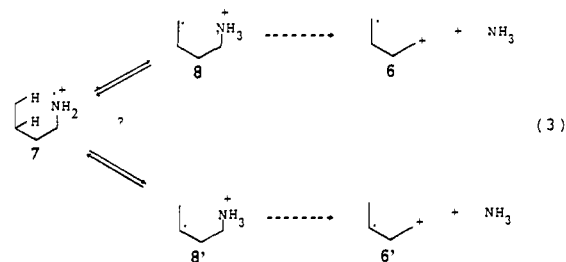
ostensibly at the same site, e.g., ionized butanoic acid (1) and 1-butanol (4). Distonic radical ions,<sup>1,2</sup> in which the radical and



charge sites are separated, are instead formed in secondary reactions. For many years distonic structures have been inferred as intermediates in isomerization ( $1 \rightarrow 2$ ,  $4 \rightarrow 5$ ), dissociation ( $2 \rightarrow 3$ ,  $5 \rightarrow 6$ ), and ion-molecule reactions, mainly based on isotopic labeling<sup>3</sup> and theory<sup>4</sup> (eq 1,<sup>3c,4a</sup> eq 2<sup>3a,h</sup>). Recently our understanding of these has been increased greatly by definitive ab initio theoretical studies<sup>1,5</sup> and direct experimental characterization<sup>6,7</sup> utilizing secondary mass spectra from collisionally activated dissociation (CAD).<sup>8</sup> Unsaturated distonic ions (e.g., **2**) have been the predominant type investigated with these techniques.<sup>6</sup> The saturated distonic radical ions characterized by CAD have been the ylide ions,<sup>7d</sup> such as  $\cdot\text{CH}_2\text{O}^+\text{H}_2$ ,<sup>5a,7b,c</sup> and  $\cdot\text{CH}_2\text{N}^+\text{H}_3$ ,<sup>7f</sup> and their homologues  $\cdot\text{CH}_2\text{CH}_2\text{O}^+\text{H}_2$  (**10**),<sup>5c,7a</sup>  $\cdot\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3$  (**13**),<sup>7f</sup>  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{O}^+\text{H}_2$  (**16**),<sup>7e</sup> and  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3$  (**18**).<sup>7g</sup>

This report describes a more extensive study of the  $\text{C}_2$ - $\text{C}_4$  saturated acyclic radical ions containing oxygen and nitrogen (Table I), including the relative stabilities of the normal and distonic forms and of the transition states for interconversion of these forms, such as eq 2. In this major fragmentation of **4**, typical of ionized primary alkanols,<sup>3e</sup> the rearranged hydrogen atom

originates 4:1 from the 4 and 3 positions.<sup>3a,h</sup> Although the corresponding loss of  $\text{NH}_3$  from ionized *n*-butylamine (**7**) (eq 3)



produces  $\text{C}_4\text{H}_8^+$  in only  $\sim 1\%$ , the abundance found from **4**, and theoretical calculations<sup>5d</sup> indicate  $7 \rightarrow 8$  to be unfavorable, deuterium scrambling gives evidence for the 1,5-H rearrangement  $7 \rightarrow 8$ <sup>3f,g</sup> analogous to that of the Hofmann-Löffler reaction.<sup>3f,9</sup> The possibility of such isomerization of normal and distonic ions can seriously compromise their structural differentiation using CAD mass spectra,<sup>8</sup> as collisional activation can induce this isomerization prior to dissociation.<sup>7g</sup> To avoid this these ionic structures are also investigated here with neutralization-reionization (NR)<sup>10</sup> mass spectra; neutralization<sup>11</sup> of the distonic form produces a hypervalent species, such as  $8 \rightarrow \cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3$ , which should dissociate before isomerization.

### Experimental Section

Measurements were made with a tandem mass spectrometer described previously,<sup>10a-c</sup> which contains a Hitachi RMH-2 double-focusing instrument as the first mass analyzer (MS-I) and an electrostatic sector as MS-II, using 70-eV electron ionization and 10-kV ion acceleration. For NR mass spectra<sup>10</sup> the ions exiting MS-I undergo charge-exchange neutralization<sup>11</sup> with mercury vapor (25 °C, 90–95% transmittance) or helium gas (50% transmittance); the remaining ions are deflected electrostatically, and the resulting fast neutrals are reionized by collision with a molecular beam of oxygen or other collision gas ( $\sim 50\%$  transmittance of neutrals); complete details are reported elsewhere.<sup>12</sup> Neutrals from 10-keV ions of mass 50 reach the collision region in  $\sim 10^{-6}$  s. Note that neutrals formed by CAD and metastable ion (MI) dissociation can also be collisionally ionized. A "Hg/O<sub>2</sub> NR" spectrum is one obtained with mercury neutralization and oxygen reionization. The relative values of total ion currents after neutralization and reionization (Table I) were determined the same day under the same experimental conditions; these values were used to calculate the isomeric ion compositions reported in the text. For normal CAD spectra ions exiting MS-I undergo collisions

(9) Wolff, M. E. *Chem. Rev.* **1963**, *63*, 55. Green, M. M.; Moldovan, J. M.; Armstrong, M. W.; Thompson, T. L.; Sprague, K. J.; Hass, A. J.; Artus, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 849.

(10) (a) Danis, P. O.; Wesdemiotis, C.; McLafferty, F. W. *J. Am. Chem. Soc.* **1983**, *105*, 7454. (b) McLafferty, F. W.; Todd, P. J.; McGilvery, D. C.; Baldwin, M. A. *Ibid.* **1980**, *102*, 3360. (c) Todd, P. J.; McGilvery, D. C.; Baldwin, M. A.; McLafferty, F. W. In ref 86, pp 271–286. (d) Clair, R.; Holmes, J. L.; Mommers, A. A.; Burgers, P. C. *Org. Mass Spectrom.* **1985**, *20*, 207–212.

(11) Gellene, G. I.; Porter, R. F. *Acc. Chem. Res.* **1983**, *16*, 200–207. Gellene, G. I.; Kleinrock, N. S.; Porter, R. F. *J. Chem. Phys.* **1983**, *78*, 1795–1800.

(12) Danis, P. O.; Feng, R.; McLafferty, F. W. *Anal. Chem.*, submitted for publication. Danis, P. O., Ph.D. Thesis, Cornell University, Aug 1985.

(13) (a) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. No. 1. (b) Lias, S. G.; Liebman, J. F.; Levin, R. D. *Ibid.* **1984**, *13*, 695. (c) Benson, S. W. "Thermochemical Kinetics"; Wiley-Interscience: New York, 1976. (d) Holmes, J. L.; Fingas, M.; Lossing, F. P. *Can. J. Chem.* **1981**, *59*, 80. (e) Krassig, R.; Reinke, H.; Braunnagel, H. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 425.

(14) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311. Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol 2, pp 1–51.

(15) Calculated from  $\Delta H_f^\circ(\text{CH}_2=\text{O}^+\text{H}) + \Delta H_f^\circ(\text{C}_2\text{H}_5) = 169^{13a} + 27^{13c} = 196 \text{ kcal mol}^{-1}$ , and  $\Delta H_f^\circ(\cdot\text{CH}_2\text{CH}_2\text{CH}_2^+) + \Delta H_f^\circ(\text{H}_2\text{O}) = 253 + (-58)^{13a} = 195 \text{ kcal mol}^{-1}$  if  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2^+$  is the water loss product, based on  $\Delta H_f^\circ(\cdot\text{CH}_2\text{CH}_2\text{CH}_2^+) = 253 \text{ kcal mol}^{-1}$ , estimated from  $\Delta H_f^\circ(\cdot\text{CH}_3\text{CH}_2\text{CH}_2^+) = 207 \text{ kcal mol}^{-1}$  by additivity.<sup>13c,d</sup> Formation instead of ionized cyclopropane ( $\Delta H_f^\circ(\cdot\text{C}_3\text{H}_6^+) = 241 \text{ kcal mol}^{-1}$ )<sup>13c</sup> during water loss is 12 kcal mol<sup>-1</sup> more favorable thermodynamically; even though the cyclization involved should require a substantial activation energy, this may be the threshold energy reaction, as metastable ion dissociation is mainly by H<sub>2</sub>O loss.<sup>7e</sup>

(16) Tajima, S.; Van der Greef, J.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1978**, *13*, 551.

(1) As proposed by: (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805. (b) Radom, L.; Bouma, W. J.; Nobes, R. H.; Yates, B. F. *Pure Appl. Chem.* **1984**, *56*, 1831.

(2) Radom et al.<sup>1b</sup> restrict the "distonic" definition to species which arise from neutral systems best written as zwitterions or ylides. We would extend this to include species such as **6** arising from diradicals.

