J. Am. Chem. Soc. 1987, 109, 4810-4818

to determine whether the more severe thermal treatment and catalytic reaction at 800 °C was responsible for the improved yield, we prepared used catalysts (20% Na/MgO) in this manner and then quenched them from 750 °C. Again, there was no spectral evidence for $[Na^+O^-]$ centers after quenching or after subsequent irradiation.

A comparison of the catalytic results for Li/MgO, Na/MgO and pure MgO, as depicted in Figure 2, indicates that among the three catalysts Na/MgO was unique in that C_2 selectivity began to develop only at temperatures greater than 675 °C and continued to increase at 700 °C. When the conversion and selectivity are extrapolated to 750 °C, the C_2 yield is about 15%, which is comparable to the value of 16% reported by Aika and co-workers.[11] Similarly a 20% Na/MgO catalyst prepared and operated under the same conditions as employed by the Japanese group gave a C_2 yield of 11% at 750 °C. Since no $[Na^+O^-]$ centers were detected in this material, it appears reasonable that another type of active site was formed, such as $Na^+O_2^-$ which resulted from the decomposition of the Na_2CO_3 phase at the higher temperatures. By contrast, the activity and selectivity patterns obtained for Na/CaO are more similar to Li/MgO (Figure 2) than to Na/MgO,[12] which supports the role of $[M^+O^-]$ centers in the former catalysts.

Thus, although $[M^+O^-]$ centers appear to be involved in the activation of CH_4 on catalysts where the cation size match is appropriate, other centers involving group IA ions may be active, particularly at temperatures >700 °C. Moreover, other catalysts such as La_2O_3 are effective in generating $CH_3^\bullet$ radicals, yet they do not contain group IA ions.[13,14] It should be noted, however, that thermally generated O_2^- ions have been detected on La_2O_3, and this may be the reactive form of oxygen on the lanthanide oxides.[15]

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Generation of the Distonic Ion $CH_2NH_3^{\bullet+}$: Nucleophilic Substitution of the Ketene Cation Radical by Ammonia and Unimolecular Decarbonylation of Ionized Acetamide[†]

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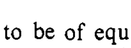
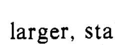
Abstract: The combined application of Fourier-transform ion cyclotron resonance and tandem mass spectrometries, complemented by ab initio MO calculations, provides a relatively detailed description of crucial aspects of the potential energy surface of ionized acetamide ($CH_3CONH_2^{\bullet+}$, **6**) and the complexes formed in ion/molecule reactions of ionized ketene ($CH_2CO^{\bullet+}$, **5**) with ammonia. Both the unimolecular decarbonylation of **6** and the bimolecular substitution of **5** generate the distonic ion $CH_2NH_3^{\bullet+}$, which is fully characterized by proton-transfer reactions and collision-induced dissociations. Although the two fundamentally different reactions are linked by common intermediates, which are suggested to be hydrogen-bridged complexes, there are some distinct differences. The reaction of ammonia with $CH_2CO^{\bullet+}$ to generate $CH_2NH_3^{\bullet+}$ and CO occurs in a region of the potential energy surface which does not result in the formation of hydrogen-scrambled product ions. In contrast, starting from $CH_3CONH_2^{\bullet+}$ the isomerization steps involve intermediates which, prior to the formation of $CH_2NH_3^{\bullet+}$ and CO, permit hydrogen-exchange processes to occur. The enol of ionized acetamide ($CH_2{=}C(OH)NH_2^{\bullet+}$, **8**) is separated by a significant barrier from $CH_3CONH_2^{\bullet+}$. If **8** is internally excited it also dissociates to $CH_2NH_3^{\bullet+}$ and CO, presumably via $CH_3CONH_2^{\bullet+}$. Recent suggestions that nucleophilic substitutions involving radical cations are "forbidden" processes and should therefore have an inherent, low reactivity are not confirmed. The substitution reaction $NH_3 + CH_2{=}C{=}O^{\bullet+} \rightarrow CO + CH_2NH_3^{\bullet+}$ is relatively facile.

Distonic ions[1] such as **1** are species where the charge and radical sites are, in a formal sense, centered at different atoms. Such radical ions have been known in mass spectrometry and radiation chemistry for quite some time.[1d] In the past, distonic ions were often proposed as high-energy, though stable, intermediates to account for specific unimolecular decompositions or rearrangements of radical cations, and only recently they were recognized as species in their own right.[1-3] In the last years these ions have regained experimental interest[1d,2] because calculations[3] predicted some of them to be of equal, if not larger, stability than the corresponding conventional isomers such as **2**.[4]


$\dot{C}H_2-\overset{+}{N}H_3$

1


$CH_3-\overset{+\,\cdot}{N}H_2$

2

[†] Dedicated to Professor Th. J. de Boer on the occasion of his retirement from the University of Amsterdam.

[‡] Berlin.

[⊥] Amsterdam.

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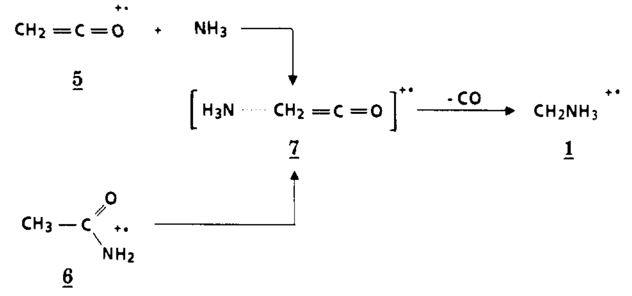
Scheme I



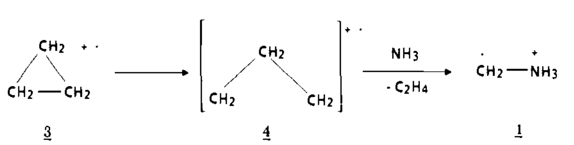
For **1** and **2** Radom et al.[4b–d] found, on the basis of high-level ab initio molecular orbital (MO) calculations, an energy difference of 2 kcal/mol in favor of the distonic ion **1**. Moreover, **1** is predicted[4] to have substantial barriers for rearrangement (42 kcal/mol) and fragmentation processes (48 kcal/mol). The lowest energy decomposition pathway for $CH_2NH_3^{\bullet+}$ has a barrier of 42 kcal/mol and involves hydrogen migration (via **2**), followed by loss of a hydrogen radical to give $CH_2NH_2^+ + H^\bullet$. In fact, there is now compelling theoretical and experimental evidence[1–3] that distonic ions $CH_2XH^{\bullet+}$ (X = NH_2, OH, F, PH_2, SH, Cl) do exist as stable species.

