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Ion/Molecule Reactions of Ammonia with Two Translationally Excited $C_2H_5O^+$ Isomers

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Abstract: Two isomers of $C_2H_5O^+$ were accelerated by up to 35 eV (laboratory frame) into N_2 and NH_3 in a triple quadrupole instrument. Ion yields were obtained as a function of ion kinetic energy and used to determine ion kinetic energy thresholds for all endothermic processes. These thresholds were used as indicators of the ion and neutral structure. The efficiency of conversion of translational energy into the internal energy at the threshold ranged from 60 to 100%; the percentage of conversion appears to qualitatively reflect the tightness of the activated complex.

The interpreter of a mass spectrum uses the structures of observed fragment ions to deduce the structure of the molecular ion.[1] The determination of the structures of these fragment ions is, therefore, important both to understand their gas-phase ion chemistry and to interpret mass spectra with increased sophistication. Fragmentation reactions, either metastable or collisionally activated, of the ion of interest have often been used to determine its structure. In some cases, however, the differences in either the metastable or the collisional activation spectra of isomeric ions are subtle and inconclusive.[2] In some cases, ion/molecule reactions may be of use because they may allow the investigator, through careful selection of the neutral, to take advantage of some characteristic reactivity present in a proposed structure.[3] Spectra due to exothermic ion/molecule reactions, however, may also differ because of differences in the energy content of the ions.[4]

Most early studies of ion/molecule reactions utilized ion cyclotron resonance (ICR),[5] high-pressure mass spectrometry,[6] or flowing afterglow.[7] Recently, several studies have been reported using double and triple quadrupole mass spectrometers.[8-13] Two particularly attractive features of double and triple quadrupole instruments are, first, that the reacting neutral is introduced at a distance from the ion source and can be chosen completely independently of the reacting ion and, second, that a low center-of-mass (COM) translational energy can be imparted to the reacting ion to provide access to reactions that are either endothermic or have a large activation barrier, that is, reactions that require excess energy. In addition, spectra may be obtained as a function of ion kinetic energy, giving so-called "energy-resolved" data.[14-17] Trajectory calculations and experiments by other investigators have shown that the acceleration by the rf field of the collision cell does not contribute significantly to the energy of the collision.[18,19] These "energy-resolved" data allow the observation of threshold ion kinetic energy (TIKE) values which can provide limits for the onset potentials of products.[19-24]

Several stable isomers of $C_2H_5O^+$ have been identified.[25] The two most stable $C_2H_5O^+$ isomers have been the subject of numerous investigations. These include theoretical calculations,[26] collisionally activated decompositions (CAD),[27] and ion/molecule reactions by ICR[4] and by double-quadrupole mass spectrometry.[8] This system is then an attractive starting point because the structures, $CH_3OCH_2^+$ and CH_3CHOH^+, are well-established. In addition, specific differences in reactivity may be predicted from differences in the structures. For example, efficient proton transfer from CH_3CHOH^+ but not $CH_3OCH_2^+$ to a base with a proton affinity greater than that of CH_3CHO (188.9 kcal/mol[28]) is expected. Under what conditions does $CH_3OCH_2^+$ protonate the same base? This difference in reactivity illustrates the broader range of questions that now can be asked about ion/molecule reactions and readdresses their use in targeting specific aspects of ion structure.

We report differences in the reactivity of the major $C_2H_5O^+$ isomers, $CH_3OCH_2^+$ and CH_3CHOH^+, with ammonia in the collision cell of a triple-quadrupole mass spectrometer. These differences are clear indicators of ion structure. The thermochemistry of reactions requiring excess kinetic energy is discussed

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(1) McLafferty, F. W. "Interpretation of Mass Spectra", 3rd ed.; University Science: Mill Valley, CA, 1980.

(2) For example: (a) Cooks, R. G.; Beynon, J. H.; Litton, J. F. *Org. Mass Spectrom.* **1975**, *10*, 503. (b) Bowen, R. D.; Barbalas, M. P.; Pagano, F. P.; Todd, P. J.; McLafferty, F. W. *Org. Mass Spectrom.* **1980**, *15*, 51. (c) Holmes, J. L.; Terlouw, J. K.; Burgers, P. C.; Rye, R. T. B. *Org. Mass Spectrom.* **1980**, *15*, 149. (d) Lay, J. O., Jr.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 3445.

(3) (a) Gross, M. L. *J. Am. Chem. Soc.* **1972**, *94*, 3744. (b) Diekman, J.; MacLeod, J.; Djerassi, C.; Baldeschwieler, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 2069.

(4) Beauchamp, J. L.; Dunbar, R. C. *J. Am. Chem. Soc.* **1970**, *92*, 1477.

(5) Lehman, T. A.; Bursey, M. M. "Ion Cyclotron Resonance Spectrometry"; Wiley Interscience: New York, 1976.

(6) Field, F. H. *Acc. Chem. Res.* **1968**, *1*, 42.