(3) (a) Benz, W.; Biemann, K. *J. Am. Chem. Soc.* **1964**, *86*, 2375. (b) Gross, M. L.; McLafferty, F. W. *Ibid.* **1971**, *93*, 1267. (c) Smith, J. S.; McLafferty, F. W. *Org. Mass Spectrom.* **1971**, *5*, 483. (d) McLafferty, F. W. "Interpretation of Mass Spectra", 3rd ed.; University Science Books: Mill Valley, CA, 1980. (e) McLafferty, F. W. *Ibid.*, pp 51, 57, 68. (f) Hammerum, S. *Tetrahedron Lett.* **1981**, *22*, 157. Hammerum, S.; Christensen, J. B.; Egsgaard, H.; Larsen, E.; Derrick, P. J.; Donchi, K. F. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *47*, 351. (g) Audler, H. E.; Milliet, A.; Denhez, J. P. *Org. Mass Spectrom.* **1983**, *18*, 131; (h) Bukovits, G. J.; Budzikiewicz, H. *Ibid.* **1983**, *18*, 219.

(4) (a) Boer, F. P.; Shannon, T. W.; McLafferty, F. W. *J. Am. Chem. Soc.* **1968**, *90*, 7239. (b) Bouma, W. T.; Poppinger, D.; Radom, L. *Ibid.* **1977**, *99*, 6643.

(5) (a) Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2929. (b) Apeloig, V.; Ciommer, B.; Frenking, G.; Karni, M.; Mandelbaum, A.; Schwarz, H.; Weisz, A. *Ibid.* **1983**, *105*, 2186. (c) Bouma, W. J.; Nobes, R. H.; Radom, L. *Ibid.* **1983**, *105*, 1743. (d) Yamamoto, M.; Takenchi, T.; Nishimoto, K. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *46*, 239–242.

(6) (a) McAdoo, D. J.; McLafferty, F. W.; Parks, T. E. *J. Am. Chem. Soc.* **1972**, *94*, 1601. (b) Van de Sande, C. C.; McLafferty, F. W. *Ibid.* **1975**, *97*, 4613–4616. (c) Hemberger, P. H.; Kleingeld, J. C.; Levens, K.; Mainzer, N.; Mandelbaum, A.; Nibbering, N. M. M.; Schwarz, H.; Weber, R.; Weisz, A.; Wesdemiotis, C. *Ibid.* **1980**, *102*, 3736. (d) Vajda, J. H.; Harrison, A. G.; Hirota, A.; McLafferty, F. W. *Ibid.* **1981**, *103*, 36. (e) Wesdemiotis, C.; Feng, R.; McLafferty, F. W. *Ibid.* **1985**, *107*, 715.

(7) (a) Terlouw, J. K.; Heerma, W.; Dijkstra, G. *Org. Mass Spectrom.* **1981**, *16*, 326. (b) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2930. (c) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *Ibid.* **1982**, *104*, 2931. (d) Schwarz, H. *Mass Spectrosc. Tokyo* **1984**, *32*, 3. (e) Holmes, J. L.; Mommers, A. A.; Szulejko, J. E.; Terlouw, J. K. *J. Chem. Soc., Chem. Commun.* **1984**, 165. (f) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *Can. J. Chem.* **1983**, *61*, 2305. (g) Hammerum, S.; Kuck, D.; Derrick, P. J. *Tetrahedron Lett.* **1984**, *25*, 893–896.

(8) (a) McLafferty, F. W.; Bente, P. F., III; Kornfield, R.; Tsai, S. -C.; Howe, I. *J. Am. Chem. Soc.* **1973**, *95*, 2120. (b) Zwinselman, J. J.; Nibbering, N. M. M.; Ciommer, B.; Schwarz, H. In "Tandem Mass Spectrometry"; McLafferty, F. W., Ed.; Wiley: New York, 1983; pp 67–104.

Table I. Thermochemical Data and Neutralization-Reionization Efficiencies for Radical Ions Studied

conventional radical ion	$\Delta H_f^\circ$ <sup>a</sup>	$\Sigma[I^+]^b$	distonic radical ion	$\Delta H_f^\circ$ <sup>c</sup>	$\Sigma[I^+]^b$	$\Delta H_f^\circ$ (products) <sup>d</sup>	
						$\alpha$ -cleavage <sup>e</sup>	H <sub>2</sub> O or NH <sub>3</sub> loss
CH <sub>3</sub> CH <sub>2</sub> OH <sup>+</sup> (9)	185	0.035	·CH <sub>2</sub> CH <sub>2</sub> O <sup>+</sup> H <sub>2</sub> (10)	168	0.008	203	197
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH <sup>+</sup> (15)	173	0.022	·CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> O <sup>+</sup> H <sub>2</sub> (16)	159	0.011	196	195 (183) <sup>f</sup>
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OH <sup>+</sup> (19) <sup>g</sup>	165		·CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> O <sup>+</sup> H <sub>2</sub> (20)	153		185 <sup>h</sup>	186 (166)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH <sup>+</sup> (4)	166		·CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> O <sup>+</sup> H <sub>2</sub> (5)	155		190	188 (180)
			·CH(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> O <sup>+</sup> H <sub>2</sub> (5')	152			184 (166)
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> <sup>+</sup> (12)	193	0.036	·CH <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> H <sub>3</sub> (13) <sup>i</sup>	184	0.014	212	244
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup> (17)	186	0.019	·CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> N <sup>+</sup> H <sub>3</sub> (18)	178	0.010	205	242 (230)
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> NH <sub>2</sub> <sup>+</sup> (21)	177		·CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> N <sup>+</sup> H <sub>3</sub> (22)	169		196	233 (213)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> <sup>+</sup> (7)	179		·CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> N <sup>+</sup> H <sub>3</sub> (8)	172		199	235 (227)
			·CH(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>2</sub> N <sup>+</sup> H <sub>3</sub> (8')	169			231 (213)

<sup>a</sup>  $\Delta H_f^\circ$ <sub>298</sub> values in kcal mol<sup>-1</sup> and from ref 13 unless otherwise noted. <sup>b</sup> Total ion abundance from neutralization and reionization in percent of the transmitted precursor ion abundance. <sup>c</sup> Calculated from eq 4.<sup>13,14</sup> <sup>d</sup> Major dissociation products. <sup>e</sup> R-CH<sub>2</sub>-X<sup>+</sup> → R· + CH<sub>2</sub>=X<sup>+</sup> (X = OH, NH<sub>2</sub>). <sup>f</sup> The value represents formation of the acyclic ion structure directly from the corresponding distonic ion (eq 2, 3); the value in parentheses represents formation of the cyclized product ion.<sup>15</sup> <sup>g</sup> A major dissociation path for 19 for EI and CAD spectra is CH<sub>3</sub>O<sup>+</sup>H<sub>2</sub> formation by allyl loss ( $\Delta H_f^\circ$  (products) = 177 kcal mol<sup>-1</sup>).<sup>16</sup> <sup>h</sup> The  $\alpha$ -cleavage products of 19 are (CH<sub>3</sub>)<sub>2</sub>CH<sup>+</sup> + ·CH<sub>2</sub>OH (Stevenson's rule).<sup>3d</sup> <sup>i</sup> Base peak in the CAD spectrum of 13 is N<sup>+</sup>H<sub>4</sub> formed by C<sub>2</sub>H<sub>3</sub>· elimination;  $\Delta H_f^\circ$  (products) = 218 kcal mol<sup>-1</sup>.<sup>7f</sup>

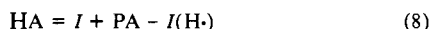
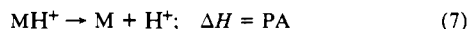
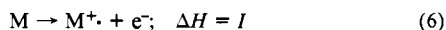
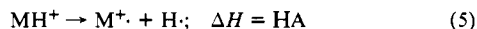
with a molecular beam of helium (the same beam location used for O<sub>2</sub> reionization with NR spectra) whose pressure is adjusted to give 50% ion transmittance. CAD spectra using mercury (which also include MI products) were measured as described for NR spectra, but without ion deflection and neutral reionization.

O-*d* and N-*d*<sub>2</sub> samples were prepared via in situ H/D exchange in the ion source with D<sub>2</sub>O. *n*-Butylamine-*l,l-d*<sub>2</sub> was synthesized via LiAlD<sub>4</sub> reduction of butyramide.