In contrast, the neutral counterparts $^-CH_2X^+H$ (the so-called ylides) are very often unknown; this holds in particular for those ylides for which X corresponds to a molecular fragment containing a first-row element and which are better described as weak complexes of methylene with the polar molecule XH.[5]

There exist several ways[1d,2] to generate ions like **1**. A quite convenient route involves dissociative ionization of suitable precursors, whose unimolecular decomposition (loss of small, stable molecules like CO, C_2H_4, CH_2O, etc.) may be accompanied by hydrogen rearrangement. An example is given in eq 1.[6] Loss of formaldehyde from ionized 2-aminoethanol generates the methyleneammonium ylidion **1**.

$$\overset{+\bullet}{HOCH_2CH_2NH_2} \longrightarrow \underset{\mathbf{1}}{\overset{\bullet}{C}H_2-\overset{+}{N}H_3} + CH_2O \qquad (1)$$

Another route to generate distonic ions involves ion/molecule reactions, for example, in the case of ion **1**, by reaction of the radical cation of cyclopropane **3** with NH_3 under expulsion of ethylene (eq 2).[7] The reactive form of ionized cyclopropane is supposed to be the ion **4**, which can also be viewed as a vibrationally excited form of the one-electron-bond structure of **3**.[8]



(2)

In this paper we describe two novel routes (Scheme I) to generate ion **1**. These involve (i) the ion/molecule reaction of ionized ketene **5** with neutral NH_3 and (ii) the unimolecular decarbonylation of ionized acetamide **6**.[9] Moreover, we will demonstrate that both the bimolecular reaction $CH_2CO^{\bullet+} + NH_3 \rightarrow \mathbf{1} + CO$ and the unimolecular process $CH_3CONH_2^{\bullet+} \rightarrow \mathbf{1} + CO$ do proceed via the same central intermediate (**7** and isomers thereof). Attention will be drawn to the fact that the gas-phase chemistry of **6** represents another example for the *increasing role hydrogen-bridged intermediates play in unimolecular processes*.[11] And, last but not least, our study is directly related to the recently raised question: "Can nucleophiles attack radical cations directly?".[12] This problem has been analyzed by using elements of the configuration mixing model,[13] and not withstanding gas-phase experimental data which point to the contrary[14] it was concluded[12] that the reaction of a nucleophile, like NH_3, with a radical cation, like ionized ketene **5**, is a "forbidden" process and

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cannot lead to nucleophilic substitution. The theoretical analysis[12] was in part inspired by the extensive experimental findings on the reactions of nucleophiles (Nu) with cation radicals ($A^{\bullet+}$) in solution, which in contrast to polar reactions of closed-shell/closed-shell systems are very often characterized by a relatively low reactivity, as noted by Eberson.[15d] An explanation was provided by Parker,[15a,b] who suggested that the low reactivity in the half-regeneration mechanism (3) may be due to a disproportionation of the radical cation $A^{\bullet+}$ to a dication A^{2+} and a neutral A. While such a disproportionation may take place in solution (although the disproportionation constant of the reaction $2A^{\bullet+} \rightarrow A^{2+} + A$ is as small as ca. 10^{-9}),[12] such a process most certainly does not occur in the gas phase, as dications are extremely unstable thermochemically.[16] Moreover, the products formed by reactions of Nu with A^{2+} could in the gas phase easily be distinguished from those obtained from reaction 3.

$$A^{\bullet+} + \mathrm{Nu} \rightarrow (A\text{-}\mathrm{Nu})^{\bullet+} \rightarrow \text{products} \qquad (3)$$

According to Pross,[12] the low reactivity for reaction 3 is due to the fact that direct nucleophilic attack on the radical cation in terms of the configuration mixing model would generate a *doubly excited* intermediate and should therefore be a high-energy process. We will demonstrate that this generalization cannot account for the reactions described in Scheme I. Our experimental findings, which are based on experiments using Fourier-transform ion cyclotron resonance (FTICR[17]) and tandem mass spectrometry methodologies (MSMS[18]), are complemented by ab initio MO calculations.

Experimental Section

The FTICR experiments were performed on a home-built instrument described in detail in ref 19. Low-pressure conditions were used to suppress charge exchange with diketene and proton transfer of the ketene radical cation to diketene. The latter was used as a precursor to generate ionized ketene. Low-pressure conditions also had to be applied in order to prevent proton transfer of the distonic ions formed to ammonia. Typical pressures wer 6×10^{-6} Pa for diketene and 2×10^{-6} Pa for ammonia. The S/N ratio was improved by a relatively long duration of the electron beam pulse (20 ms) and signal averaging by accumulation of ca. 600 transients prior to Fourier transformation. The ketene radical cation was generated by 40-eV electron-impact ionization of diketene. To suppress ionization of He, which was used as a collision gas in collision-induced dissociation (CID) experiments,[20] the electron energy was reduced to 20 eV. Positive ions were trapped in the cubic FTICR cell (15.6 cm^3) at a magnetic field of 1.1 T by application of a small positive potential (+1 V) to the trapping plates. Immediately after the electron beam pulse, the ketene radical cation was isolated by creation of a notch in the wave form of a relatively slow excitation pulse (scan speed 68 kHz × ms^{-1}).[21] After a typical 200-ms reaction time, the product ion of the ion/molecule reaction of ionized ketene with ammonia, i.e., the ion $CH_5N^{\bullet+}$, was isolated and its reaction with neutral molecules studied. Typical pressures of these neutrals were 3×10^{-5} Pa. CID experiments were performed with He as collision gas with an additional pressure of 9×10^{-5} Pa. A short, but intense, radio-frequency pulse at the cyclotron frequency of the ions was used (0.02-ms duration, 10-V peak) to excite the ions translationally.

