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Structures of the Adduct Ions Formed in the Ammonia Chemical Ionization of Ketones

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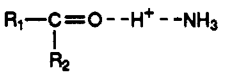
Abstract: The low-energy and high-energy collision-induced dissociation (CID) mass spectra of the adduct ions $M{\cdot}NH_4^+$, $M{\cdot}(CH_3NH_2)H^+$, $M{\cdot}((CH_3)_2NH)H^+$, and $M{\cdot}((CH_3)_3N)H^+$ (M = acetone and 3-pentanone) as well as the CID mass spectra of the higher adducts $M_2(NH_3)H^+$, $M_2(CH_3NH_2)H^+$, $M(NH_3)_2H^+$, $M(CH_3NH_2)_2H^+$, and $M((CH_3)_2NH)_2H^+$ (M = 3-pentanone) have been determined. The low-energy CID mass spectra of the adducts containing a single molecule of the ketone and the amine show only formation of the protonated amine on fragmentation, consistent with a proton-bound cluster ion structure. The high-energy CID mass spectra show formation of the protonated amine but also fragmentation by elimination of a neutral amine and neutral amine plus H, presumably representing fragmentation of very highly excited ions. The fragmentation modes of the ions containing two molecules of the amine or two molecules of the ketone also are consistent with proton-bound cluster ion structures.

Introduction

The NH_4^+ ion, which is the dominant species in ammonia under chemical ionization (CI) conditions, will transfer a proton to only very basic compounds, since the proton affinity of NH_3 is high ($PA(NH_3) = 854$ kJ mol^{-1})[1]. When proton transfer is not exothermic, clustering with the molecule M to form $M{\cdot}NH_4^+$ and, under suitable conditions, $M_2{\cdot}NH_4^+$ and $M(NH_3)NH_4^+$ frequently occurs.[2-5] The structure of these adduct or cluster ions is of considerable interest.

Some years ago, Maquestiau et al.[6] investigated the structures of the $M{\cdot}NH_4^+$, $M_2{\cdot}NH_4^+$, and $M(NH_3)NH_4^+$ ions for a series of ketones. They reported that the high-energy (keV ion energies) collision-induced dissociation (CID) of the $M{\cdot}NH_4^+$ ions resulted primarily in loss of NH_3 neutral and a neutral of 18 amu (which they assumed to be H_2O). They argued that a simple proton-bound complex **1** would fragment to form NH_4^+ since the proton affinity of NH_3 is greater than the proton affinity of any of the ketones studied. Consequently, they concluded that addition of the ammonium ion to the carbonyl bond must have occurred to form the protonated carbinolamine **2**. They further reported that the adduct ion containing two ammonia molecules fragmented primarily by loss of NH_3 to give a species which fragmented by loss of neutrals of 17 and 18 amu. Thus, they concluded that the $M(NH_3)NH_4^+$ species was a protonated carbinolamine solvated by a molecule of ammonia. Similarly, the $M_2{\cdot}NH_4^+$ species was considered to be a protonated carbinolamine solvated by a molecule of the ketone.



$R_1-\underset{R_2}{\underset{|}{C}}=O--H^+--NH_3$

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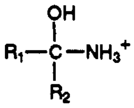

$R_1-\underset{R_2}{\underset{|}{\overset{\overset{OH}{|}}{C}}}-NH_3^+$

2

More recently, Tzeng, Wei, and Castleman[7] have prepared similar species by photoionization of neutral acetone/ammonia clusters. For $(NH_3)_n((CH_3)_2CO)_mH^+$ ($n = 1$, $m = 2$–5), they observed only loss of $(CH_3)_2CO$ in metastable unimolecular decomposition reactions, while for $(NH_3)_n((CH_3)_2CO)_mH^+$ ($n = 2$–18, m 1–5), they observed only loss of NH_3 in metastable unimolecular reactions. The simplest species, $(NH_3)((CH_3)_2H^+$, showed no metastable decomposition reactions. Tzeng et al.[7] concluded that all the species they had prepared were proton-bound cluster species and pointed out that this conclusion was at variance with the conclusions reached by Maquestiau et al.[6]

There are major differences in the methods of preparing the adduct ions in the work of Tzeng et al.[7] and Maquestiau et al.[6] The former workers prepared their ions by multi-photon photoionization of cold neutral clusters, while Maquestiau et al.[6] prepared their adduct ions by ammonia chemical ionization in a chemical ionization source operated at a temperature which was unstated but which probably was considerably higher than room temperature. It appeared possible that these differences in conditions, particularly the temperature, might be the origin of the differences observed. We recently have constructed a high-pressure source for our BEqQ tandem mass spectrometer[8] which permits preparation of cluster ions at pressures up to ca. 4 Torr and temperatures barely above room temperature.[9] Similar ions also can be prepared in a combined electron impact/chemical ionization source at pressures of ca. 0.2 Torr and source temperatures of 200–250 °C. Therefore, we undertook a study of the adduct ions formed in ketone (acetone, 3-pentanone)/ammonia mixtures and produced them in the two different sources at different temperatures and source pressures. We have used low-energy and high-energy collisional activation as a probe of the ion structures.