**Thermochemistry.** Values (Table I) for heats of formation of the conventional radical ions were taken from the literature<sup>13</sup> while those of the distonic radical ions were calculated via

$$\Delta H_f^\circ(\text{distonic}) = \Delta H_f^\circ(\text{molecular}) - \text{HA}(\text{molecular}) + D(\text{R-H}) \quad (4)$$

where HA is the hydrogen affinity of the molecular radical ion and  $D(\text{R-H})$  is the C-H bond dissociation energy of the transferred hydrogen atom.<sup>13</sup> HA values were calculated by the method of Bowers and co-workers,<sup>14</sup> utilizing eq 5-8, where  $I$  is the ionization energy of M, and PA its proton affinity.<sup>13</sup>



## Results and Discussion

As found for other distonic radical ions,<sup>5,7</sup> those of Table I are of lower energy than their corresponding normal ions. This arises<sup>1b,14</sup> from the fact that the hydrogen affinities of ionized alcohols and primary amines are greater than the C-H bond dissociation energies of the transferred hydrogen atom (eq 4). However, these relative exothermicities of isomerization are greater for the oxygen (11-17 kcal mol<sup>-1</sup>) than for the nitrogen (7-10 kcal mol<sup>-1</sup>)<sup>17</sup> species, in contrast to the conclusion<sup>3e</sup> that reactions involving radical sites on nitrogen (e.g., 7 → 8) are favored over those on oxygen (e.g., 4 → 5). The loss of H<sub>2</sub>O from the distonic oxonium ions requires 28-31 kcal mol<sup>-1</sup> less than the loss of NH<sub>3</sub> from the corresponding ammonium ions, consistent with the conclusion that reactions involving charge sites on oxygen (e.g., 5 → 6) are favored over those on nitrogen (e.g., 8 → 6).<sup>3d,e</sup>

**C<sub>2</sub>H<sub>6</sub>O<sup>+</sup> Isomers.** Confirming the report of Terlouw et al.,<sup>7a</sup> our CAD (helium) mass spectra (not shown) of ionized ethanol (9) and of the distonic ethene oxonium ion (10) (formed by CH<sub>2</sub>O loss from ionized 1,3-propanediol) demonstrate that 9 and 10 are distinct, stable ionic species. The dominant  $\alpha$  cleavage of 9 to form CH<sub>2</sub>=OH<sup>+</sup> shows that <1% of this isomer accompanies the formation of 10.<sup>7a</sup> Similarly, the dominant CAD H<sub>2</sub>O loss forming C<sub>2</sub>H<sub>4</sub><sup>+</sup> from 10 shows that <5% of ionized ethanol has undergone isomerization to 10 before CAD. The neutralization-reionization (NR)<sup>10</sup> mass spectra of 9 and 10 (Figure 1A,B) extend these

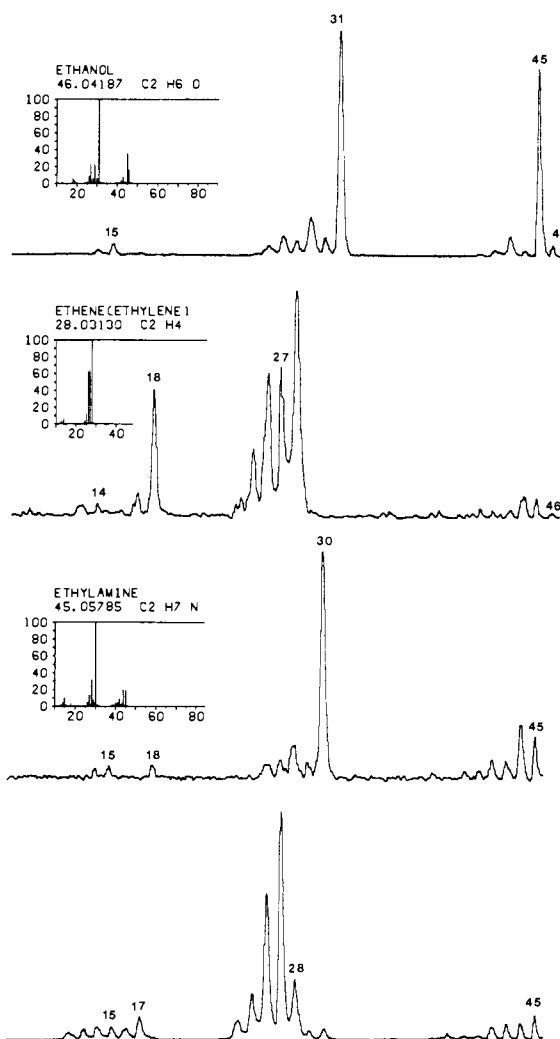


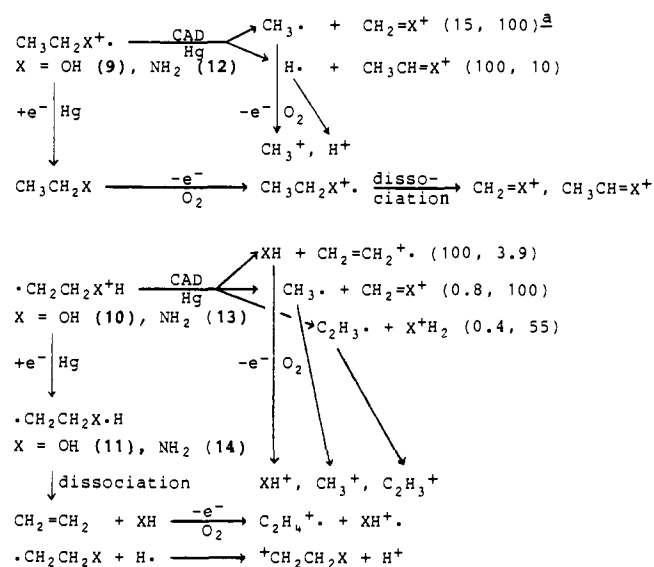
Figure 1. Hg/O<sub>2</sub> NR mass spectra of, top to bottom: (A) ionized ethanol, 9; (B) ·CH<sub>2</sub>CH<sub>2</sub>O<sup>+</sup>H<sub>2</sub>, 10; (C) ionized ethylamine, 12; and (D) ·CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>H<sub>3</sub>, 13. Inserted are EI mass spectra as labeled.

conclusions, confirming that <3% of ionized ethanol has undergone isomerization to 10 before NR, but demonstrating a <0.5% value for 10 → 9. Thus the exothermic isomerization 9 → 10 requires >12 kcal mol<sup>-1</sup> (Table I).

As observed in similar cases,<sup>10a,d,12</sup> the neutralization and reionization of C<sub>2</sub>H<sub>5</sub>OH<sup>+</sup> produces a NR mass spectrum (Figure 1A) which is closely similar to the 70-eV electron ionization (EI) mass spectrum<sup>18</sup> of ethanol, having large peaks at  $m/z$  31 and

(17) MP2/6-31G\* calculations by Radom<sup>1b</sup> show the same energy differences for 12/13, 17/18, and 7/8.

Scheme 1



<sup>a</sup> Relative abundances, percent, for X = OH and NH<sub>2</sub>, respectively.

45 and smaller ones at 27, 29, 43, and 46. Interaction of the 9 ions with the Hg target also causes their collisional activation; direct measurement (CAD/Hg data, Scheme I, measured by omitting both ion deflection and reionization) indicates that CH<sub>3</sub>· and H· are the main neutral products formed by CAD. Their reionization has little effect<sup>19</sup> on the NR spectrum of 9 (Figure 1A, H<sup>+</sup> not measured); this shows a 4% peak at mass 15, part of which could arise from the reionization of C<sub>2</sub>H<sub>5</sub>OH. Similarly, the main peaks in the NR mass spectrum of the distonic radical ion 10 are consistent with the products from the exothermic dissociation of ·CH<sub>2</sub>CH<sub>2</sub>O·H<sub>2</sub>, 11 (Scheme I,  $\Sigma\Delta H_f^\circ = -46$  kcal mol<sup>-1</sup>),<sup>13a</sup> matching the EI mass spectra of water and ethene as well as the NR mass spectra (not shown) of H<sub>2</sub>O<sup>+</sup> and CH<sub>2</sub>=CH<sub>2</sub><sup>+</sup> obtained separately. The minor peaks at masses 45 and 44 in the NR spectrum of 10 could be formed from reionization of undissociated ·CH<sub>2</sub>CH<sub>2</sub>O·H<sub>2</sub>,<sup>20</sup> or from its dissociation to ·CH<sub>2</sub>CH<sub>2</sub>OH + H· ( $\Sigma\Delta H_f^\circ = +42$  kcal mol<sup>-1</sup>).<sup>13</sup> The most favored CAD reaction with Hg (Scheme I, yielding C<sub>2</sub>H<sub>4</sub><sup>+</sup>) produces H<sub>2</sub>O, which should also contribute to *m/z* 17 and 18 in the NR spectrum.