The unimolecular chemistry of acetamide was probed by using a Vacuum Generator ZAB-HF-3F mass spectrometer. This is a triple-sector instrument of B(1)EB(2) configuration (B magnetic and E electric sector), whose performance is described in detail in ref 11r and 22. Briefly, ions are generated by 70-eV electron-impact ionization (ion trap current 100 μA, accelerating voltage 8 kV). Ions of 8-keV kinetic energy are mass selected by using B(1)E (at a mass resolution of 1000–3000 for the primary ion beam), and their unimolecular dissociations are recorded by scanning B(2). Spectra in the range of 10–100 were accumulated by using the Vacuum Generator 250/11 data system. CID spectra of the decarbonylation product of $CH_3CONH_2^{\bullet+}$, i.e., $CH_5N^{\bullet+}$, were recorded by mass selecting the metastable ion, m*, of this process and then subjecting this ion to collisional activation with He as the collision gas. Kinetic energy release, *T*, data were observed for ions dissociating unimolecularly in the field-free region between B(1) and E and recorded by scanning E (MIKE methodology[23]). The ZAB-HF-3F instrument was also used to perform some preliminary[24] low-energy collision experiments of $CH_5N^{\bullet+}$ generated from $CH_3CONH_2^{\bullet+}$. To this end $CH_5N^{\bullet+}$ ions, mass selected by B(1), were decelerated to ca. 15-eV kinetic energy (laboratory energy) and reacted with CO in a collision chamber located in the second field-free region (CO pressure ca. 4×10^{-2} Pa). After reacceleration, the resulting ionic products of the ion/molecule reactions were energy selected by E and recorded by scanning B(2).

The ab initio MO calculations were performed by using the GAUSSIAN 82 program.[25] Geometries were optimized with the split-valence 3-21G basis set.[26] Single-point calculations were performed with the 6-31G-(d,p) basis set.[27] (The notation 6-31G(d,p) is identical with Pople's 6-31G** notation; we prefer, however, the former one, which is more informative.) The effects of electron correlation were accounted for by Møller–Plesset perturbation theory[28] terminated at third order (MP3). Open-shell systems were treated with the unrestricted UHF formalism.[29] Stationary points were rigorously characterized by analyzing the harmonic force constant matrix at the 3-21G//3-21G level of theory (minima zero and transition structures (TS) one negative eigenvalue). Zero-point energies (ZPE) were obtained at the same level of theory and corrected by 10% in order to account for the overestimation of the vibrational frequencies.[30] In the discussion we refer (if not otherwise stated) to the following level of theory: MP3/6-31G-(d,p)//3-21G + ZPE.

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Scheme II

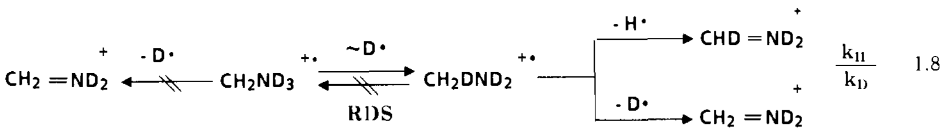


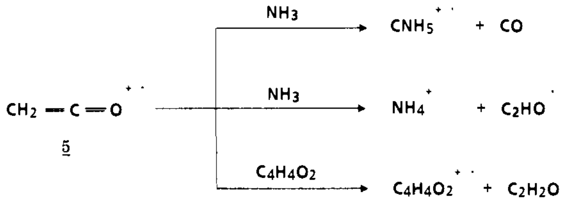
Table I. Collision-Induced $H^{\bullet}/D^{\bullet}$ Loss from $CH_2ND_3^{\bullet+}$ (m/z 34) as a Function of Trapping Time in FTICR[a,b]

t, ms	loss of, % $H^{\bullet}$	loss of, % $D^{\bullet}$
50	78	22
100	78	22

[a] Abundances are normalized to 100%. [b] Due to nonreactive translational–translational energy exchange, the translational excitation of $CH_2ND_3^{\bullet+}$ is damped out relatively fast, which may explain why there is no measurable effect on the lossess of $H^{\bullet}/D^{\bullet}$ as a function of time. Moreover, the ratio of the ion intensities m/z 34/(m/z 33 + m/z 32) is also relatively insensitive to the trapping time. The ratio corresponds to 0.87 at 50 ms and 0.84 at 100 ms.

Results and Discussion

Under FTICR conditions ionized ketene **5** is found to undergo with neutral ammonia two processes (eq 4 and 5), i.e., CO substitution accompanied by the formation of $CNH_5^{\bullet+}$ (m/z (calcd) 31.0422 dalton; m/z (measured) 31.0422 ± 0.0002 dalton) and proton transfer to NH_3 to give NH_4^+. A third process (eq 6) of **5** corresponds to charge exchange with diketene to give $C_4H_4O_2^{\bullet+}$.



$$CH_2=C=O^{+\bullet} \xrightarrow{NH_3} CNH_5^{+\bullet} + CO \quad (4)$$
$$CH_2=C=O^{+\bullet} \xrightarrow{NH_3} NH_4^{+} + C_2HO^{\bullet} \quad (5)$$
$$CH_2=C=O^{+\bullet} \xrightarrow{C_4H_4O_2} C_4H_4O_2^{+\bullet} + C_2H_2O \quad (6)$$

5

The structure of the ion $CNH_5^{\bullet+}$ has been probed by further ion/molecule reactions of the isolated species. Upon reaction with ammonia, $CNH_5^{\bullet+}$ transfers a proton to generate NH_4^+; the same process is observed for authentic $CH_2NH_3^{\bullet+}$, **1**, generated according to eq 2.[7] If in reaction 4 NH_3 is replaced by ND_3, the resulting $CNH_2D_3^{\bullet+}$ ions specifically transfer a deuterium in the further reaction with ammonia; i.e., a reversible interconversion between ion structures **1** and **2** does not take place.