The studies soon revealed that the source conditions had no influence on the results obtained. Our initial high-energy CID results for the $M{\cdot}NH_4^+$ adducts were in essential agreement with the results presented by Maquestiau et al.[6] in apparently showing loss of neutrals of 17 and 18 amu from the adduct ion as the main fragmentation processes. However, these results were in sharp contrast with the low-energy CID results for $M{\cdot}NH_4^+$ which showed formation of the NH_4^+ as the dominant fragmentation process. Our initial interpretation[10] of this difference in behavior invoked electronic excitation of the ketone moiety of the $M{\cdot}NH_4^+$

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complex on high-energy collisional activation, thus increasing the proton affinity of the ketone and leading to preferential formation of $MH^+ + NH_3$ upon fragmentation. However, further experimentation led to a much more prosaic explanation of the difference, viz., severe discrimination against detection of low-energy fragment ions in high-energy CID experiments as recorded by the mass analyzed ion kinetic energy spectroscopy (MIKES) technique.[11] The evidence which leads to this conclusion will be presented in the following analysis. In part, this conclusion is derived from studies of the collisionally-induced fragmentation of the adducts with the methylamines and the higher adducts containing two molecules of the amine base or two molecules of the ketone; these results also are presented in the following analysis.

Experimental Section

All experimental work was carried out using a VG Analytical ZAB-2FQ hybrid BEqQ mass spectrometer which has been described in detail previously.[8] Briefly, the instrument is a reversed-geometry (BE) double-focusing mass spectrometer with a third stage consisting of a deceleration lens system, a radio frequency-only (rf-only) quadrupole collision cell, and a quadrupole mass analyzer. Of particular note is the fact that the instrument is equipped with conversion dynodes and off-axis electron multipliers for ion detection following the single-focusing focal point (before the electric sector), following the double-focusing focal point (after the electric sector), and following the quadrupole mass analyzer.

For high-energy collisional activation experiments, the ion of interest was mass selected at 8-keV ion kinetic energy by the magnetic sector and underwent collision with He in a collision cell located at the focal point between the magnetic and electric sectors. The helium pressure was 2×10^{-7} Torr as read by the ionization gauge attached to the pumping line for the region. The fragment ions produced were analyzed according to their kinetic energy by scanning the electric sector (the so-called MIKES technique[11]). An essential feature of the present experiments was the application of a positive voltage, V_c, to the collision cell. The application of this voltage has three effects. First, the kinetic energy of the ions undergoing collisional activation is decreased from zV_a to $z(V_a - V_c)$, where V_a is the ion accelerating voltage and z is the charge on the ion. More important is the effect of the applied voltage on the kinetic energy of the fragment ion, m_2, formed in the fragmentation process

$$m_1^+ \rightarrow m_2^+ + m_3 \qquad (1)$$

For fragmentation reactions occurring outside the collision cell, the fragment ion will be observed at a kinetic energy $(m_2/m_1)zV_a$. However, for fragmentation reactions occurring within the collision cell, the fragment ion m_2^+ will enter the electric sector with a kinetic energy given by

$$KE(m_2^+) = (m_2/m_1)z(V_a - V_c) + zV_c \qquad (2)$$

Thus, fragment ions formed outside the cell (mostly by unimolecular fragmentation reactions) will be separated on the kinetic energy scale from fragment ions formed inside the cell by collision-induced dissociation. Further, the kinetic energy of the fragment ions formed inside the cell will be increased, relative to the situation where no voltage is applied to the cell, and as will be shown below, on our instrument, this leads to an increased efficiency for detection of fragment ions of low kinetic energy.

In the low-energy collisional activation studies, the ions of interest were mass selected by the double-focusing BE segment of the instrument at 6-keV ion energy, decelerated to the appropriate kinetic energy, and introduced into the rf-only quadrupole cell where they underwent collision with N_2 at ion energies in the range 2–50 eV (laboratory scale). The fragment ions produced were mass analyzed by the final quadrupole. The N_2 pressure was 3×10^{-7} Torr as read by the ionization gauge attached to the pumping line for the quadrupole region. In both the high-energy and low-energy CID studies, the output signal was fed to a multichannel analyzer and the results presented represent the accumulation of 15–25 2-s scans.

The adduct ions were prepared in an EI/CI source (operating in the CI mode) by using ammonia or one of the methylamines as the reagent gas and introducing the ketone through a heated inlet line. In these experiments, the source temperature was 200–250 °C, the ionizing electron energy was 100 eV, and the total source pressure was in the range 0.1–0.3 Torr. Alternatively, the adduct ions were prepared in the high-pressure source recently described[9] at a temperature of ca. 40 °C by introducing the appropriate amine containing a trace of the ketone into the source at a total pressure in the range 2–4 Torr. The method of preparation had no effect on the collision-induced dissociation mass spectra obtained. The high-pressure source gave better yields of the higher adducts.