**C<sub>2</sub>H<sub>7</sub>N<sup>+</sup> Isomers.** Confirming the report of Holmes and co-workers,<sup>7f</sup> CAD mass spectra of ionized ethylamine (12) and the distonic ethene ammonium ion (13, formed by CH<sub>2</sub>=NH loss from H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub><sup>+</sup>) are distinctly different, with base peaks corresponding to CH<sub>2</sub>=N<sup>+</sup>H<sub>2</sub> and H<sub>4</sub>N<sup>+</sup>, respectively (formed in part by metastable decomposition). The 2% relative abundance of H<sub>4</sub>N<sup>+</sup> in the CAD spectrum of 12 indicates that C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> ionization gives a negligible amount of the distonic form 13, and that upon collisional activation most 12 ions dissociate directly, not via 13. However, the CAD spectrum of 13 is less definitive, showing an upper limit of ~32% 12 based on the CH<sub>2</sub>=N<sup>+</sup>H<sub>2</sub> peak abundance. On the other hand, the NR mass spectra of 12 and 13 (Figure 1C,D) clearly show the absence of 12 in the 13 ions (<1% based on *m/z* 30) as well as of 13 in 12 (<7% based on *m/z* 17); thus the activation energy for 12 → 13 must be >19 kcal mol<sup>-1</sup> (Table I). Collisional activation of ·CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>H<sub>3</sub> (13) has produced the misleading CH<sub>2</sub>=N<sup>+</sup>H<sub>2</sub>

by causing the isomerization of 13 to 12. Neutralization of 13 yields the hypervalent ·CH<sub>2</sub>CH<sub>2</sub>N·H<sub>3</sub>, 14,<sup>20</sup> whose dissociation energy must be appreciably below its energy of isomerization to C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>, an obvious advantage of NR over CAD mass spectra for ion structure characterization.

Again the EI and NR spectra of C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub><sup>+</sup> (12) are strikingly similar (Figure 1C). CAD by Hg accompanying NR, which should produce mainly ·CH<sub>3</sub>, has had little effect on the NR spectrum, which shows only 4% CH<sub>3</sub><sup>+</sup>; in keeping with the previously observed<sup>12</sup> tendency for He to produce a much higher proportion of CAD vs. charge exchange than Hg produces, in the He/O<sub>2</sub> NR spectrum of 12 (not shown) the base peak represents CH<sub>3</sub><sup>+</sup>. The NR spectrum of ·CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>H<sub>3</sub> (13, Figure 1D) shows peaks at 45, 44, 28, and 17 corresponding to those from reionization of the expected (Scheme I) neutral molecule C<sub>2</sub>H<sub>7</sub>N and its dissociation products C<sub>2</sub>H<sub>6</sub>N, C<sub>2</sub>H<sub>4</sub>, and NH<sub>3</sub>; in the He/O<sub>2</sub>-NR spectrum of 13 their abundances (except [17<sup>+</sup>]) are substantially reduced, [45<sup>+</sup>] by more than an order of magnitude. However, the Hg (and He)/O<sub>2</sub> NR spectra of 13 are dominated by *m/z* 27 and 26, which would be expected from reionization of the C<sub>2</sub>H<sub>3</sub>· formed by CAD/Hg (Scheme I).<sup>21</sup> The *m/z* 27 of Figure 1D does not arise in major part from C<sub>2</sub>H<sub>6</sub>N (*m/z* 44); [27<sup>+</sup>]/[26<sup>+</sup>] = <0.5 in the NR spectra of CH<sub>3</sub>CH=N<sup>+</sup>H<sub>2</sub> and protonated ethylenimine. As found for similar species,<sup>22</sup> for the ammonium ion 13 the cross section for neutralization, relative to that for CAD, apparently is much lower than that for its molecular isomer 12 or the oxonium ion 10.

The NR mass spectra of the distonic radical ions 10 and 13 (Figure 1B,D) bear ions of the precursor masses *m/z* 46 (C<sub>2</sub>H<sub>6</sub>O<sup>+</sup>) and 45 (C<sub>2</sub>H<sub>7</sub>N<sup>+</sup>), respectively. These cannot be ionized ethanol or ethylamine because of the absence of intense α-cleavage fragments at *m/z* 31 (CH<sub>2</sub>=O<sup>+</sup>H) and 30 (CH<sub>2</sub>=N<sup>+</sup>H<sub>2</sub>), expected from Figure 1, parts A and C. These appear to be due to reionized ·CH<sub>2</sub>CH<sub>2</sub>O·H<sub>2</sub> and ·CH<sub>2</sub>CH<sub>2</sub>N·H<sub>3</sub> neutrals which survived the ~10<sup>-6</sup> s between neutralization and reionization. Further characterization of such hypervalent neutrals will be reported separately.<sup>20</sup>

**n-C<sub>3</sub>H<sub>8</sub>O<sup>+</sup> Isomers.** Holmes and co-workers<sup>7e</sup> have demonstrated that ·CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O<sup>+</sup>H<sub>2</sub> ions (16), formed by CH<sub>2</sub>O loss from HO(CH<sub>2</sub>)<sub>4</sub>OH<sup>+</sup>, contain little CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH<sup>+</sup> (15), as the CAD spectra of 16 and 15 show CH<sub>2</sub>=O<sup>+</sup>H abundances of 2.2 and 83%, respectively. However, the CAD spectrum of 16 has no characteristic peaks to define the upper limit of 16 formed in the ionization of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH; C<sub>3</sub>H<sub>6</sub><sup>+</sup> (H<sub>2</sub>O loss) is the base peak in both spectra. Fortunately, the NR spectra (Figure 2A,B) show a characteristic *m/z* 31 peak for 15, and *m/z* 18, 39, 41, and 42 peaks for 16, demonstrating that both 15 and 16 are formed with <5% of the other isomer (based on the abundances of *m/z* 18 and 31, respectively). Thus the isomerization 15 → 16 must require ~20 kcal mol<sup>-1</sup> (Table I).<sup>15,23</sup> This result is consistent with the fact that metastable CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OD<sup>+</sup> ions lose only HDO, and CD<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH<sup>+</sup> ions eliminate specifically (>98%) HDO in both the ion source<sup>25</sup> and the metastable time window,<sup>7e</sup> and with recent ab initio MO calculations of Nishimoto et al.<sup>25</sup> predicting an activation energy of 25 kcal mol<sup>-1</sup>. The NR spectrum of 15 is closely similar to the EI spectrum of 1-propanol;

(21) The Hg/O<sub>2</sub> NR spectrum of C<sub>2</sub>H<sub>3</sub><sup>+</sup> (from CH<sub>2</sub>=CHBr<sup>+</sup> of 6 keV, the kinetic energy of C<sub>2</sub>H<sub>3</sub><sup>+</sup> produced by CAD/Hg from 10-keV 13 ions) shows [27<sup>+</sup>]/[26<sup>+</sup>] = 0.7, vs. 1.5 in the NR spectrum of 13 (Figure 1D). The higher H loss in the NR spectrum of C<sub>2</sub>H<sub>3</sub><sup>+</sup> indicates that a substantial proportion of C<sub>2</sub>H<sub>3</sub><sup>+</sup> is formed with the more stable bridged structure; vertical neutralization would then produced excited ·C<sub>2</sub>H<sub>3</sub> (for which the open structure is more stable), leading to enhanced H loss.<sup>20</sup> This effect lowers the recombination energy for C<sub>2</sub>H<sub>3</sub><sup>+</sup>, lowering the neutralization cross section: Shields, G. C.; Wennberg, L.; Wilcox, J. B.; Moran, T. F., submitted for publication.