(7) Depuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146.

(8) Glish, G. L.; Hemberger, P. H.; Cooks, R. G. *Anal. Chim. Acta* **1980**, *119*, 137.

(9) Bately, J. H.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1263.

(10) Mitchell, A. L.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1984**, 667.

(11) Fetterolf, D. D.; Yost, R. A.; Eyler, J. R. *Org. Mass Spectrom.* **1984**, *19*, 104.

(12) Schmit, J. P.; Dawson, P. H.; Beaulieu, N. *Org. Mass Spectrom.* **1985**, *20*, 269.

(13) Schmit, J. P.; Dawson, P. H. *Org. Mass Spectrom.*, in press.

(14) Dawson, P. H., personal communication.

(15) Fetterolf, D. D.; Yost, R. A. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *44*, 37.

(16) McLuckey, S. A.; Sallans, L.; Cody, R. B.; Barnier, R. C.; Verma, S.; Freiser, B. S.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *44*, 215.

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

(18) Dawson, P. H.; Fulford, J. E. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *42*, 195.

(19) Dawson, P. H. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *50*, 287.

(20) Dawson, P. H.; Douglas, D. J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *47*, 121.

(21) Douglas, D. J. *J. Phys. Chem.* **1982**, *86*, 185.

(22) Dawson, P. H. *Int. J. Mass Spectrom. Ion Process.* **1985**, *63*, 305.

(23) Dawson, P. H. *Int. J.* Mass *Spectrom. Ion Phys.* **1983**, *43*, 195.

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

(25) Burgers, P. C.; Terlouw, J. K.; Holmes, J. L. *Org. Mass Spectrom.* **1982**, *17*, 369.

(26) Nobes, R. H.; Rodwell, W. R.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1981**, *102*, 1913.

(27) McLafferty, F. W.; Kornfeld, R.; Haddon, W. F.; Levsen, K.; Sakai, I.; Bente, P. F., III; Tsai, S.-C.; Schuddemage, H. D. R. *J. Am. Chem Soc.* **1973**, *95*, 3886.

(28) Aue, D. H.; Bowers, M. T. "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 1.

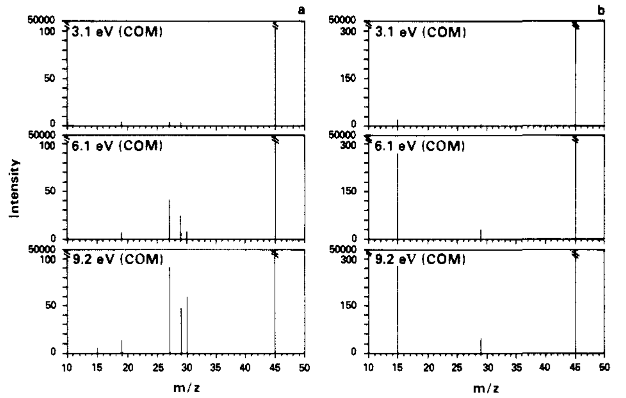

Figure 1. Spectra of (a) CH_3CHOH^+ and (b) $CH_3OCH_2^+$ at several ion kinetic energies using N_2 collision gas.

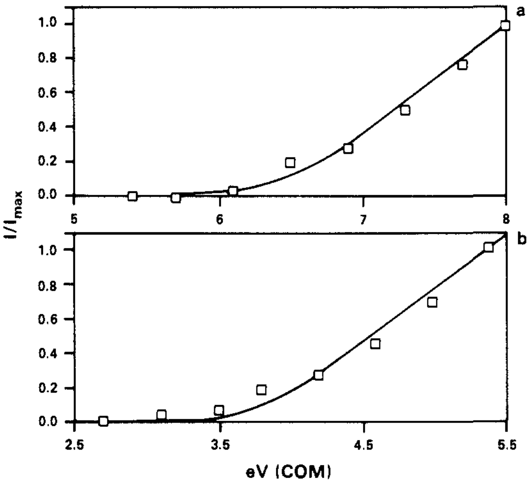

Figure 2. Ion yields of m/z 15 from (a) CH_3CHOH^+ and (b) $CH_3OCH_2^+$ as a function of ion kinetic energy using N_2 collision gas. The line represents the best fit to the theoretical doppler-broadened appearance curve (linear cross-sectional model).

in relation to their threshold ion kinetic energies and the implications concerning the ion chemistry involved.