Thus, we conclude that the gas-phase substitution of CO (of ionized ketene **5**) by NH_3 results in the formation of the methyleneammonia ion $CH_2NH_3^{\bullet+}$, **1**. We stress, with regard to the experiments to be described below, that the labeling experiment proves that (i) replacement of CO by ND_3 is not accompanied by H/D scrambling and (ii) the NH protons of $CH_2NH_3^{\bullet+}$ are more acidic than the CH protons.[42]

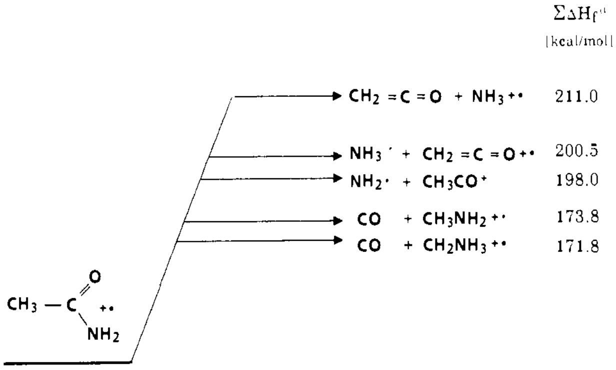
Ion/molecule reactions of $CH_2NH_3^{\bullet+}$ with electrophilic neutrals, aimed at probing the *radical site* of **1**, were also tried. However, in contrast to other systems,[31] no processes were observed under the described experimental FTICR conditions, for example, with NO (eq 7), bromine, phenyl bromide, and phenyl chloride.

$$CH_2NH_3^{\bullet+} + NO \rightarrow CH_2NO^+ + NH_3 \quad (7)$$

The reverse of reaction 4, i.e., regeneration of ionized ketene by reacting $CH_2NH_3^{\bullet+}$ with CO, could not be detected either under the applied FTICR conditions but was observed in beam experiments (see below).

Collision-induced dissociations were used to characterize the $CNH_5^{\bullet+}$ ions. In contrast to the beam experiment, where high kinetic energy (3-8 keV) collisions are employed, under FTICR the kinetic energy is much smaller (typically, under our experimental conditions, ca. 0.1 keV). If the isolated $CH_2ND_3^{\bullet+}$ ions (generated from **5** and ND_3) are translationally excited via the application of appropriate radio-frequency pulses[32] we observe collision-induced losses of both $H^{\bullet}$ and $D^{\bullet}$. The data given in Table I differ substantially from a ratio predicted for statistical losses of $H^{\bullet}$ and $D^{\bullet}$; this would correspond to 40% loss of $H^{\bullet}$ and 60% loss of $D^{\bullet}$ ignoring the operation of any kinetic isotope effects.

Scheme III



The experimental data can be explained by assuming that $CH_2ND_3^{\bullet+}$ does not split off directly $H^{\bullet}$ or $D^{\bullet}$ but first rearranges to $CH_2DND_2^{\bullet+}$ as suggested by theory.[4] The CH_2D group of the latter then serves as an immediate "source" for the losses of both $H^{\bullet}$ and $D^{\bullet}$. This mechanism (Scheme II) has two implications, which are fully in line with the theoretical predictions of Bouma et al.:[4b] (i) The isomerization $CH_2ND_3^{\bullet+} \rightarrow CH_2DND_2^{\bullet+}$ constitutes the rate-determining step (RDS); the reaction is irreversible. (ii) Losses of $H^{\bullet}/D^{\bullet}$ from the internally excited intermediate $CH_2DND_2^{\bullet+}$ are associated with a kinetic isotope effect. From the data, reported in Table I, we calculate an isotope effect $k_H/k_D = 1.8$. We should mention that, while *direct loss* of $H^{\bullet}$ from $CH_2ND_3^{\bullet+}$ is out of the question as it would generate the highly energetic species HC^+NH_3, an additional pathway of direct loss of $D^{\bullet}$ from unrearranged $CH_2ND_3^{\bullet+}$ to generate $CH_2{=}ND_2^{\bullet+}$ cannot be excluded on principal grounds. If this, however, would be the case, the "real" isotope effect affecting losses of $H^{\bullet}/D^{\bullet}$ from intermediate $CH_2DND_2^{\bullet+}$ would then be larger than the value of 1.8 mentioned above. However, as stated previously the ab initio calculations of Bouma et al.[4b] predict that direct loss of $H^{\bullet}$ from $CH_2NH_3^{\bullet+}$ would require at least 6 kcal/mol more energy than isomerization of $CH_2NH_3^{\bullet+}$ to $CH_3NH_2^{\bullet+}$.