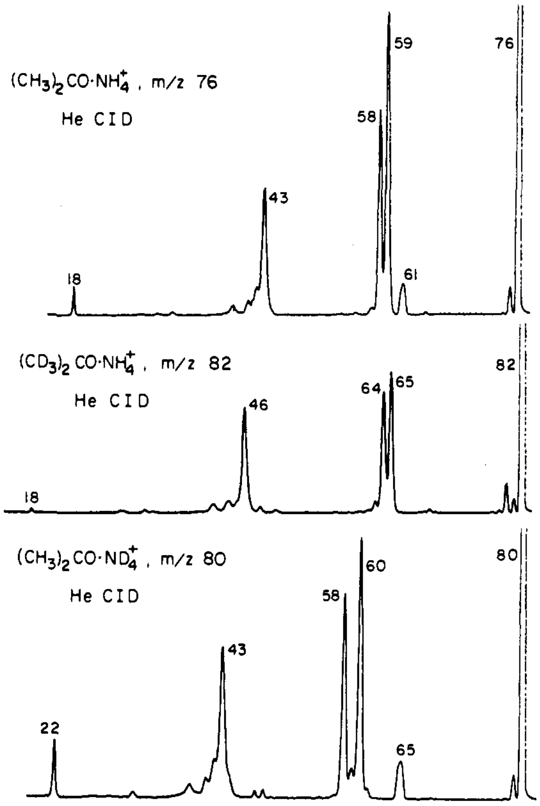

Figure 1. High-energy CID mass spectra of $(CH_3)_2CO{\cdot}NH_4^+$ (top trace), $(CD_3)_2CO{\cdot}NH_4^+$ (middle trace), and $(CH_3)_2CO{\cdot}ND_4^+$ (lower trace). Reactant ions were mass selected at 8-keV ion kinetic energy, and no voltage was applied to the collision cell.

All unlabeled gases were commercial samples of high purity as were the ketones, acetone, and 3-pentanone. Acetone-d_6 was obtained from Aldrich Chemical Co., while ammonia-d_3 was obtained from the Matheson Co.

Results

Our initial experiments showed that we obtained high-energy CID mass spectra in agreement with those reported by Maquestiau et al.[6] irrespective of which source was used (but see below for discussion of the effect of cell voltage on the observed spectra). Our attention then turned to characterizing definitively the ion formed by loss of 18 amu from the $M{\cdot}NH_4^+$ species. Figure 1 shows the high-energy CID mass spectra of the $(CH_3)_2CO{\cdot}NH_4^+$, $(CD_3)_2CO{\cdot}NH_4^+$, and $(CH_3)_2CO{\cdot}ND_4^+$ adducts. The CID spectrum of the unlabeled adduct ion (top trace) shows loss of neutrals of masses 15 (CH_3), 17 (NH_3), and 18 (?) from the adduct ion as well as formation of NH_4^+ in apparent low yield and formation of CH_3CO^+ (m/z 43). For the $(CD_3)_2CO{\cdot}NH_4^+$ adduct (middle trace), losses of neutrals of masses 17 and 18 still are observed, indicating that the hydrogens involved originate entirely from the "ammonium" portion of the adduct ion. Note that loss of methyl is now loss of CD_3 and corresponds also to loss of 18 amu. For the $(CH_3)_2CO{\cdot}ND_4^+$ adduct (bottom trace), losses of neutrals of masses 15 (CH_3), 20 (ND_3 and D_2O (?)), and 22 ((ND_3 + D)/ND_4) clearly are observed. Thus, at least part of the loss of 18 amu in the unlabeled case must correspond to loss of (NH_3 + H)/NH_4. However, elimination of H_2O has not been disproven, since, in the bottom spectrum, elimination of either ND_3 or D_2O will lead to the product of m/z 60. To

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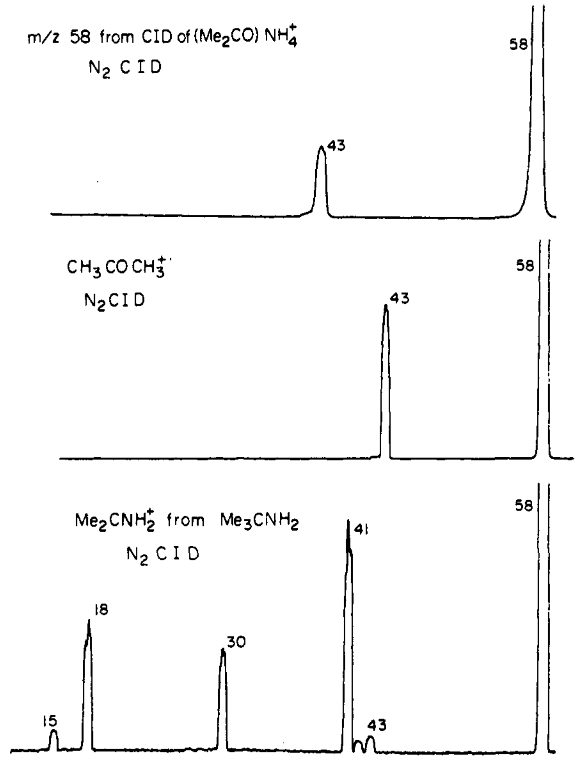

Figure 2. 50-eV CID mass spectra of *m/z* 58 produced from high-energy CID of $(CH_3)_2CO{\cdot}NH_4^+$ (top trace), from ionization of acetone (middle trace), and from dissociative ionization of $(CH_3)_3CNH_2$ (bottom trace).

provide further evidence, the *m/z* 58 ion produced in the high-energy CID of $(CH_3)_2CO{\cdot}NH_4^+$ was transmitted through the electric sector and decelerated and underwent collision with N_2 in the quadrupole cell at 50-eV collision energy. The CID mass spectrum of this ion is shown as the top trace in Figure 2. For comparison, the middle trace shows the 50-eV CID mass spectrum of the acetone molecular ion, while the bottom trace shows the CID mass spectrum of $(CH_3)_2CHNH_2^+$, the species that would be formed by loss of H_2O from the protonated carbinolamine. Clearly, the *m/z* 58 ion formed in the high-energy CID of $(CH_3)_2CO{\cdot}NH_4^+$ is the acetone molecular ion formed by loss of $(NH_3 + H)/NH_4$ from the adduct ion. Further support for this conclusion comes from the high-energy CID mass spectra of the adducts of $CH_3NH_3^+$ and $(CH_3)_2NH_2^+$ with acetone (Figure 3) which show no signal corresponding to loss of H_2O from the adduct ions but do show signals for loss of the neutral amine and the neutral amine plus H.