Experimental Section

All experiments were performed by using an Extranuclear Laboratories triple-quadrupole mass spectrometer. The ion kinetic energies were varied from approximately 4 to 35 eV in the laboratory frame of reference (lab), corresponding to energies of approximately 1–15 eV and approximately 1–10 eV in the center-of-mass frame of reference (COM) for N_2 and NH_3, respectively. The energies were set by changing the mean dc level (pole zero) of the second quadrupole (Q2) relative to the source potential. The pole zero of the first quadrupole (Q1) was set at approximately −10 V relative to the source potential to provide needed main beam intensity with adequate resolution, and the pole zero of the third quadrupole (Q3) was set at approximately −5 V relative to the pole zero of the second quadrupole to remove low mass discrimination and yet provide adequate resolution throughout the range of ion kinetic energies used. The effects of the various experimental and instrumental parameters have been previously discussed by Dawson.[29,30] The collision cell pressure was set to give between 95 and 100% transmission of the main beam and was on the order of 2×10^{-6} torr (ion gauge). Attenuation on this order[31] is consistent with the assumption of single-collision conditions; our calculations of collision frequency also support this assumption. The parent ions were formed by electron impact using 11.0–11.5-eV electrons, which are approximately 0.8–1.3 eV above the appearance thresholds for the formation of $C_2H_5O^+$ from 2-propanol and 1,2-dimethoxyethane, obtained from commercial sources, of 10.26 and 10.27 eV, respectively.[32] Experimental results were deconvoluted for doppler broadening due to the thermal motion of the neutral by the method of Chantry using a linear cross-section model.[33] Curves were fitted to the nearest 0.1 eV, and the quality of results also obtained can be judged from later figures to be excellent.

Table I. Daughter Ions Observed Using N_2 as the Collision Gas

m/z	product ion	ΔH°_r, lit., eV	TIKE,[a] obsd, eV, COM	% conversion
		CH_3CHOH^+		
15	CH_3^+	6.5	6.5	100
19[b]	H_3O^+	2.0	2.8	71
27[c]	$C_2H_3^+$	3.1	4.0	78
29[d]	HCO^+	1.6	2.6	62
30	H_2CO^+	5.1	6.2	82
30	$HCOH^+$	8.0		
		$CH_3OCH_2^+$		
15	CH_3^+	3.5	3.8	93
29[e]	HCO^+	1.0	1.7	59

[a] Reproducibility ±0.2 eV. [b] $CH_3CHOH^+ \rightarrow H_3O^+ + HCCH$. [c] $CH_3CHOH^+ \rightarrow C_2H_3^+ + H_2O$. [d] $CH_3CHOH^+ \rightarrow HCO^+ + CH_4$. [e] $CH_3OCH_2^+ \rightarrow HCO^+ + CH_4$.

Table II. Daughter Ions Observed Using NH_3 Collision Gas

m/z	product ion	ΔH°_r, lit., eV	TIKE,[a] obsd, eV, COM	% conversion
		CH_3CHOH^+		
15	CH_3^+	3.7	4.2	89
18	NH_4^+	−0.8		
19	H_3O^+	2.0	3.0	67
27	$C_2H_3^+$	3.1	3.9	79
29	HCO^+	1.6	2.5	64
30	H_2CO^+	5.1	6.0	85
		$CH_3OCH_2^+$		
15	CH_3^+	3.1	3.0 ± 0.3	100
18	NH_4^+	2.5	2.4	100
29	HCO^+	1.0	1.4	71
30	$CH_2NH_2^+$	−0.5		
32	$CH_3NH_3^+$	−1.1		

[a] Reproducibility ±0.2 eV except where listed.

Results and Discussion

N_2 Collision Gas. Both isomers were accelerated into N_2, which was assumed to be unreactive. Spectra obtained at ion kinetic energies of 3.1, 6.1, and 9.2 eV (COM) (Figure 1) contained daughter ions at m/z 15 and 29 for $CH_3OCH_2^+$ and at m/z 15, 19, 27, 29, and 30 for CH_3CHOH^+. These ions are the products of collisionally activated decompositions and are consistent with previous low-energy CAD experiments.[8]

Thresholds of 3.8 and 6.5 eV (COM) (Figure 2) were observed for the formation of CH_3^+ from $CH_3OCH_2^+$ and CH_3CHOH^+, respectively. This difference in threshold ion kinetic energies indicates a difference for the enthalpy of the two reactions of at least 2.7 eV. Since the ΔH°_f of the two isomers differs by only 0.6 eV,[34] most of this difference in reaction enthalpies must be due to a difference in the ΔH°_f of the neutral products. This difference is consistent with the formation of H_2CO from $CH_3OCH_2^+$ and HCOH from CH_3CHOH^+ (eq 1 and 2).

$$\begin{array}{lcccc} & CH_3O{=}CH_2^+ & \longrightarrow & CH_3^+ \; + & H_2CO \\ \Delta H^\circ_f & 6.7\text{ eV} & & 11.4\text{ eV} & -1.2\text{ eV} \\ & & & \multicolumn{2}{c}{\Delta H^\circ_r = 3.5\text{ eV}} \end{array} \qquad (1)$$

$$\begin{array}{lcccc} & CH_3{-}CH{=}OH^+ & \longrightarrow & CH_3^+ \; + & HCOH \\ \Delta H^\circ_f & 6.1\text{ eV} & & 11.4\text{ eV} & 1.2\text{ eV} \\ & & & \multicolumn{2}{c}{\Delta H^\circ_r = 6.5\text{ eV}} \end{array} \qquad (2)$$

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(29) Dawson, P. H.; French, J. B.; Buckley, J. A.; Douglas, D. J.; Simmons, D. *Org. Mass Spectrom.* **1982**, *17*, 205.