Metastable $CH_3CONH_2^{\bullet+}$ ions (m/z 59) produce in the third field-free region of the tandem mass spectrometer ZAB-HF-3F the products described in Table II. For comparison, we also give the corresponding data for the enol of acetamide, i.e., $CH_2{=}C(OH)NH_2^{\bullet+}$ (**8**); this ion can be conveniently generated via a McLafferty rearrangement of the amide of n-hexanoic acid. From the data reported in Table II we conclude, in passing, that **6** and **8** must be separated by a substantial barrier which prevents facile isomerization **6** $\rightleftarrows$ **8**. This result is in line with observations on many other ionized keto/enol tautomers.[33]

In the following we will not discuss all unimolecular processes described in Table II but will rather focus on the unimolecular decarbonylation of $CH_3CONH_2^{\bullet+}$ and its relation to the *ion/molecule reactions* of $CH_2CO^{\bullet+}$ with NH_3 mentioned above. Loss of CO to generate $CH_5N^{\bullet+}$ constitutes the most favored decomposition reaction of $CH_3CONH_2^{\bullet+}$. In fact, simple thermochemical considerations would predict that this reaction is indeed

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Table II. Unimolecular Dissociations of Metastable $CH_3CONH_2^{\bullet+}$, **6**, and Its Enol $CH_2{=}C(OH)NH_2^{\bullet+}$, **8**[a]

dissociation products of m/z 59	precursor: $CH_3CONH_2^{\bullet+}$, **6** rel abundances, %	$CH_3CONH_2^{\bullet+}$, **6** $T_{0.5}$, meV	$CH_2{=}C(OH)NH_2^{\bullet+}$, **8** rel abundances, %	$CH_2{=}C(OH)NH_2^{\bullet+}$, **8** $T_{0.5}$, meV
$CH_3^{\bullet} + CH_2NO^+$ (m/z 44)	13.0	11 ± 1	54.3	21 ± 2
$NH_2^{\bullet} + C_2H_3O^+$ (m/z 43)	2.1	30 ± 2	25.2	26 ± 3
$NH_3 + C_2H_2O^{\bullet+}$ (m/z 42)	0.6	40 ± 8	2.4	37 ± 1
$CO + CH_5N^{\bullet+}$ (m/z 31)	74.1	200 ± 5	13.6	231 ± 9
$C_2HO^{\bullet} + NH_4^+$ (m/z 18)	10.2	18 ± 2	4.8	24 ± 2

[a] Abundances (peak areas) are normalized to 100%. Spectra were recorded in the third field-free region. The kinetic energy release, $T_{0.5}$, data refer to dissociations occurring in the second field-free region.

favored energetically over its many competing processes, some of which are mentioned in Scheme III, together with the sum of the heats of formation of the products.[34]

What is the structure of the $CH_5N^{\bullet+}$ ions generated from $CH_3CONH_2^{\bullet+}$? Is it the distonic ion $CH_2NH_3^{\bullet+}$ (**1**) or ionized methylamine $CH_3NH_2^{\bullet+}$ (**2**)? Although the thermochemical data favor the former by ca. 2 kcal/mol (Scheme III), this difference does not prove the formation of **1**, as the generation of the $CH_5N^{\bullet+}$ products might be associated with barriers of different magnitudes. Moreover, the formation of $CH_2NH_3^{\bullet+}$ from $CH_3CONH_2^{\bullet+}$ requires an isomerization step (hydrogen migration onto the nitrogen).

An unambiguous structure assignment is, however, provided by the high-energy collision-induced reactions of mass-selected $CH_5N^{\bullet+}$. The CID spectra of $CH_3NH_2^{\bullet+}$ (generated via electron-impact ionization of CH_3NH_2HCl) and of $CNH_5^{\bullet+}$ generated either from $HOCH_2CH_2NH_2^{\bullet+}$ (via loss of CH_2O[6a]) or from $CH_3CONH_2^{\bullet+}$ (**5**) are reported in Figure 1. A comparison of the spectra leaves no doubt that the $CH_5N^{\bullet+}$ species formed from $CH_3CONH_2^{\bullet+}$ are distinct from ionized methylamine ($CH_3NH_2^{\bullet+}$) but have a CA spectrum very close to that of $CH_5N^{\bullet+}$ generated from $HOCH_2CH_2NH_2^{\bullet+}$. The latter precursor has been shown to generate the distonic ion $CH_2NH_3^{\bullet+}$.[6a,b] Note in particular the sharp signal at m/z 15.5 which corresponds to the charge-stripping reaction[37] $CH_5N^{\bullet+} \rightarrow CH_5N^{2+}$; this process is much more favored for the distonic ion $CH_2NH_3^{\bullet+}$ than for its conventional isomer $CH_3NH_2^{\bullet+}$.[6] Moreover, the CA mass spectra reported in Figure 1 also reflect the structural differences between the two $CH_5N^{\bullet+}$ isomers; see, for example, the structure-diagnostic intensity differences of the ions at m/z 14 ($CH_2^{\bullet+}$) and 15 (CH_3^+). At this point it should also be noted that $CH_3CONH_2^{\bullet+}$ is much better suited as a precursor to generate $CH_5N^{\bullet+}$ than $HOCH_2CH_2NH_2^{\bullet+}$, as the latter cogenerates the isobaric CH_3O^+ ion.