The elimination of $(NH_3 + H)/NH_4$ (reaction 3) from the adduct ion $M{\cdot}NH_4^+$ in competition with elimination of NH_3 (reaction 4) is surprising, since available thermochemical data[1]

$$(CH_3)_2CO{\cdot}NH_4^+ \rightarrow (CH_3)_2CO^{\cdot+} + (NH_3 + H)/NH_4 \quad (3)$$

$$\rightarrow (CH_3)_2COH^+ + NH_3 \quad (4)$$

indicate that reaction 3 is thermochemically more demanding than reaction 4 by about 450 kJ mol^{-1}. (It should be noted, however, that formation of $NH_4^+ + M$ is the most favorable fragmentation route thermochemically.) The NH_4 species is estimated[12] to be about 41 kJ mol^{-1} more stable than $NH_3 + H$, so even with formation of NH_4, reaction 3 is thermochemically unfavorable. It is not clear, in the present situation, which neutral product(s) is (are) formed. Herzberg[13] has presented spectroscopic evidence that NH_4 is a stable neutral species. In neutralization–reionization[14] experiments, Porter and co-workers[12,15,16] have observed ND_4 to be a stable neutral although neutral NH_4 was not observed; it was concluded that NH_4 dissociated by tunneling.

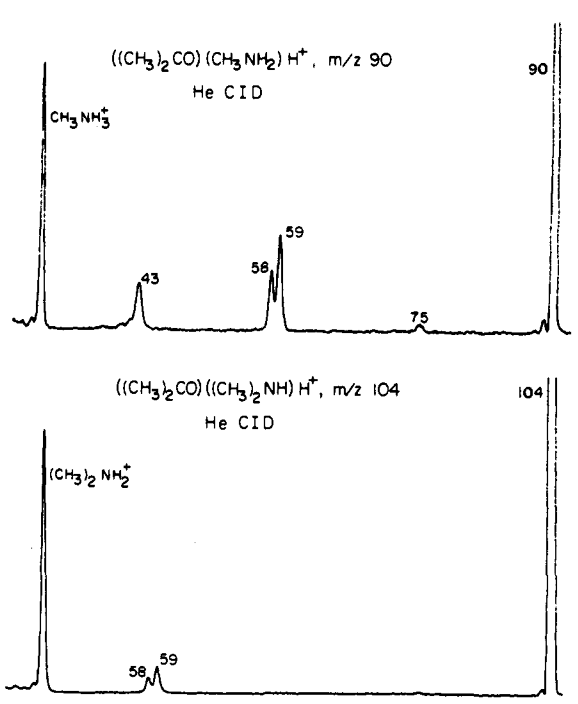

Figure 3. High-energy CID mass spectra of $((CH_3)_2CO)(CH_3NH_2)H^+$ (top trace) and $((CH_3)_2CO)((CH_3)_2NH)H^+$ (bottom trace). Reactant ions were selected at 8-keV ion energy, and no voltage was applied to the collision cell.

While the CID mass spectra of Figure 1 show only a low-intensity signal for NH_4^+/ND_4^+, the signals for the protonated amine are much more prominent in the spectra of Figure 3. Indeed, for $(CH_3)_2CO((CH_3)_2NH)H^+$, the $(CH_3)_2NH_2^+$ ion signal dominates the CID mass spectrum. In the low-energy (50 eV) CID mass spectra of the adducts of ammonia and the methylamines with acetone, only the protonated ammonia/amine ions were observed. Similar results were obtained with the ketone, 3-pentanone. Figure 4 compares the 8-keV and the 50-eV CID mass spectra of the ammonium ion adduct with 3-pentanone. In the former spectrum (top trace), no ammonium ion is observed, while in the 50-eV CID mass spectrum (bottom trace), it is the dominant ion in the spectrum. This discrepancy between the low-energy and high-energy CID results for the ammonium ion adducts led us to carry out high-energy CID experiments in which the positive voltage on the collision cell was varied. We observed that as the voltage on the cell was increased the intensities of the peaks corresponding to elimination of NH_3 and $(NH_3 + H)/NH_4$ from $M{\cdot}NH_4^+$ remained essentially constant, while the peak corresponding to NH_4^+ increased greatly in intensity until the kinetic energy of the NH_4^+ fragment leaving the cell was greater than 3 keV; beyond that point there was no change in relative ion intensities. Figure 5 shows the spectra obtained for the NH_4^+ adducts of acetone and 3-pentanone with +2 kV applied to the collision cell. Clearly, the spectra are much different from those shown in Figures 1 and 4 and now are in agreement with the low-energy CID experiments in showing NH_4^+ as the favored fragmentation product, although there is minor fragmentation

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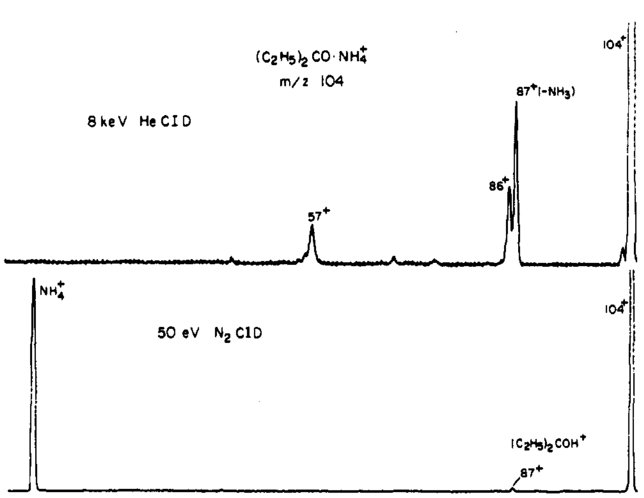

Figure 4. Comparison of 8-keV (top trace) and 50-eV (bottom trace) CID mass spectra of $(C_2H_5)_2CO{\cdot}NH_4^+$. No voltage was applied to the collision cell in high-energy CID experiments.