(22) Ions with no unfilled orbitals adjacent to the charge, such as R<sub>4</sub>N<sup>+</sup>, apparently have a much lower cross section for charge exchange vs. CAD.<sup>20</sup>

(23) The 1,2-hydrogen rearrangement required to form the even more stable CH<sub>2</sub>=CHCH<sub>3</sub><sup>+</sup> should have an activation energy comparable to that of its formation from cyclopropane<sup>+</sup> of ~40 kcal mol<sup>-1</sup>.<sup>24</sup>

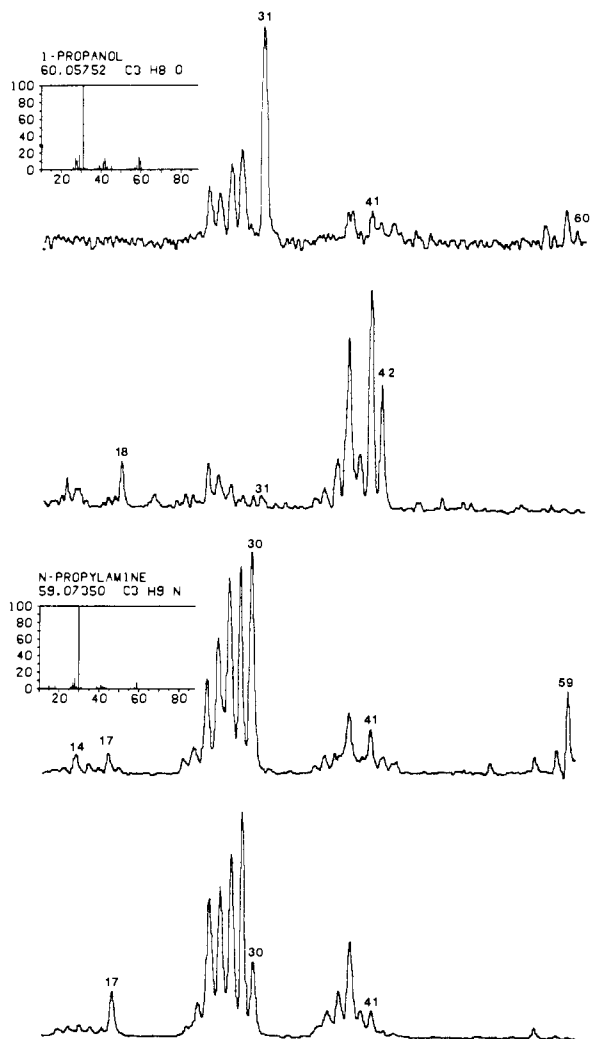
(24) McLafferty, F. W.; Barbalas, M. P.; Turecek, F. *J. Am. Chem. Soc.* **1983**, *105*, 1.

(25) Takeuchi, T.; Veno, S.; Yamamoto, M.; Matsushita, T.; Nishimoto, K. *Int. J. Mass Spectrom. Ion Phys.* **1985**, *64*, 33.

(18) Stenhagen, E.; Abrahamsson, S.; McLafferty, F. W. "Registry of Mass Spectral Data"; Wiley-Interscience: New York, 1974.

(19) The reionization and collection efficiency can be relatively poor for a small neutral formed from a large ion with a substantial release of kinetic energy. For the dissociation of CH<sub>3</sub>COCH<sub>3</sub><sup>+</sup>, this efficiency for CH<sub>3</sub>· is less than one-tenth that for CH<sub>3</sub>CO·: ref 12 and Todd, P. J., Ph.D. Thesis, Cornell University, May 1980.

(20) Wesdemiotis, C.; Danis, P. O.; Feng, R.; McLafferty, F. W., to be submitted for publication.



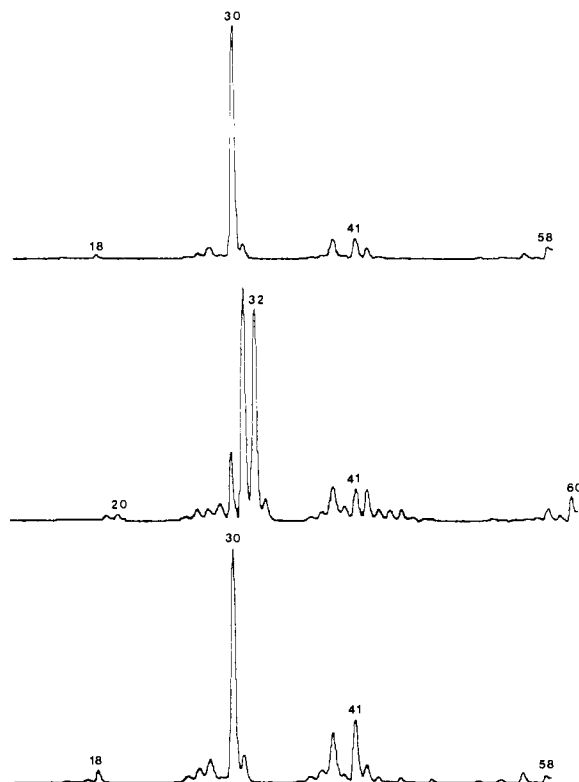
**Figure 2.** Hg/O<sub>2</sub> NR mass spectra of, top to bottom: (A) ionized 1-propanol, **15**; (B)  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{O}^+\text{H}_2$ , **16**; (C) ionized *n*-propylamine, **17**; and (D)  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3$ , **18**. Inserted are corresponding EI mass spectra.

$\cdot\text{C}_2\text{H}_5$ , a major neutral product expected by CAD/Hg, contributes to the  $m/z$  29 also formed by reionization of propanol. In the NR spectrum of **16** the major peaks at  $m/z$  18, 39, 41, and 42 correspond to those from reionization of the expected neutral products H<sub>2</sub>O and C<sub>3</sub>H<sub>6</sub>. CAD/Hg also can contribute to the H<sub>2</sub>O<sup>+</sup> NR peak.

***n*-C<sub>3</sub>H<sub>9</sub>N<sup>+</sup> Isomers.** The CAD spectra (Figure 3) of *n*-propylamine (**17**) and its distonic isomer **18**, prepared from H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub><sup>+</sup>, are quite similar, dominated by CH<sub>2</sub>=N<sup>+</sup>H<sub>2</sub>. This  $\alpha$ -cleavage pathway requires 37 kcal mol<sup>-1</sup> less than NH<sub>3</sub> loss (Table I), while  $\alpha$ -cleavage of **15/16** requires 1 kcal mol<sup>-1</sup> more than H<sub>2</sub>O loss.

In contrast, the NR spectra of **17** and **18** (Figure 2C,D) are distinctive for these isomers. The large abundance difference shown by these spectra for reionized propylamine ( $m/z$  59) demonstrates that the formation of **18** produces little (<2%) **17**. Neither NR nor CAD of **17** should produce NH<sub>3</sub><sup>+</sup>, by analogy to its EI spectrum and the behavior of C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub><sup>+</sup> (Figure 1C and Scheme I); under this assumption Figure 2C indicates that nearly 70% of the molecular **17** ions have isomerized to **18**. In confirmation, C(H,D)<sub>4</sub>N<sup>+</sup> ions in the CAD spectrum (Figure 3B) of CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>ND<sub>2</sub><sup>+</sup> (lifetimes before collision  $\sim 15$   $\mu$ s) indicate that 62%<sup>26</sup> of the molecular **17** ions undergo H/D exchange, presumably via **17**  $\rightleftharpoons$  **18**. Thus the majority of **17** ions formed

(26) As indicated by the NR and CAD spectra of *n*-C<sub>4</sub>H<sub>9</sub>OD, little of this scrambling occurs after collision (vide infra).



**Figure 3.** CAD mass spectra of, top to bottom: (A) ionized *n*-propylamine, **17**; (B) its N-*d*<sub>2</sub> isotopomer, and (C)  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3$ , **18**.

with internal energies of <19 kcal mol<sup>-1</sup> (the  $\alpha$ -cleavage barrier) isomerize to **18**, indicating that  $< \sim 9$  mol<sup>-1</sup> is required<sup>27</sup> for **17**  $\rightarrow$  **18**. This is in sharp contrast to the  $\sim 20$  kcal mol<sup>-1</sup> value for the more exothermic isomerization involving the oxygen analogues, **15**  $\rightarrow$  **16**.

As found for the homologous  $\cdot\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3$ ,<sup>22</sup> in the Hg/O<sub>2</sub>-NR spectrum of **18** charge exchange appears to be dominated by CAD. This gives mainly (Figure 3C) C<sub>2</sub>H<sub>5</sub><sup>+</sup> + CH<sub>2</sub>=N<sup>+</sup>H<sub>2</sub>; reionization of C<sub>2</sub>H<sub>5</sub><sup>+</sup> accounts for the abundant  $m/z$  26–29 peaks in Figure 2D. The neutralized **18** should dissociate into NH<sub>3</sub> and  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\cdot$ . Possibly the latter is more excited than that produced from **16**, accounting for peaks such as C<sub>3</sub>H<sub>5</sub><sup>+</sup> and C<sub>3</sub>H<sub>3</sub><sup>+</sup>. The intermediate formation of  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  could lead to the NR  $m/z$  30 peak.