The fact that the same product, i.e., $CH_2NH_3^{\bullet+}$, is generated via two fundamentally different processes (substitution of CO by NH_3 from $CH_2{=}CO^{\bullet+}$ vs. unimolecular decarbonylation of $CH_3CONH_2^{\bullet+}$) suggests that common intermediates, **7** (Scheme I) or isomers thereof, *may link the ion/molecule reactions in the* $[CH_2{=}C{=}O/NH_3]^{\bullet+}$ *system with the unimolecular chemistry of* $CH_3CONH_2^{\bullet+}$. While this is indeed the case (see below), there are, however, distinct differences which shed further light on the details of the potential energy surface. As already mentioned, reaction of ND_3 with $CH_2{=}C{=}O^{\bullet+}$ gives pure $CH_2ND_3^{\bullet+}$. This indicates that the excess internal energy of the ion/molecule complex $(NH_3/CH_2CO^{\bullet+})^*$ is not more than the energy of the intermediate structures for H/D exchange. A different behavior is, however, observed for those $CD_3CONH_2^{\bullet+}$ ions which undergo loss of CO in the beam experiment; the resulting $CH_2D_3N^{\bullet+}$ ions, when subjected to collisions (10–15 eV of laboratory energy) with CO, eliminate NH_2D (62.9%), NHD_2 (33.3%), and ND_3 (3.8%), respectively. Obviously, decarbonylation of $CD_3CONH_2^{\bullet+}$ involves intermediates which enable the system to partially equilibrate the H/D atoms in the course of this reaction. (A complete exchange of H and D would correspond to losses of NH_2D (30%), NHD_2 (60%), and ND_3 (10%), respectively.)[43] Moreover, the region of the potential energy surface containing the starting ion $CH_3CONH_2^{\bullet+}$ must be separated by a barrier, significantly large enough to prevent the $[ND_3/CH_2{=}C{=}O]^{\bullet+}$ system from an efficient communication with the intermediates initially generated from $CD_3CONH_2^{\bullet+}$.

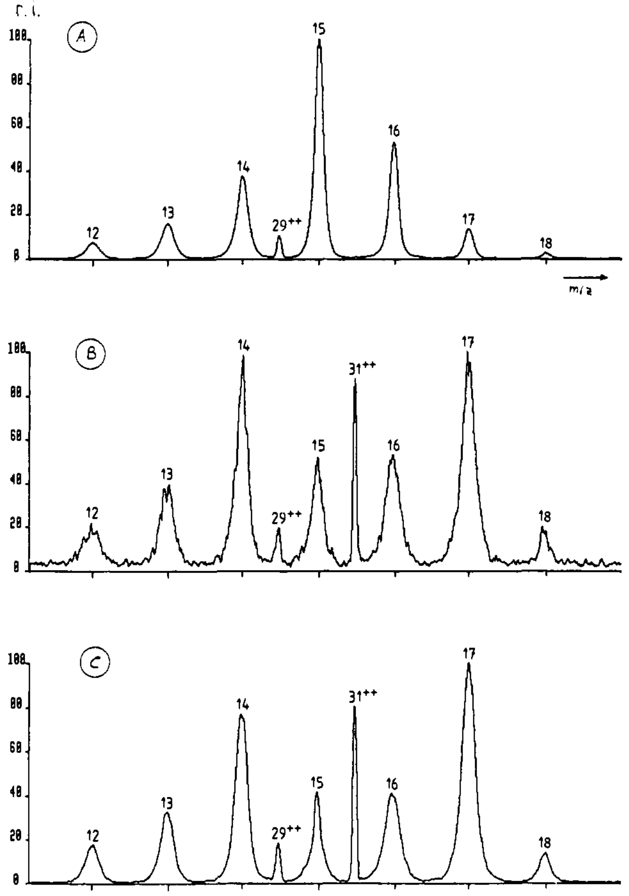

Figure 1. Collisional activation mass spectra of $CH_5N^{\bullet+}$ ions generated form several precursors: A, $CH_3NH_2HCl^{\bullet+}$ (loss of HCl); B, $HOCH_2CH_2NH_2^{\bullet+}$ (loss of CH_2O); C, $CH_3CONH_2^{\bullet+}$ (ion source decarbonylation). The CA mass spectrum of $CH_5N^{\bullet+}$ generated from metastably dissociating $CH_3CONH_2^{\bullet+}$ is practically identical with the CA mass spectrum given under C.

How does the potential energy surface look in these two regions, and what are the most likely pathways connecting them? Answers to these questions cannot be provided by experiments, but they may be accessible by ab initio MO calculations. We are fully aware that the size of the system does not permit us to explore

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(34) The following thermochemical data (in kcal/mol) were used. CO, -27.2[35a] $CH_2NH_3^{\bullet+}$, 199,[4b,6b] $CH_3NH_2^{\bullet+}$, 201[4d,6b] $NH_2^{\bullet}$, 41;[35a] CH_3CO^+, 157;[36] NH_3, -9.3[35a] $CH_2{=}C{=}O^{\bullet+}$, 209.8;[35a,b] $CH_2{=}C{=}O$, -11.4[35b] $NH_3^{\bullet+}$, 225.[35a]

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Table III. Total Energies (in hartrees) and Zero-Point Energies[a] (ZPE in kcal/mol)

species	3-21G//3-21G	6-31G(d,p)//3-21G	MP2/6-31G(d,p)//3-21G	MP3/6-31G(d,p)//3-21G	ZPE//3-21G
8	−206.543 71	−207.713 78	−208.295 54	−208.321 47	44.0
6	−206.534 71	−207.697 64	−208.262 84	−208.295 73	44.2
9	−206.480 70	−207.649 56	−208.233 34	−208.253 97	41.6
10	−206.473 96	−207.631 85	−208.219 42	−208.238 41	39.7
11	−206.484 55	−207.645 13	−208.256 80	−208.271 83	45.1
12	−206.501 60	−207.669 33	−208.272 47	−208.291 12	45.0
TS **8/6**	−206.444 03	−207.612 12	−208.212 15	−208.234 59	40.8
TS **6/9**	−206.478 89	−207.651 42	−208.232 91	−208.254 13	39.8
TS **9/10**	−206.470 97	−207.627 87	−208.221 42	−208.239 04	37.7
TS **10/11**	−206.463 39	−207.624 54	−208.213 29	−208.232 15	40.9
TS **11/12**	−206.483 83	−207.641 89	−208.254 89	−208.270 26	45.5
TS **12/1**	−206.489 10	−207.654 82	−208.251 86	−208.271 50	43.0
$CH_2CO^{\bullet+}$	−150.569 21	−151.427 76	−151.826 50	−151.833 62	18.6
CH_3CO^+	−151.201 31	−152.064 01	−152.497 67	−152.503 71	26.9
$CH_2NH_3^{\bullet+}$ (**1**)	−94.417 30	−94.944 10	−95.237 17	−95.262 44	41.7
NH_3	−55.872 20	−56.194 03	−56.381 05	−56.393 78	20.1
$NH_2^\bullet$	−55.245 38	−55.564 39	−55.709 66	−55.725 39	10.9
CO	−112.093 30	−112.737 26	−113.020 13	−113.018 37	2.9

[a] Scaled by 0.89.