(30) Dawson, P. H.; French, J. B.; Buckley, J. A.; Douglas, D. J.; Simmons, D. *Org. Mass Spectrom.* **1982**, *17*, 212.

(31) Todd, P. J.; McLafferty, F. W. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *38*, 371.

(32) Levin, R. D.; Lias, S. G. "Ionization Potential and Appearance Potential Measurements 1971–1981"; U. S. Government Printing Office: Washington, DC, 1982.

(33) Chantry, P. J. *J. Chem. Phys.* **1971**, *55*, 2746.

(34) Lossing, F. P. *J. Am. Chem. Soc.* **1977**, *99*, 7526.

Table III. Heats of Formation Used

structure	ΔH_f°, kcal/mol	ΔH_f°, eV/mol	ref
	Ions		
$CH_3OCH_2^+$	153	6.7	34
CH_3CHOH^+	140	6.1	34
CH_3^+	262	11.4	*a*
H_2CO^+	224	9.7	*a*
$HCOH^+$	290	12.6	*b*
NH_4^+	149	6.5	*c*
$CH_2NH_2^+$	178	7.7	*a*
$CH_3NH_3^+$	142	6.2	*d*
H_3O^+	134	5.8	*e*
$C_2H_3^+$	269	11.7	*a*
CHO^+	195	8.5	*a*
H^+	365	15.9	*a*
	Neutrals		
H_2CO	-28	-1.2	*a*
HCOH	27	1.2	*f*
$CH_3\cdot$	34	1.5	*a*
CH_3CHO	-40	-1.7	*a*
$\cdot CH_2OCH_2\cdot$	51	2.2	*g*
CH_3OH	-48	-2.1	*a*
H_2NCH_2OH	-48	-2.1	*h*
HCCH	54	2.3	*a*
H_2O	-58	-2.5	*a*
CH_4	-18	-0.8	*a*
NH_3	-11	-0.5	*a*
CH_3NH_2	-6	-0.3	*a*

[a] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1. [b] Pires, M. V.; Galloy, C.; Lorquet, J. C. *J. Chem. Phys.* **1978**, *69*, 5242. [c] Calculated by using $\Delta H_f^\circ(NH_3) = -0.5$ eV/mol; $\Delta H_f^\circ(H^+) = 15.9$ eV/mol; $PA(NH_3)^{28} = 8.9$ eV/mol. [d] Calculated by using $\Delta H_f^\circ(CH_3NH_2) = -0.3$ eV/mol; $\Delta H_f^\circ(H^+) = 15.9$ eV/mol; $PA(CH_3NH_2)^{28} = 9.3$ eV/mol. [e] Calculated by using $\Delta H_f^\circ(H_2O) = -2.5$ eV/mol; $\Delta H_f^\circ(H^+) = 15.9$ eV/mol; $PA(H_2O)^{28} = 7.5$ eV/mol. [f] Goodard, J. D.; Schaefer, H. F., III, *J. Chem. Phys.* **1979**, *70*, 5117. [g] Calculated by using ΔH_f°(oxirane molecular ion)[a] = 10.2 eV/mol; ΔH_r°(C–C) bond cleavage in oxirane molecular ion)[i] = 0.9 eV/mol; $IP(\cdot CH_2OCH_2\cdot)^j = 7.1$ eV/mol. [h] Calculated by using $\Delta H_f^\circ(CH_3NH_2) = -0.3$ eV/mol; $\Delta H_f^\circ(CH_3OH) = -2.1$ eV/mol; $\Delta H_f^\circ(CH_4) = -0.8$ eV/mol; $\Delta H_f^\circ(CH_3NH_2 + CH_3OH \rightarrow CH_4 + HOCH_2NH_2)^k = 0.5$ eV/mol. [i] Bouma, W. J.; Poppinger, D.; Saebo, S.; MacLeod, J. K.; Radom, L. *Chem. Phys. Lett.* **1984**, *104*, 198. [j] Caramella, P.; Gaudon, R. W.; Hall, J. A.; Deville, C. G.; Houk, K. N., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 385. [k] Schleyer, P. von R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141.

Similarly, thresholds were observed for the formation of all other ions in the CAD spectrum of each isomer. The observed thresholds, the calculated heats of reaction, and the calculated percentages of translational energy converted into the internal energy at the threshold are summarized in Table I. From these data, one can see that for each isomer, the formation of CH_3^+ at the threshold proceeds with approximately 100% conversion of translational energy into internal energy. Conversely, all other CAD reactions for these isomers proceed with only 60%–80% conversion at the threshold. This difference in conversion efficiency parallels the observation that the formation of CH_3^+ from each isomer is the result of simple cleavage, while the other ions are formed by more complex processes with tight activated complexes. The complexity of these reactions, compared to CH_3^+ formation, may inherently lead to thresholds in excess of the calculated heat of reaction because of the reverse activation energy. The reactions may also have significant kinetic shifts. Since the magnitude of an experimental kinetic shift is difficult to predict a priori,[35] it is as yet impossible to determine the cause of the high threshold.