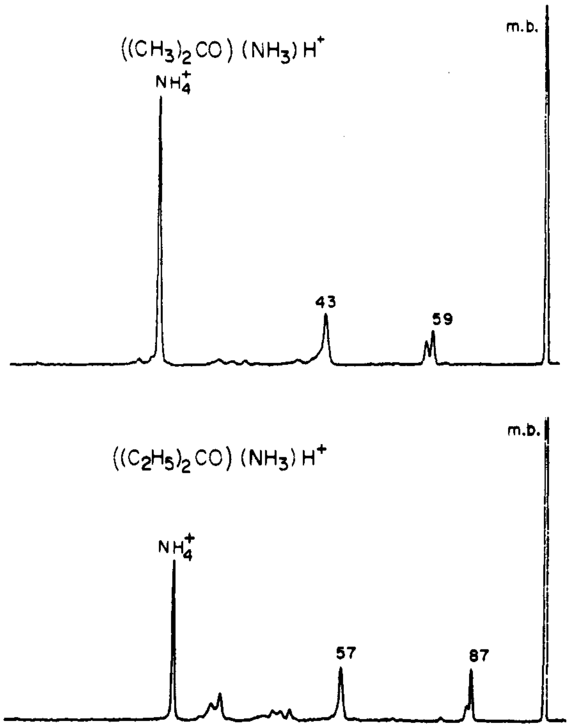

Figure 5. High-energy CID mass spectra of $(CH_3)_2CO{\cdot}NH_4^+$ (top trace) and $(C_2H_5)_2CO{\cdot}NH_4^+$ ions with +2 kV applied to the collision cell. Main beam (m.b.) ions were mass selected at 8-keV ion energy, so collisions in the cell occurred at 6-keV ion energy.

by loss of NH_3 and $(NH_3 + H)/NH_4$. Figure 6 shows similar results for the adducts of protonated methylamine, dimethylamine, and trimethylamine with 3-pentanone. The protonated amine is the only significant fragmentation product; for the dimethylamine and trimethylamine adducts, there is a significant unimolecular fragmentation of the adduct to give the protonated amine. The low-energy CID mass spectra of these adducts showed the protonated amine as the only fragmentation product at laboratory collision energies from 2 to 50 eV.

We also have examined the collision-induced fragmentation of the adducts of 3-pentanone containing two molecules of the amine. Figure 7 shows the high-energy CID mass spectra for $((C_2H_5)_2CO)(NH_3)_2H^+$, $((C_2H_5)_2CO)(CH_3NH_2)_2H^+$, and $((C_2H_5)_2CO)((CH_3)_2NH)_2H^+$ obtained with 1 kV applied to the collision cell. Figures 8–10 show the low-energy CID mass spectra of the same ions in the forms of breakdown graphs expressing the fragment ion abundances as a function of the center-of-mass collision energy.

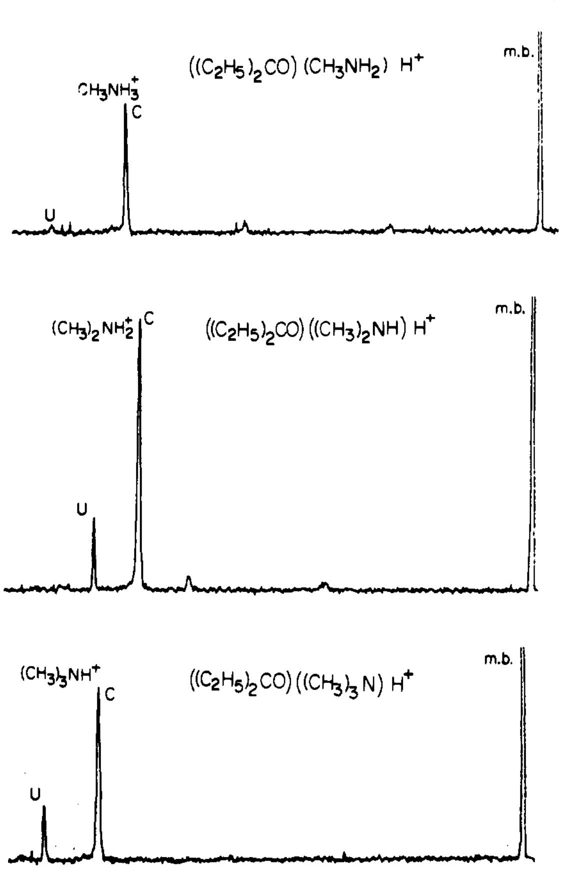

Figure 6. High-energy CID mass spectra of $((C_2H_5)_2CO)(CH_3NH_2)H^+$ (top), $((C_2H_5)_2CO)((CH_3)_2NH)H^+$ (middle), and $((C_2H_5)_2CO)((CH_3)_3N)H^+$ (bottom) with +1 kV on the collision cell. Main beam (m.b.) ions were mass selected at 8-keV ion energy so collisions in the cell occurred at 7-keV ion energy. Fragmentation reactions occurring outside the collision cell (labeled U) are separated in the ion kinetic energy scan from fragmentation reactions occurring inside the collision cell (labeled C).