**Isobutanol<sup>+</sup> (19) and Isobutylamine<sup>+</sup> (21).** Although the distonic forms  $\cdot\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{O}^+\text{H}_2$  (**20**) and  $\cdot\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{N}^+\text{H}_3$  (**22**) were not examined directly, CAD and NR spectra of **19** and **21** indicate (as found for **15** and **17**) that the 1,4-H rearrangement to nitrogen (**21**  $\rightarrow$  **22**) is more favorable than that to oxygen (**19**  $\rightarrow$  **20**).<sup>28</sup> In the CAD spectrum of (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>OH<sup>+</sup> (**19**) the products (CH<sub>3</sub>)<sub>2</sub>CH<sup>+</sup> and CH<sub>2</sub>=O<sup>+</sup>H arise directly from **19**, and CH<sub>3</sub>O<sup>+</sup>H<sub>2</sub><sup>16</sup> and C<sub>4</sub>H<sub>8</sub><sup>+</sup> come through rearrangement to **20**. However, the NR spectrum of **19** (Figure 4B) resembles the EI spectrum of isobutanol; by analogy to **16**, any **20** present should produce C<sub>4</sub>H<sub>8</sub><sup>+</sup>, which is small. The CAD contribution to the NR spectrum cannot be large; CAD/Hg peaks at  $m/z$  33, 43, and 56 predict NR contributions at  $m/z$  41,

(27) The 9-kcal mol<sup>-1</sup> value is based on the distribution of the internal energies of the molecular ions estimated from the corresponding photoelectron spectra: Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. "Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules"; Halsted Press: New York, 1981; pp 116–118. The actual value must be <9 kcal mol<sup>-1</sup> due to the kinetic shift, as demonstrated (vide infra) for **7**.

(28) The CAD spectrum of the -O-*d*<sub>1</sub> isotopomer of **19** shows that water loss proceeds only with minor H-exchange (<5%),<sup>16</sup> although almost complete H/D scrambling between the methyl and hydroxylic hydrogens takes place prior to allyl loss.<sup>16,29</sup>

(29) Nibbering, N. M. M. *Philos. Trans. R. Soc. London, A Ser.* **1979**, 293, 103. Bowen, R. D.; Williams, D. H. *J. Chem. Soc., Chem. Commun.* **1981**, 836.

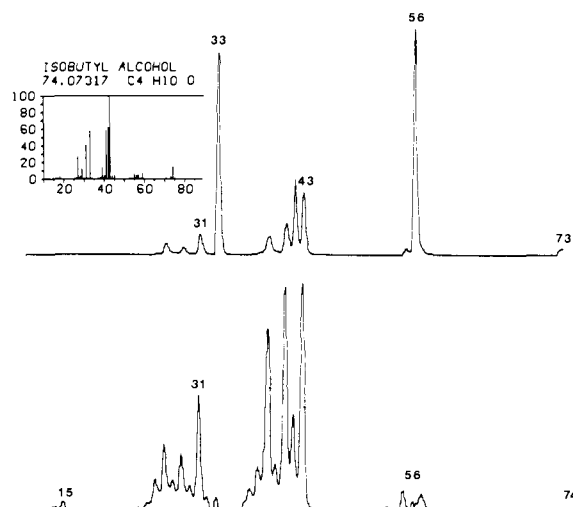


Figure 4. (A) CAD and EI (top), and (B) Hg/O<sub>2</sub> NR mass spectra (bottom) of ionized isobutanol, **19**.

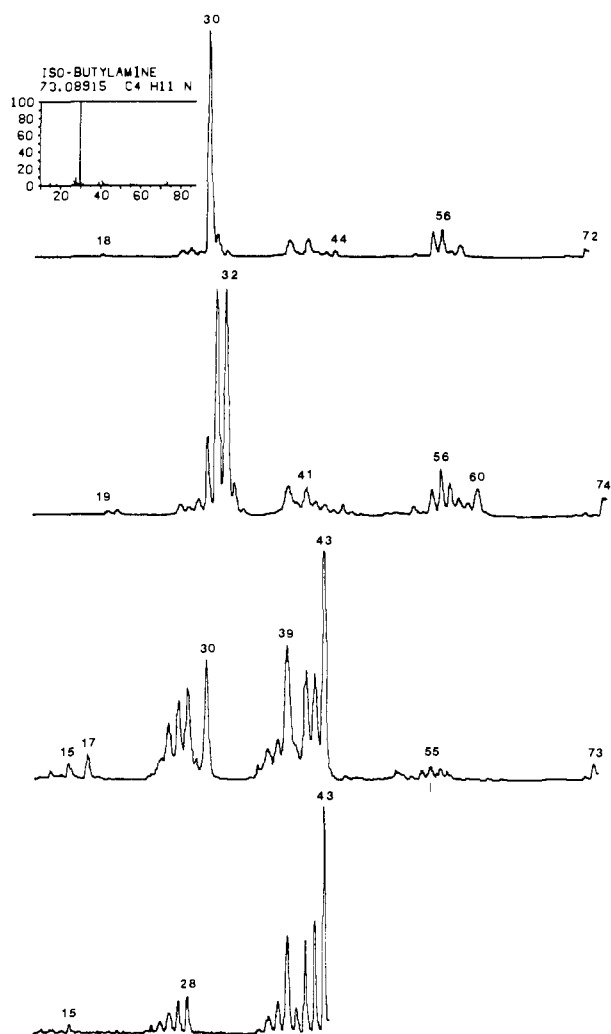


Figure 5. CAD mass spectra of, top to bottom: (A) ionized isobutylamine, **21** (EI mass spectrum inserted); and (B) its *N-d*<sub>2</sub> isotopomer. Hg/O<sub>2</sub> NR mass spectra of (C) **21** and of (D) *i*-C<sub>3</sub>H<sub>7</sub><sup>+</sup> ions.

31, and 18,<sup>19</sup> all of which would be expected also by reionization of isobutanol from its EI spectrum.

The CAD spectra of (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>NH<sub>2</sub><sup>+</sup> (**21**) and -ND<sub>2</sub><sup>+</sup> (Figure 5A,B) show clearly the occurrence of H/D exchange, presumably through **21** → **22**. The data are very similar to those for **17**, indicating that ~62%<sup>26</sup> of the nondecomposing (<19 kcal mol<sup>-1</sup> internal energy, Table I) molecular ions **21** are formed with

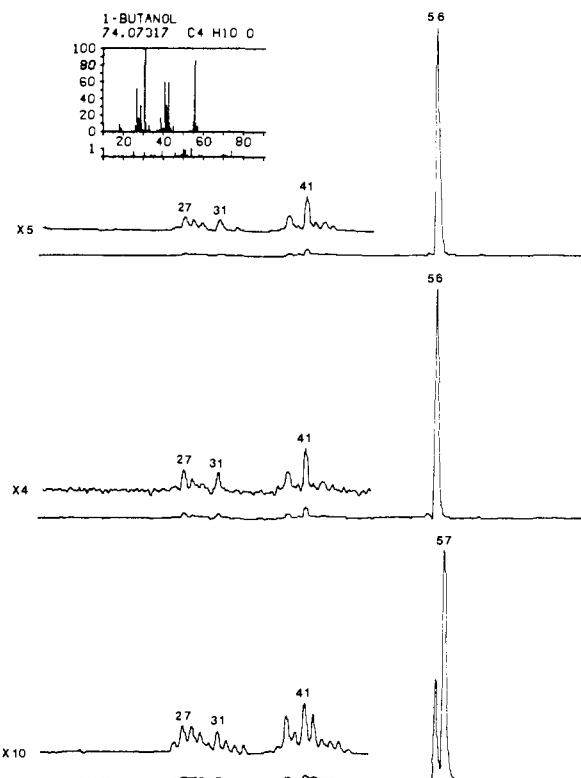


Figure 6. CAD mass spectra of, top to bottom: (A) ionized 1-butanol, **4**; (B) ·CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O<sup>+</sup>H<sub>2</sub>, **5**; and (C) ionized 1-butanol-*d*.

internal energies greater than the isomerization barrier, which thus is <~9 kcal mol<sup>-1</sup>.<sup>27</sup> The NR spectrum of **21** (Figure 5C) is dominated by peaks which resemble closely the NR spectrum of (CH<sub>3</sub>)<sub>2</sub>CH<sup>+</sup> (Figure 5D). This presumably arises from the reionization of (CH<sub>3</sub>)<sub>2</sub>CH· formed with CH<sub>2</sub>=N<sup>+</sup>H<sub>2</sub> in the dominant CAD/Hg reaction of both **21** and **22**. Analogous to **13** and **18**,<sup>22</sup> the cross section for charge exchange neutralization of **22** appears to be relatively low from the NR abundances corresponding to the expected products NH<sub>3</sub> and ·CH<sub>2</sub>CH-(CH<sub>3</sub>)CH<sub>2</sub>, although the latter may be excited and undergo extensive dissociation.