The guideline that simple cleavage reactions are more efficient, i.e., consume more of the apparently available kinetic energy than reactions that involve a degree of rearrangement, is useful for correlating the observed threshold ion kinetic energy for the formation of the *m/z* 30 product from CH_3CHOH^+ with the product ion structure. For CH_3CHOH^+, simple cleavage of the C–C bond without charge migration would be expected to yield $CHOH^{+\cdot}$ as the *m/z* 30 ion. This reaction (eq 3), however, would be 8.0-eV endothermic and, because of the high efficiency of simple cleavage reactions, would be expected to show a threshold ion kinetic energy of approximately 8.0 eV (COM). The observed threshold of 6.2 eV (COM), significantly below the ΔH_r° of 8.0 eV, indicates that $CHOH^{+\cdot}$ is not the structure of the ion formed. Formation of $H_2CO^{+\cdot}$ from CH_3CHOH^+ (eq 4), which is only 5.1-eV endothermic, would require some rearrangement and therefore would be expected to be less efficient. The observed threshold of 6.2 eV (COM) would then represent an 80% conversion of translational energy into the internal energy consistent with our observations above.

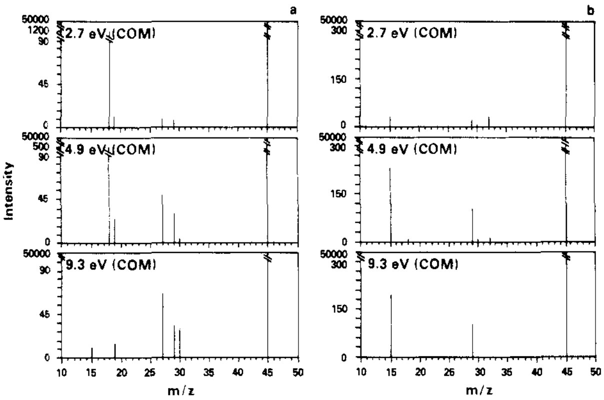

Figure 3. Spectra of (a) CH_3CHOH^+ and (b) $CH_3OCH_2^+$ at several ion kinetic energies using NH_3 collision gas.

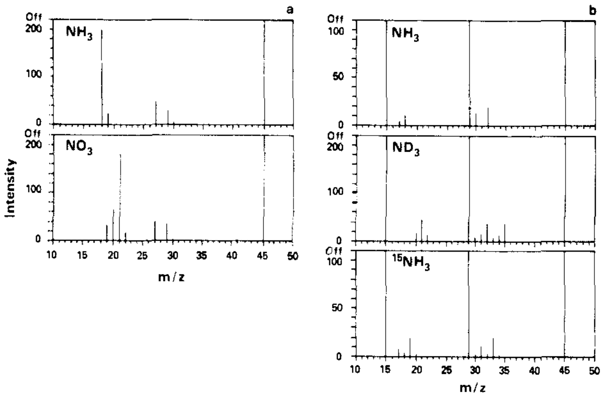

Figure 4. Spectra of (a) CH_3CHOH^+ and (b) $CH_3OCH_2^+$ at 4 eV (COM) using NH_3, ND_3, and $^{15}NH_3$ collision gases.

$$\begin{array}{lccc} & CH_3{-}CH{=}OH^+ \longrightarrow & HCOH^{+\cdot} + \cdot CH_3 & (3) \\ \Delta H_f^\circ & 6.1\ \text{eV} & 12.6\ \text{eV} \quad 1.5\ \text{eV} & \\ & & \Delta H_r^\circ = 8.0\ \text{eV} & \end{array}$$

$$\begin{array}{cc} \longrightarrow H_2CO^{+\cdot} + \cdot CH_3 & (4) \\ 9.7\ \text{eV} \quad 1.5\ \text{eV} & \\ \Delta H_r^\circ = 5.1\ \text{eV} & \end{array}$$

NH_3 Collision Gas. Ammonia was chosen as a reactive collision gas to take advantage of the lability of the oxygen-bound proton of the CH_3CHOH^+ isomer. In spectra obtained at 2.7, 4.9, and 9.3 eV (COM) (Figure 3), all CAD products previously noted in N_2 collisions were still observed and additional product ions were found at *m/z* 18, 30, and 32 from $CH_3OCH_2^+$ and *m/z* 18 from CH_3CHOH^+. For ease of discussion, the observed ion/molecule reactions have been divided into three categories: proton-transfer reactions, condensation reactions, and dissociative additions.