Table IV. Relative Energies (in kcal/mol) for Some $C_2H_5NO^{\bullet+}$ Isomers and Reaction Products

species	3-21G// 3-21G	6-31G(d,p)// 3-21G	MP2/6-31G(d,p)// 3-21G	MP3/6-31G(d,p)// 3-21G	MP3/6-31G(d,p)// 3-21G + ZPE
8	0	0	0	0	0
6	5.7	10.2	20.6	16.2	16.4
9	39.6	40.4	39.1	42.4	40.0
10	43.8	51.5	47.8	52.2	47.9
11	37.2	43.2	24.4	31.2	32.3
12	26.5	27.9	14.5	19.1	20.1
$CH_2CO^{\bullet+} + NH_3$	64.3	57.8	55.3	59.1	53.8
$CH_3CO^+ + NH_2^\bullet$	61.0	53.7	55.4	58.1	51.9
$CH_2NH_3^{\bullet+} + CO$	20.8	20.4	24.0	25.6	26.2
TS **8/6**	62.7	64.0	52.4	54.6	51.4
TS **6/9**	40.7	39.2	39.4	42.3	38.1
TS **9/10**	45.8	54.0	46.6	51.8	45.0
TS **10/11**	50.5	56.1	51.7	56.1	53.0
TS **11/12**	37.6	45.2	25.6	32.2	33.7
TS **12/1**	34.3	37.1	27.5	29.3	28.3

the *complete* potential energy surface of $CH_5N^{\bullet+}$ at a sufficiently high level of theory. We are, however, encouraged by previous experimental/theoretical studies[38] that at least a *qualitative insight* can be obtained concerning the chemically most feasible pathways of the system in question, provided that a split-valence basis set is employed for geometry optimizations and that the final energy comparisons include the effects of polarization functions and of correlation energies. We think that the level of theory used (MP3/6-31G(d,p)//3-21G + ZPE) suffices to serve this function.

The total and zero-point energies of minima and transition structures (TS) relevant in the present context are given in Table III, relative energies are reported in Table IV, and structural data (bond lengths in angstroms, bond angles in degrees) are given in Chart I.

As already mentioned in the discussion of the experimental results, one of the key questions is concerned with the rearrangement of **6** to give eventually species of the general structure **7** (complexes of NH_3 with $CH_2{=}C{=}O^{\bullet+}$), from which CO may be expelled to generate $CH_2NH_3^{\bullet+}$. The energetic requirement of these multistep reactions should be comparable with or smaller than the energy required to dissociate $CH_3CONH_2^{\bullet+}$ directly to $CH_3CO^+ + NH_2^\bullet$. At the 3-21G//3-21G level of theory we locate a pathway by which $CH_3CONH_2^{\bullet+}$ eventually rearranges to **11**. The hydrogen-bridged ions **9** and **10**, which are minima at this level of theory, serve as intermediates to link $CH_3CONH_2^{\bullet+}$ with the $[NH_3/CH_2{=}C{=}O]^{\bullet+}$ complexes. From **11**, after bending of the CCO unit (**11** → **12**), CO can be liberated to generate $CH_2NH_3^{\bullet+}$. The inspection of the data reported in Table IV demonstrates that the multistep sequence $CH_3CONH_2^{\bullet+} \rightarrow$ **9** → **10** → **11** → **12** → $CH_2NH_3^{\bullet+}$ requires less energy than direct dissociation of $CH_3CONH_2^{\bullet+}$ to $CH_3CO^+ + NH_2^\bullet$. For the latter process 10.5 kcal/mol more energy is needed. At the 3-21G//3-21G level of theory we locate a transition structure (C_s symmetry) for the hydrogen scrambling with a relative energy of 51.7 kcal, close in energy to that of TS **10/11**.

At the highest level of theory used (MP3/6-31G(d,p)//3-21G + ZPE) some of the crucial features of the 3-21G//3-21G-calculated potential energy surface are preserved, in that **6** is separated from **11**, **12** and the products $CH_2NH_3^{\bullet+}$/CO by a significant barrier (TS **10/11**). The latter is comparable in energy to the calculated sum of the heats of formation of CH_3CO^+ and $NH_2^\bullet$ and is likely to be lowered at even higher levels of theory (see below). Notable changes are, however, found for the hydrogen-bridged intermediates **9** and **10**, the heats of formation of which are now *above* those of the transition states TS **6/9** and TS **9/10** connecting them. Such a situation is by no means unique