**1-Butanol<sup>+</sup> Isomers.** For ionized 1-butanol (**4**) and its distic isomer ·CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O<sup>+</sup>H<sub>2</sub> (**5**, formed by CH<sub>2</sub>O loss from HO(CH<sub>2</sub>)<sub>3</sub>OH<sup>+</sup>), both the CAD (Figure 6A,B) and NR (Figure 7A,B) spectra are very similar, suggesting facile isomerization. This is borne out by the CAD and NR spectra of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OD<sup>+</sup>, for which (-HDO)/(-H<sub>2</sub>O) = 0.62<sup>30</sup> and 0.6 ± 0.1, respectively (the latter shows that only a minor amount of scrambling occurs after collisional activation). This indicates that the scrambling is 1,4 as well as 1,5; complete equilibration of D with the three δ-H atoms would give a ratio of 1.0, while equilibration also with the two γ-H atoms would give 0.5. However, the *m/z* 74 molecular ion presence<sup>31</sup> in the NR spectrum of **4** (and of C<sub>4</sub>H<sub>9</sub>OD<sup>+</sup>) shows that the 1-butanol ionization yields a significant amount of **4** ions with insufficient energy to undergo this exothermic isomerization. The absence of *m/z* 74 in the NR spectrum of **5** confirms that the equilibrium **4** ⇌ **5** lies far to the right.

Thus the NR spectra of Figure 7A,B arise mainly from the distic isomers **5** and **5'**. Any CAD/Hg of these (Scheme II) would give predominantly H<sub>2</sub>O neutrals whose reionization would contribute to *m/z* 18.<sup>19</sup> Neutralization and dissociation of **5/5'** should yield ·C<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub> (+H<sub>2</sub>O); its presence is indicated by

(30) Corrected for the contribution from metastable ion dissociation, in which H/D scrambling is statistical for all hydrogens.

(31) The apparent stability of the **4** molecular ion in Figure 7A is surprising in view of those in Figures 1A, 2A, and 4B and in the EI mass spectrum of Figure 6A. However, in other cases (e.g., ·CH<sub>2</sub>Cl-H) we have found that O<sub>2</sub> reionization produces surprisingly abundant molecular ions.<sup>20</sup>

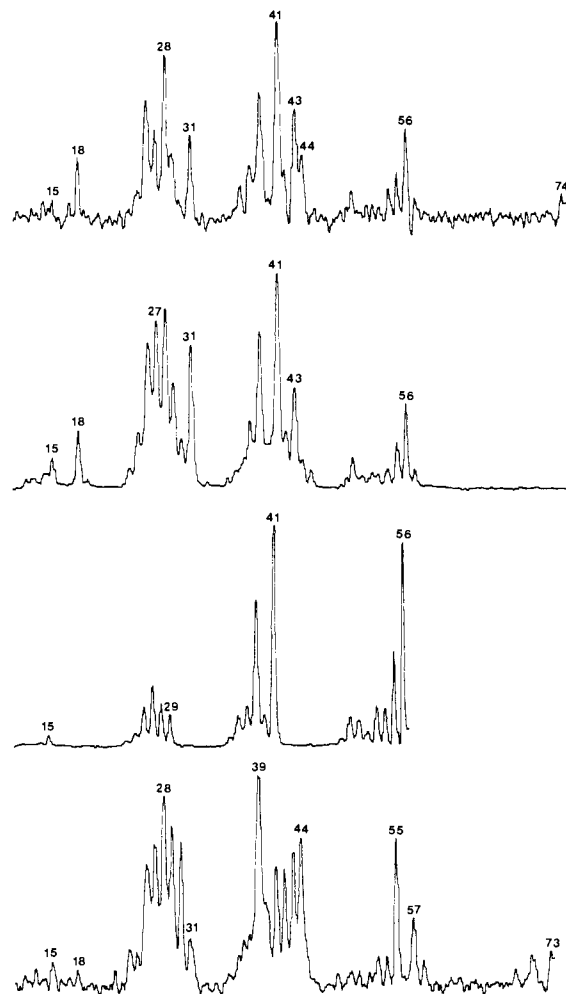
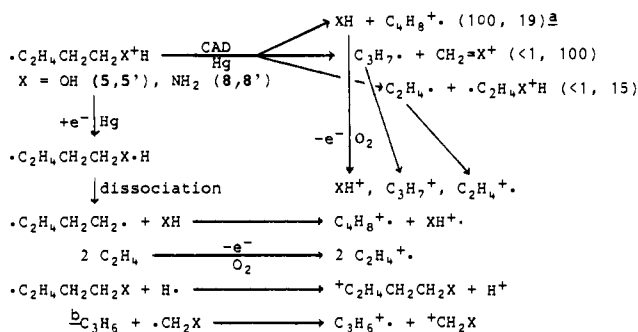


Figure 7. Hg/O<sub>2</sub> NR mass spectra of, top to bottom: (A) 4; (B) 5; (C) ionized methylcyclopropane; and (D) protonated oxolane ions.

#### Scheme II



<sup>a</sup> See Scheme I. <sup>b</sup> This reaction should be favored for  $\cdot\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{X}$ .

*m/z* 56, 41, and 39 (compare the NR reference spectrum of ionized methylcyclopropane, Figure 7C) and by *m/z* 28 from its C<sub>2</sub>H<sub>4</sub> dissociation product. Some of the remaining NR peaks could arise from 5/5' → ·C<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>OH (+H·); compare the NR spectrum of the C<sub>4</sub>H<sub>9</sub>O<sup>+</sup> ion, presumably protonated oxolane, formed by loss of HOCH<sub>2</sub>· from HO(CH<sub>2</sub>)<sub>5</sub>OH<sup>+</sup>· (Figure 7D). Further dissociation of these neutrals to produce ·CH<sub>2</sub>OH, ·C<sub>2</sub>H<sub>3</sub>O, and C<sub>2</sub>H<sub>4</sub>O could account for other, less abundant peaks of Figure 7A,B (Scheme II).

***n*-Butylamine<sup>+</sup>· Isomers.** The similarity of the CAD spectra (Figure 8) of ionized *n*-butylamine (7) and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>H<sub>3</sub> (8, formed by CH<sub>2</sub>O loss from HOCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>NH<sub>2</sub><sup>+</sup>) suggests extensive isomerization prior to CAD. This is confirmed by the CAD spectrum (Figure 8C) of

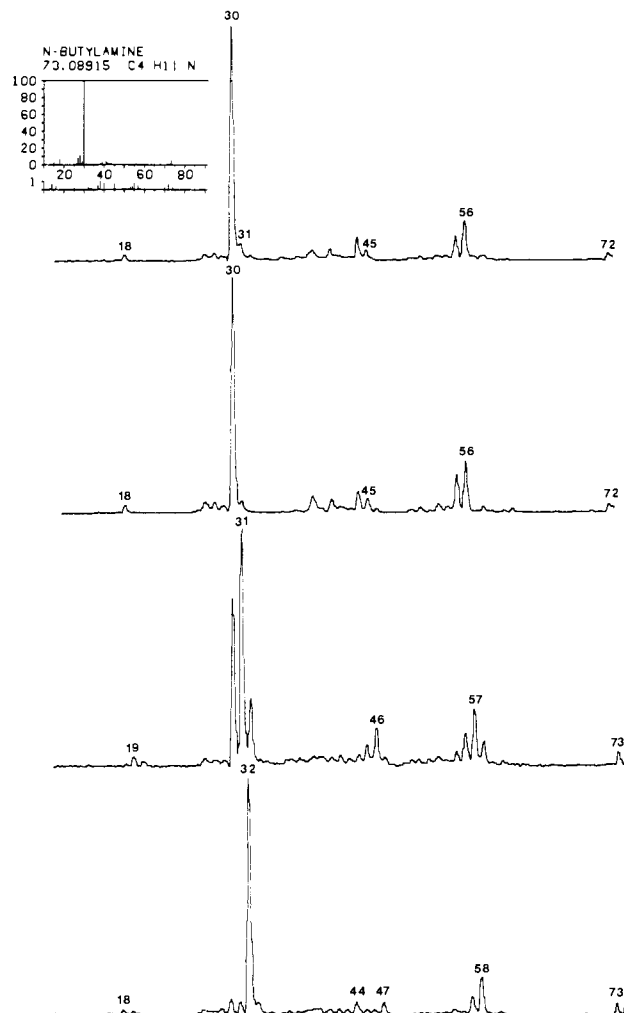


Figure 8. CAD mass spectra of, top to bottom: (A) ionized *n*-butylamine, 7; (B) ·CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>H<sub>3</sub>, 8; and ionized (C) *n*-butylamine-*N*-d<sub>2</sub> and (D) *n*-butylamine-1,1-d<sub>2</sub>.

ionized CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>ND<sub>2</sub><sup>+</sup> (7'); its C(H,D)<sub>4</sub>N<sup>+</sup> abundances are consistent with ~10% of 7' formed with insufficient energy to isomerize,<sup>26</sup> and the deuterium atoms of the remaining 7' exchanging with ca. four hydrogen atoms. Presumably these are from the five γ and δ hydrogens; the α hydrogens are not involved (Figure 8D). The lower degree of scrambling in (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>ND<sub>2</sub><sup>+</sup>· (Figure 5B) indicates that δ-H migration is favored over that of the γ-H. Increasing the ion lifetimes before CAD by a factor of 2.2 (2-keV acceleration) reduces the unisomerized 7 ions (*m/z* 32) to <5%, indicating a negligible barrier to isomerization of <3 kcal mol<sup>-1</sup>.<sup>27</sup>