Proton-Transfer Reactions. Additional experiments using ND_3 and $^{15}NH_3$ as the collision gas (Figure 4) indicate that the ion at *m/z* 18 for both isomers is NH_4^+, the product of a proton-transfer reaction. The protonation of ammonia by CH_3CHOH^+ is expected; the reaction is 0.8-eV exothermic (eq 5). The pro-

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

$$\begin{array}{lllll} & CH_3{-}CH{=}OH^+ + & NH_3 \longrightarrow & NH_4^+ + & CH_3CHO \quad (5) \\ \Delta H_f^\circ & 6.1\ eV & -0.5\ eV & 6.5\ eV & -1.7\ eV \\ & & & \multicolumn{2}{l}{\Delta H_r^\circ = -0.8\ eV} \end{array}$$

$$\begin{array}{lllll} & CH_3{-}O{=}CH_2^+ + & NH_3 \longrightarrow & NH_4^+ + & CH_2OCH_2 \quad (6) \\ \Delta H_f^\circ & 6.7\ eV & -0.5\ eV & 6.5\ eV & 2.2\ eV \\ & & & \multicolumn{2}{l}{\Delta H_r^\circ = 2.5\ eV} \end{array}$$

tonation of ammonia by $CH_3OCH_2^+$, however, is not expected; the reaction is endothermic by 2.5 eV (eq 6), using a reasonable value for the ΔH_f° of the likely neutral product $\cdot H_2COCH_2\cdot$. The "energy-resolved" curves for *m/z* 18 (Figure 5) show a threshold ion kinetic energy of 2.4 eV (COM) for the $CH_3OCH_2^+$ isomer, within experimental error of the 2.5-eV heat of reaction. This again represents 100% conversion of the translational energy into the internal energy at the threshold, reflecting the facility of the proton-transfer mechanism.

The "energy-resolved" curves for these reactions (Figure 5) provide typical examples of the behavior of exothermic and endothermic reactions in our experiments. In these experiments, the products of exothermic reactions should be observed even as the ion kinetic energy approaches zero, provided the pole zero of the third quadrupole (Q3) is sufficiently negative with respect to the second quadrupole to transmit the product ions through Q3. The products of endothermic reactions should be observed only at ion kinetic energies high enough to provide the internal energy needed for the reaction.

Condensation Reactions. The labeling experiments (Figure 4) also indicate ion structures of $CH_2NH_2^+$ and $CH_3NH_3^+$ for *m/z* 30 and 32, respectively, for $CH_3OCH_2^+$ reacting with NH_3. These ions would also be the products of exothermic reactions (eq 7 and 8). Again the expected behavior is seen for the "energy resolved" plots (Figure 6), with *m/z* 30 and 32 being observed even as the ion kinetic energy approaches zero.

$$\begin{array}{lllll} & CH_3{-}O{=}CH_2^+ + & NH_3 \longrightarrow & CH_2NH_2^+ + & CH_3OH \quad (7) \\ \Delta H_f^\circ & 6.7\ eV & -0.5\ eV & 7.7\ eV & -2.1\ eV \\ & & & \multicolumn{2}{l}{\Delta H_r^\circ = -0.6\ eV} \\ & & \longrightarrow & CH_3NH_3^+ + & H_2CO \quad (8) \\ & & & 6.1\ eV & -1.2\ eV \\ & & & \multicolumn{2}{l}{\Delta H_r^\circ = -1.1\ eV} \end{array}$$

The exothermic ion/molecule reactions in our experiments have maximum intensities at the lowest translational energies used, and the intensity falls off with increasing ion kinetic energy. This behavior is consistent with the predictions of average dipole orientation theory that ion/molecule reactions proceed via formation of a long-lived collision complex.[36] The very low intensity of the NH_4^+ product from $CH_3OCH_2^+$ likewise may reflect the reduction of the lifetime of the necessary collision complex by the ion kinetic energy needed for the reaction. The number of potentially observable reactions of the complex thus is limited by reaction endothermicity. Products are formed only if the complex lives long enough; as kinetic energy increases, the complex lifetime becomes too short to form products. Intuitively, this failure to react should occur for rearrangements (which require longer lifetimes of the complex because of the infrequency of reaching appropriate geometry) before failures for simple cleavages as the system kinetic energy is increased, other things being equal. (Other things, specifically the large reverse activation barrier for the rearrangement, are not equal, but if one is comparing a rearrangement and a simple cleavage of the same ΔH_r°, the effects of the barrier and of the reduced lifetime of the complex both work to favor the observation of the cleavage.)

Also of interest is the large relative cross section (greater by a factor of 18) for the formation of *m/z* 18 vs. *m/z* 27 as products of CH_3CHOH^+ and NH_3. The ion–molecule reaction product, NH_4^+, is much more intense than the collisionally activated decomposition product, $C_2H_3^+$. With the widespread use of CAD in ion structure confirmation, it has occurred to us that use of exothermic ion/molecule reactions could be an even more sensitive tool in some cases under experimental conditions such as those that we are using. The possible use of reactive collision gases to provide exothermic ion/molecule reactions for single-reaction monitoring in GC/MS/MS analysis is currently under investigation in our laboratory.