The high-energy CID mass spectrum of $((C_2H_5)_2CO(NH_3)_2H^+$ (top trace, Figure 7) is in agreement with the results of Maquestiau et al.[6] in showing dominant fragmentation by loss of ammonia. The apparent unimolecular loss of ammonia also is consistent with the observations of Tzeng et al.[7] for the analogous acetone complex. We also observe a significant ion signal for formation of $(NH_3)_2H^+$, consistent with a simple proton-bound structure for the ion. The breakdown graph obtained from the low-energy CID data (FIgure 8) shows that elimination of NH_3 is favored at low collision energies with formation of $(NH_3)_2H^+$ and NH_4^+ increasing in importance as the collision energy increases.

The high-energy CID mass spectrum of $((C_2H_5)_2CO)(CH_3NH_2)_2H^+$ (middle trace of Figure 7) also shows significant fragmentation by loss of a neutral amine molecule: the application of a voltage to the cell shows this fragmentation reaction also occurs unimolecularly. Formation of $(CH_3NH_2)_2H^+$ also is observed as a significant collision-induced fragmentation, consistent with a proton-bound complex structure for the ion. The low-energy CID mass spectra, summarized in Figure 9, show formation of both $((C_2H_5)_2CO)(CH_3NH_2)H^+$ and $(CH_3NH_2)_2H^+$ at the lowest collision energies, with the first product decreasing in importance with a concomitant increase in the yield of $CH_3NH_3^+$ as the collision energy increases.

The high-energy CID mass spectrum of the adduct containing two molecules of dimethylamine (bottom trace, Figure 7) obtained with 1 kV applied to the cell, shows elimination of both a molecule of the ketone and a molecule of the amine in unimolecular reactions; this was confirmed by obtaining the metastable ion

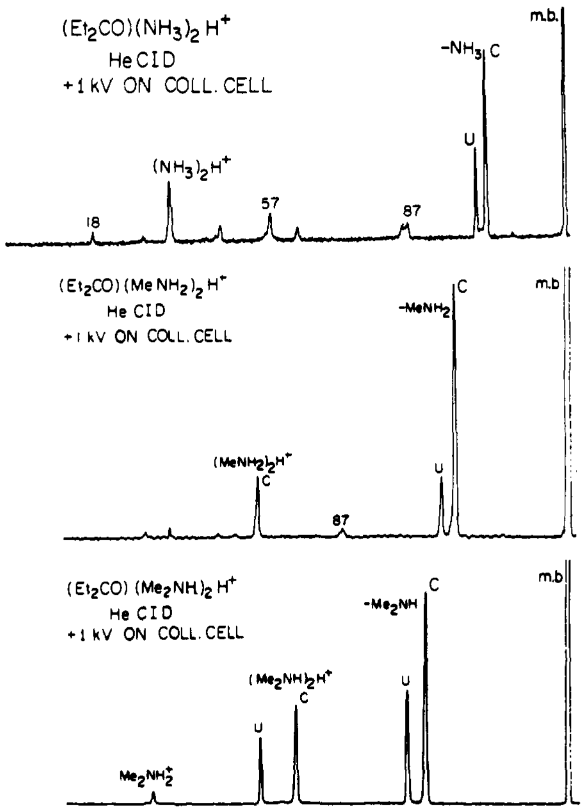

Figure 7. High-energy CID mass spectra of $((C_2H_5)_2CO)(NH_3)_2H^+$ (top), $((C_2H_5)_2CO)(CH_3NH_2)_2H^+$ (middle), and $((C_2H_5)_2CO)((CH_3)_2NH)_2H^+$ (bottom). Main beam ions were selected at 8 keV with +1 kV on the collision cell. Collisions in the cell occurred at 7 keV. For designations of U and C see the caption to Figure 6.

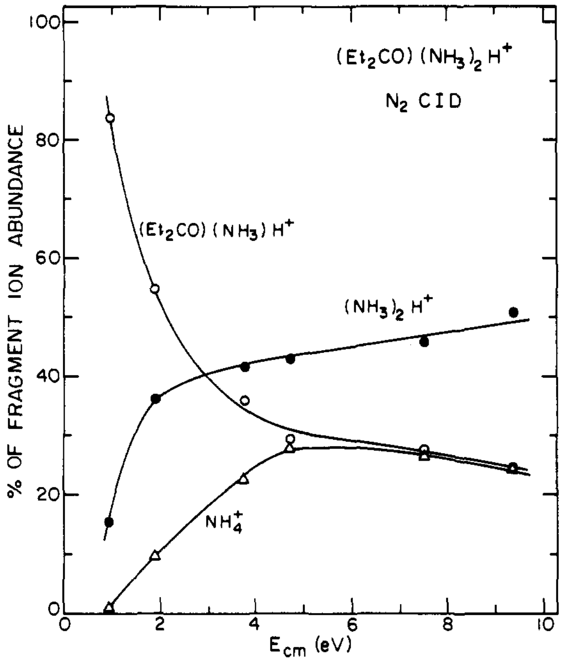

Figure 8. Breakdown graph for $((C_2H_5)_2CO)(NH_3)_2H^+$. E_{cm} is the center-of-mass collision energy.

mass spectrum with no collision gas in the cell. Collisional activation leads to formation of the same two products and to formation of $(CH_3)_2NH_2^+$ in lower yield. The low-energy CID mass spectra, summarized by the breakdown graph of Figure 10, show formation of $((CH_3)_2NH)_2H^+$ and $((C_2H_5)_2CO)((CH_3)_2NH)H^+$ at the lowest collision energies, with the former product in greater yield. With increasing collision energy, the yield of these two products decreases and the lower mass product $(CH_3)_2NH_2^+$ increases in importance.