The *m/z* 30 peak in the Hg/O<sub>2</sub> NR spectrum of ionized *n*-butylamine (Figure 9A)<sup>32</sup> is larger than that in the spectrum of 8; the extra *m/z* 30 should originate from unisomerized 7, which should yield data resembling the EI mass spectrum of *n*-butylamine (Figure 8A). On the other hand, dissociation of ·C<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> produced by H· loss from neutralized 8/8' (Scheme II) could account for the *m/z* 30 peak in the NR spectrum of 8 (Figure 9B). The near absence of *m/z* 30 in the He/O<sub>2</sub> NR spectrum (Figure 9C) shows that this arises largely by neutralization and reionization; helium produces a much lower proportion of charge exchange vs. CAD than does mercury.<sup>12</sup> However, the base peak in the NR spectra of 7 and 8 is *m/z* 43, which appears to arise mainly from the C<sub>3</sub>H<sub>7</sub><sup>+</sup> (see Figure 5D) produced with the major CAD/Hg peak, CH<sub>2</sub>=N<sup>+</sup>H<sub>2</sub> (Scheme

(32) The Hg/O<sub>2</sub> NR spectrum of ions from ionizing *n*-butylamine with 20-eV electrons shows a ~20% increase in the *m/z* 30 abundance; however, the experimental error in this measurement is nearly this large. The 20-eV value for *m/z* 42 is 80 ± 10% of that of 70 eV.

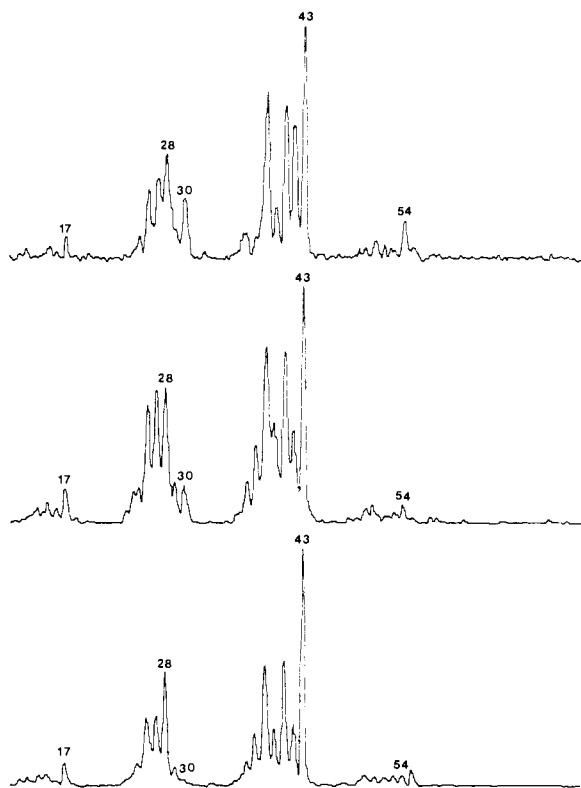


Figure 9. Hg/O<sub>2</sub> NR mass spectra of, top to bottom: (A) 7 and (B) 8. (C) He/O<sub>2</sub> NR mass spectrum of 7.

II). By analogy to the smaller distonic homologues CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>H<sub>3</sub> (13) and ·CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>H<sub>3</sub> (18), it is the distonic isomer 8, not 7, which should show this high tendency for CAD.<sup>22</sup> Thus the close similarity of the Hg/O<sub>2</sub> NR spectra of 7 and 8 indicates that the distonic isomer 8 is the dominant species resulting from the equilibrium 7 ⇌ 8. The *m/z* 26–28 could arise (Scheme II) from the C<sub>2</sub>H<sub>4</sub> neutral formed with 13 by CAD/Hg (see Figure 1B). Neutralization of 7 with sodium vapor does not appreciably increase the low relative proportion of neutralization vs. CAD.<sup>12</sup>

**Lower Isomerization Barrier of Ionized Amines vs. Alcohols.** The transition state for the more exothermic rearrangement of

alcohol molecular ions must be much less favorable than that of amine molecular ions, with activation energy values of ~20 and <9 kcal mol<sup>-1</sup> for C<sub>3</sub>H<sub>7</sub>OH<sup>+</sup> (15) and C<sub>3</sub>H<sub>7</sub>NH<sub>2</sub><sup>+</sup> (17), respectively. Recent ab initio calculations of Nishimoto et al.<sup>5d,25</sup> indicate that the transition states for these isomerizations are approached from the gauche conformations of 15 and 17. The positive charge for both is distributed over the entire molecule, primarily on the hydrogen periphery, so that the migrating γ hydrogen has a net positive charge. However, the net charge on the heteroatom accepting the hydrogen is positive for the alcohol (15) and negative for the amine (17). The resulting coulombic repulsion for 15, and attraction for 17, should then lead to a much higher activation energy for 15 → 16 vs. 17 → 18, as observed.<sup>33</sup>

### Summary

The distonic oxonium and ammonium radical ions are more stable than their molecular ion isomers, as shown by the isomerization direction for 4 → 5/5', 17 → 18, 21 → 22, and 7 → 8/8'. Although isomerization to form the oxonium ions is more exothermic (by 4–8 kcal mol<sup>-1</sup>, Table I) than such formation of the ammonium ions, the latter isomerization (17 vs. 15, 21 vs. 19, 7 vs. 4) must have substantially lower activation energies than those producing the oxonium ions, consistent with previous conclusions<sup>3d,e</sup> that radical site reactions at nitrogen are favored over those at oxygen. Consistent with previous labeling evidence,<sup>3a,f-h,7g</sup> 1,5- are favored over 1,4-hydrogen rearrangements; 1,3- and 1,2-H rearrangements (e.g., Figure 8D) were not observed.

**Acknowledgment.** We are grateful to R. F. Porter, T. F. Moran, and L. Radom for helpful discussions and to the National Institutes of Health (Grant GM16609) and Army Research Office (Grant DAAG29-82-K-0179) for generous financial support.

**Registry No.** 4, 99033-61-1; 4-*d*, 99033-62-2; 5, 99033-63-3; 7, 70677-55-3; 7-*N,N*-*d*<sub>2</sub>, 99033-64-4; 7-1,1-*d*<sub>2</sub>, 99033-65-5; 8, 20694-05-7; 9, 99095-69-9; 10, 60786-90-5; 12, 65764-66-1; 13, 20694-01-3; 15, 34538-82-4; 16, 90263-55-1; 17, 70677-54-2; 18, 20694-02-4; 19, 99033-66-6; 20, 99033-67-7; 21, 99033-68-8; 21-*d*<sub>2</sub>, 99033-69-9; 22, 20694-07-9; 1-propanol, 71-23-8; ethanol, 64-17-5; ethylene, 74-85-1; ethylamine, 75-04-7; propylamine, 107-10-8; isobutyl alcohol, 78-83-1; isobutylamine, 78-81-9; 1-butanol, 71-36-3; butylamine, 109-73-9.

(33) These authors<sup>5d,25</sup> actually reached the opposite conclusion from these data, explaining the large loss of H<sub>2</sub>O from ionized propanol as due to the attraction between the positive net charge on oxygen and the negative net charge on the γ-carbon atom.

## Efficient Total Synthesis of (±)-Anatoxin *a*

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**Abstract:** A practical and efficient synthetic route to the neurotoxic alkaloid anatoxin *a* has been developed. In this new strategy, the bicyclooctanone 4 is prepared in one to two steps from either 4-cycloheptenone or the tricyclooctane 6 and is then converted to the aminobicyclooctane intermediate 3 by reductive amination. The pivotal step in the synthetic strategy involves the electrocyclic cleavage-transannular cyclization of the amine 3, which generates the 9-azabicyclo[4.2.1]nonene ring system of the target alkaloid. Overall, the synthesis involves only seven steps (17% overall yield) beginning with 4-cycloheptenone, or alternatively, eight steps (8.3% overall yield) starting with the tetrabromotricyclooctane 6.

Certain strains of the freshwater blue-green alga *Anabaena flos-aquae* produce a potent toxin which has been responsible for numerous incidents of livestock and waterfowl poisoning in the midwestern United States and Canada.<sup>2</sup> This substance, originally

designated "very fast death factor" (VFDF), rapidly causes death in a variety of species via respiratory paralysis, with an intra-

(1) Fellow of the Alfred P. Sloan Foundation, 1981–1985.