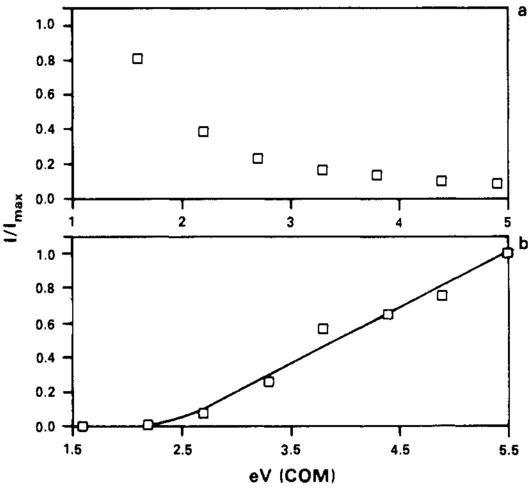

Figure 5. Ion yields of *m/z* 18 from (a) CH_3CHOH^+ and (b) $CH_3OCH_2^+$ as a function of ion kinetic energy using NH_3 collision gas. The line represents the best fit to the theoretical doppler-broadened appearance curve (linear cross-sectional model).

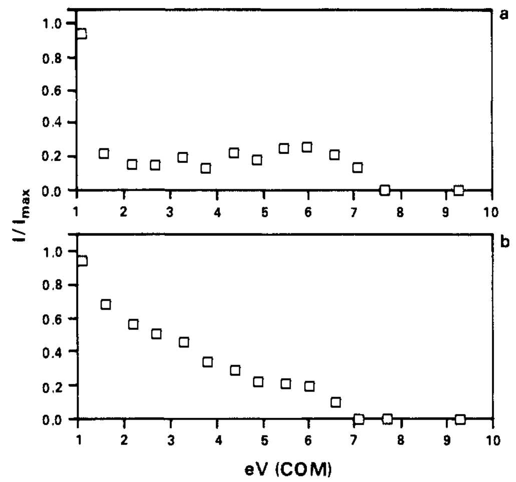

Figure 6. Ion yields of (a) *m/z* 30 and (b) *m/z* 32 from $CH_3OCH_2^+$ as a function of ion kinetic energy using NH_3 collision gas.

Dissociative Additions. Certain dissociative additions have been called reaction-induced fragmentations[12] when they result in ions also observed in CAD spectra but at ion kinetic energies below the threshold for the dissociation reaction. The formation of CH_3^+ by direct dissociation of $CH_3OCH_2^+$ and CH_3CHOH^+ (eq 1 and 2) is endothermic by 3.5 and 6.5 eV, respectively. These reactions have been shown to require ion kinetic energies of 3.8 and 6.5 eV (COM) (Figure 2). However, with NH_3 as the collision gas, *m/z* 15 appears at 3.0 eV (COM) from $CH_3OCH_2^+$ and 4.2 eV (COM) from CH_3CHOH^+ (Figure 7). The threshold for the latter process is 2.3 eV below the minimum energy required for the simple dissociation reaction. Reactions 9 and 10 are proposed for the formation of CH_3^+ using NH_3 as the collision gas. As

$$\begin{array}{lllll} & CH_3{-}O{=}CH_2^+ + & NH_3 \longrightarrow & CH_3^+ + & NH_2CH_2OH \quad (9) \\ \Delta H_f^\circ & 6.7\ eV & -0.5\ eV & 11.4\ eV & -2.1\ eV \\ & & & \multicolumn{2}{l}{\Delta H_r^\circ = 3.1\ eV} \end{array}$$

$$\begin{array}{lllll} & CH_3{-}CH{=}OH^+ + & NH_3 \longrightarrow & CH_3^+ + & NH_2CH_2OH \quad (10) \\ \Delta H_f^\circ & 6.1\ eV & -0.5\ eV & 11.4\ eV & -2.1\ eV \\ & & & \multicolumn{2}{l}{\Delta H_r^\circ = 3.7\ eV} \end{array}$$

seen in these reactions, the formation of the stable neutral NH_2CH_2OH leads to the shift of the CH_3^+ thresholds. This shift is greater for the CH_3CHOH^+ isomer because the gain in ΔH_r°

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(36) Bowers, M. T.; Su, T.; Anicich, V. G. *J. Chem. Phys.* **1973**, *58*, 5175.