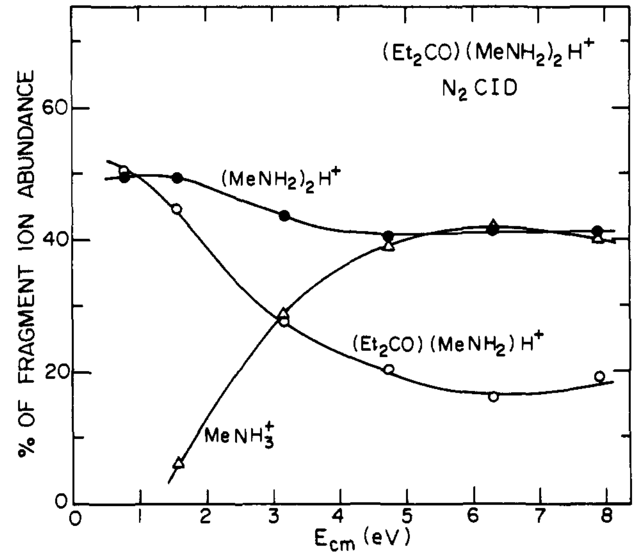

Figure 9. Breakdown graph for $((C_2H_5)_2CO)(CH_3NH_2)_2H^+$. E_{cm} is the center-of-mass collision energy.

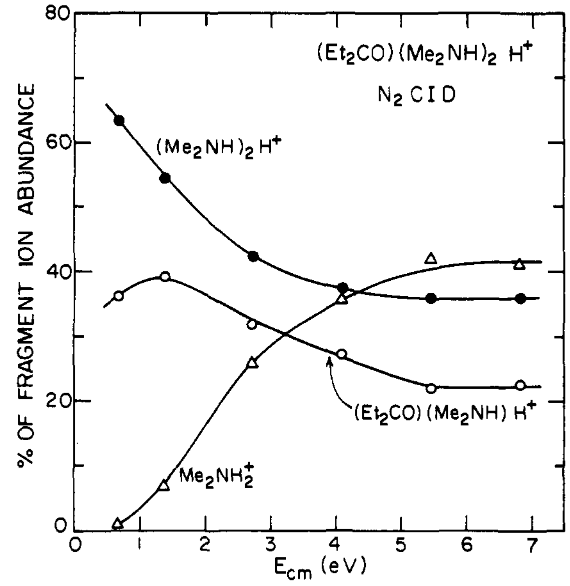

Figure 10. Breakdown graph for $((C_2H_5)_2CO)((CH_3)_2NH)_2H^+$. E_{cm} is the center-of-mass collision energy.

Finally, we also have obtained the CID mass spectra of $((C_2H_5)_2CO)_2(NH_3)H^+$ and $((C_2H_5)_2CO)_2(CH_3NH_2)H^+$. The high-energy CID mass spectra (Figure 11) show the major primary fragmentation channel is loss of a molecule of the ketone, in agreement with the results of Maquestiau et al.[6] and Tzeng et al.,[7] with very minor further fragmentation to form the protonated ketone at *m/z* 87. The low-energy CID mass spectra, summarized as breakdown graphs in Figures 12 and 13, show loss of a molecule of the ketone as the only primary fragmentation reaction with extensive further fragmentation at higher collision energies to form, respectively, the ammonium ion and the protonated amine.

Discussion

Low-energy collision-induced dissociation of the adducts of NH_4^+, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, and $(CH_3)_3NH^+$ with acetone and 3-pentanone all show the protonated amine as the only fragmentation product. This is the result that would be expected from fragmentation of a proton-bound cluster ion since, in each case, the proton affinity of the amine is greater than the proton affinity of the carbonyl compound. In particular there is no need

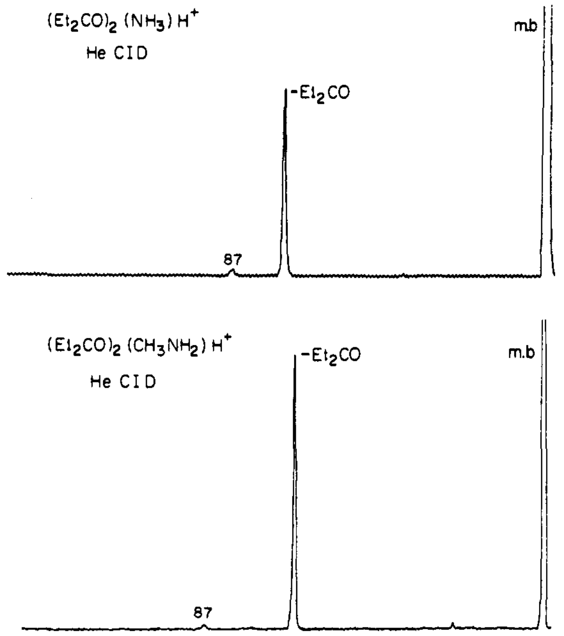

Figure 11. High-energy CID mass spectra of $((C_2H_5)_2CO)_2(NH_3)H^+$ (top) and $((C_2H_5)_2CO)_2(CH_3NH_2)H^+$ at 8-keV collision energy with no voltage applied to the collision cell.