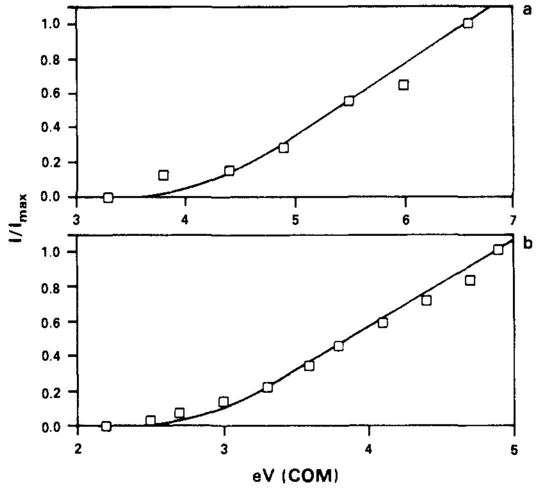

Figure 7. Ion yields of m/z 15 from (a) CH_3CHOH^+ and (b) $CH_3OCH_2^+$ as a function of ion kinetic energy using NH_3 collision gas. The line represents the best fit to the theoretical doppler-broadened appearance curve (linear cross-sectional model).

due to the formation of NH_2CH_2OH (rather than HCOH) is greater than the gain in ΔH°_{r} due to the formation of NH_2CH_2OH (rather than CH_2O) for $CH_3OCH_2^+$. Here again the threshold ion kinetic energy can be used as an indicator of not only ion structure but also neutral structure.

Conclusion

Triple-quadrupole instruments are useful for the study of ion/molecule reactions and collisionally activated decompositions by "energy-resolved" experiments. Thermochemical limits obtained from these experiments can be used as an indicator of not only parent and of daughter ion structures but also neutral structure and even the reaction mechanism. Variation in the efficiency of the conversion of the translational energy into internal energy at the threshold apparently reflects the facility of the reaction mechanism, but it also hinders the direct interpretation of observed thresholds. Efficiencies in the literature, either stated or implied, range from approximately 15 to 25% conversion,[24] for a McLafferty rearrangement in 2-pentanone, to nearly 100% conversion,[19,21-23] for simple bond cleavages. Such a wide range of conversions would make it very difficult to determine the thermochemistry of an unknown reaction exactly, but instead an upper limit to the reaction enthalpy is produced. This will sometimes still provide the information needed to establish an ion structure, neutral structure, or reaction mechanism.

This study also illustrates the targeting of a specific characteristic of an ion structure when structural analysis is the purpose of the experiment. Holmes points out that this approach should be of the greatest use in the examination of ions of known structure.[35] It should also be pointed out, however, that the CAD product ions useful for the determination of unknown ion structures are still present in spectra obtained by using a reactive collision gas.[8] Since CAD products dominate the spectrum at high ion kinetic energy and exothermic ion/molecule reaction products dominate the spectrum at low ion kinetic energy, it should be possible to identify both CAD products and ion/molecule reaction products, as well as determine the thresholds for all endothermic processes, in a single energy-resolved ion/molecule study.

Registry No. $CH_3OCH_2^+$, 23653-97-6; CH_3CHOH^+, 17104-36-8; NH_3, 7664-41-7.

Vapor-Phase X-ray Core-Photoelectron Spectra of *N*,*N*-Dimethyl-*p*-nitrosoaniline. An Experimental and Theoretical Study

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Abstract: The O1s and N1s vapor-phase photoelectron spectra of *N*,*N*-dimethyl-*p*-nitrosoaniline are reported. The O1s spectrum exhibits well-resolved intense multipeak structure. The N1s(NO) and N1s[$N(CH_3)_2$] ionizations sum to yield a considerably less structured spectrum. CNDO/S-CI equivalent-core computations yield O1s and N1s spectral functions in essential agreement with experiment. The heteroatomic spectral functions are discussed in terms of dominant singly and doubly excited electronic contributions. The vapor-phase results are compared and contrasted to existing molecular solid-state spectra to address the nature and manifestations of core-hole-induced intermolecular interactions.

It is well-known that the core-level photoelectron spectra of donor/acceptor substituted aromatic compounds in the condensed molecular solid can exhibit intense heteroatomic shakeup structure.[1-16] Although numerous quantum chemical studies have provided compelling evidence that intense shakeup satellites are indeed commonly inherent to such systems, modeling of the *solid state* spectral features is usually given in terms of electronic configurations of the isolated or vapor-phase species.[12-18] Recently, however, it was shown that the details of the core-level spectra of aromatic donor/acceptor compounds could be consid-

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(1) Siegbahn, K.; Nordling, C.; Fahlman, A.; Nordberg, R.; Hamrin, K.; Hedman, J.; Johansson, G.; Bergmark, T.; Karlsson, S. E.; Lindgren, I.; Lindberg, B. *Nova Acta Regiae Soc. Sci. Ups.* **1967**, *20*, 1.

(2) Pignataro, S.; Distefano, G. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 171-182.

(3) Pignataro, S.; Dimarino, R.; Distefano, G. *J. Electron Spectrosc. Relat.* Phenom. **1974**, *4*, 90-92.

(4) Pignataro, S.; Distefano, G. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1975**, *30*, 815-820.

(5) Distefano, G.; Jones, D.; Modelli, A.; Pignataro, S. *Phys. Scr.* **1977**, *16*, 373-377.

0002-7863/86/1508-1801$01.50/0