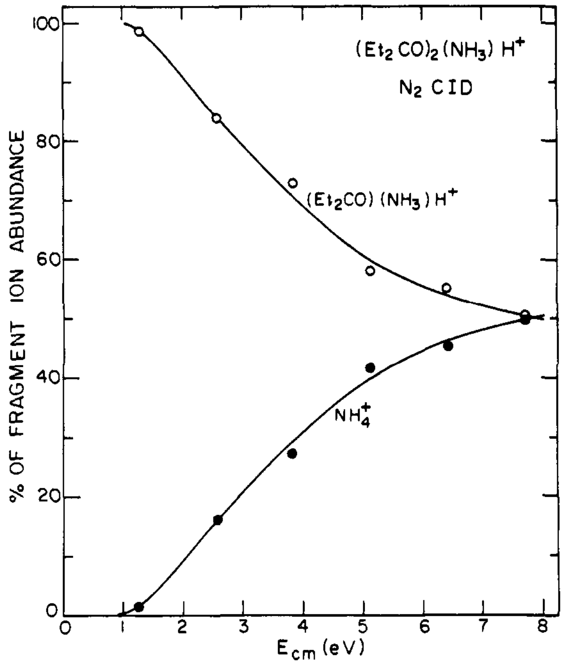

Figure 12. Breakdown graph for $((C_2H_5)_2CO)_2(NH_3)H^+$. E_{cm} is the center-of-mass collision energy.

to postulate addition of the amine to the carbonyl group to form a protonated carbinolamine.

In the same vein, the prominent formation of $(NH_3)_2H^+$, $(CH_3NH_2)_2H^+$, and $((CH_3)_2NH)_2H^+$ in the low-energy CID of the adduct ions containing two molecules of the amine also is more consistent with a proton-bound cluster ion rather than a protonated carbinolamine solvated by a molecule of the amine. The formation of significant yields of the protonated amine in the low-energy CID of the $((C_2H_5)_2CO)_2(NH_3)H^+$ and $((C_2H_5)_2CO)_2(CH_3NH_2)H^+$ ions also is entirely in line with a proton-bound cluster ion rather than a protonated carbinolamine solvated by a molecule of the ketone.

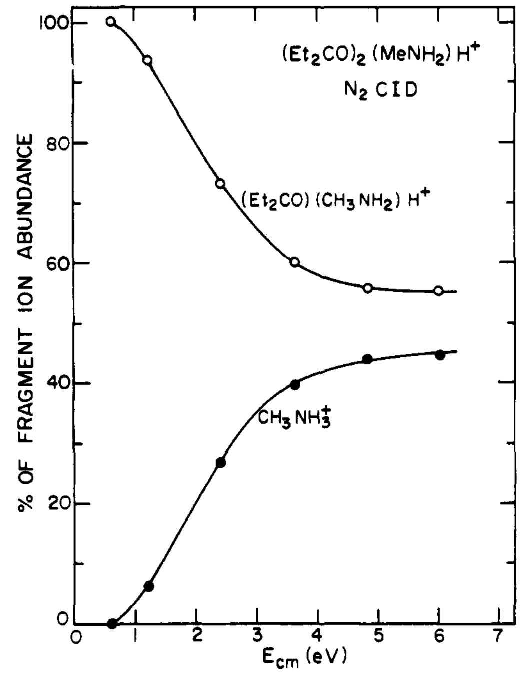

Figure 13. Breakdown graph for $((C_2H_5)_2CO)_2(CH_3NH_2)H^+$. E_{cm} is the center-of-mass collision energy.

The evidence[6] that led to the proposal that the adducts of NH_4^+ with ketones has rearranged to a protonated carbinolamine derived from the report that such adducts, on high-energy collisional activation, fragmented primarily by loss of NH_3 and by loss of a neutral of 18 amu which was assumed to be H_2O. We have shown that this neutral is, in fact, NH_4 or NH_3 + H rather than H_2O. Further, on our instrument, the conclusion that these are the dominant fragmentation pathways following high-energy collisional activation is an instrumental artifact which derives from severe discrimination against low kinetic energy ions detected by the MIKES technique. This artifact can be overcome by applying a voltage to the collision cell, and thus, we believe that Figure 5 represents a truer picture of the high-energy CID mass spectra of the ammonium ion adducts than do the spectra in Figures 1 and 4. We must conclude that the initial report[6] of the high-energy CID mass spectra of the adducts of the ammonium ion with ketones also was influenced by discrimination against low kinetic energy products. Nevertheless, fragmentation by elimination of NH_3 and $NH_4/(NH_3 + H)$ does occur following high-energy collisional activation of these adduct ions and is not observed following low-energy collisional activation. Although similar average internal energies are imparted to ions upon low- and high-energy collisional activation, the distribution of internal energies in high-energy collisional activation includes a high-energy tail.[17] We suggest that it is these highly excited ions which are undergoing the energy-demanding fragmentation by loss of ammonia and $NH_4/(NH_3 + H)$ but that fragmentation is occurring from a proton-bound cluster ion.

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(17) Wysocki, V. H.; Kenttamaa, H. I.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1987**, *75*, 181.