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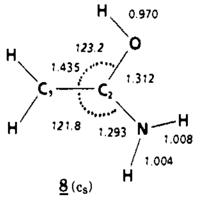
(38) (a) Reference 2. (b) Reference 3. (c) Reference 6c. (d) Reference 8. (e) Reference 11h. (f) Reference 11m. (g) Reference 11q. (h) Reference 11s. (i) Reference 11t. (j) Reference 16b. (k) Reference 16c. (l) Reference 33a. (m) Apeloig, Y.; Karni, M.; Ciommer, B.; Depke, G.; Frenking, G.; Meyn, S.; Schmidt, J.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1984**, *59*, 21. (n) Schwarz, H.; Thies, H.; Franke, W. In *Ionic Processes in the Gas Phase*; Almoster Ferreira, M. A., Ed.; D. Reidel: Dordrecht, 1984; 267. (o) Göksu, E.; Weiske, T.; Halim, H.; Schwarz, H. *J. Am. Chem. Soc.* **1984**, *106*, 1167. (p) Koch, W.; Heinrich, N.; Schwarz, H.; Maquin, F.; Stahl, D. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 305. (q) Drewello, T.; Weiske, T.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 869. (r) Weiske, T.; Halim, H.; Schwarz, H. *Chem. Ber.* **1985**, *118*, 495. (s) Uggerud, E.; Schwarz, H. *J. Am. Chem. Soc.* **1985**, *107*, 5046. (t) Koch, W.; Frenking, G.; Schwarz, H.; Maquin, F.; Stahl, D. *J. Chem. Soc., Perkin Trans* **1986**, 757. (u) Bouma, W. J.; Burgers, P. C.; Holmes, J. L.; Radom, L. *J. Am. Chem. Soc.* **1986**, *108*, 1767. (v) Hvistendahl, G.; Uggerud, E. *Org. Mass Spectrom.* **1986**, *21*, 347. (w) Drewello, T.; Koch, W.; Lebrilla, C. B.; Stahl, D.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 2922.

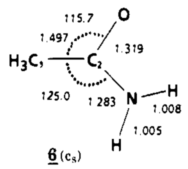
(39) For leading references, see: (a) Nobes, R. H.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 309. (b) Reference 5b.

Chart I



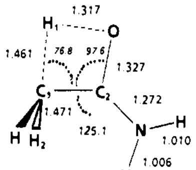
8 (c_s)

Atomic charges		Spin density	
C_1	-0.25	C_1	1.10
C_2	+0.78	C_2	0.10
O	-0.57	O	0.29
N	-0.64		



6 (c_s)

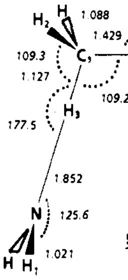
Atomic charges		Spin density	
C_1	-0.42	O	1.12
C_2	+0.76		
O	-0.18		
N	-0.66		



TS 8/6 (c_s)

Atomic charges		Spin density	
C	-0.41	C_1	0.94
C	+0.83	C_2	0.10
O	-0.45	O	0.79
N	-0.67	H_1	0.19
H	+0.35		
H	+0.27		

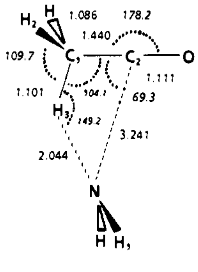
$\measuredangle H_1C_1C_2O$ 102.8°



9 (c_s)

Atomic charges		Spin density	
C_1	-0.51	N	1.19
C_2	+0.74		
O	-0.20		
N	-0.58		
H	+0.32		
H_2	+0.28		
H_3	+0.35		

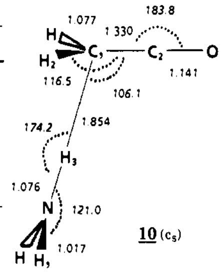
$\measuredangle H_1NC_1C_2$ 93.5°
$\measuredangle H_2C_1C_2N$ 119.7°



TS 6/9 (c_s)

Atomic charges		Spin density	
C_1	-0.48	N	1.17
C_2	+0.74		
O	-0.20		
N	-0.60		
H_1	+0.32		
H_2	+0.28		
H_3	+0.33		

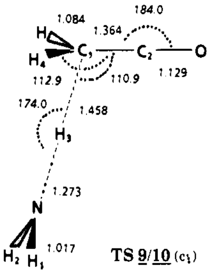
$\measuredangle H_1NC_1C_2$ 94.3°
$\measuredangle H_2C_1C_2N$ 119.1°



10 (c_s)

Atomic charges		Spin density	
C_1	-0.68	N	1.26
C_2	+0.67		
O	-0.34		
N	-0.38		
H	+0.41		
H_1	+0.42		

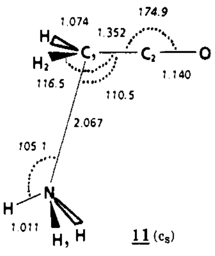
$\measuredangle H_1NC_1C_2$ 90.2°
$\measuredangle H_2C_1C_2N$ 107.6°



TS 9/10 (c_1)

Atomic charges		Spin density	
C_1	-0.68	N	1.27
C_2	+0.62		
O	-0.28		
N	-0.48		
H_3	+0.38		
H_2	+0.38		
H_1	+0.44		

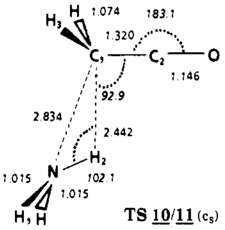
$\measuredangle H_1NH_3C_1$ 195.2°
$\measuredangle H_2NH_3C_1$ 14.8°
$\measuredangle H_4C_1C_2O$ 114.8°
$\measuredangle H_3C_1C_2O$ 0.0°



11 (c_s)

Atomic charges		Spin density	
C_1	-0.29	N	0.70
C_2	+0.64	C_1	0.55
O	-0.27	C_2	0.15
N	-0.72	O	0.39
H_1	+0.36		
H_2	+0.28		

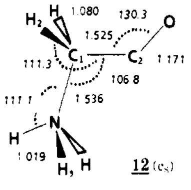
$\measuredangle H_1NC_1C_2$ 60.7°
$\measuredangle H_2C_1C_2N$ 107.4°



TS 10/11 (c_s)

Atomic charges		Spin density	
C_1	-0.62	N	1.19
C_2	+0.62		
O	-0.36		
N	-0.34		

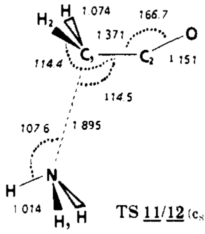
$\measuredangle H_1NH_2C_1$ 60.2°
$\measuredangle H_3C_1C_2H_2$ 112.1°



12 (c_s)

Atomic charges		Spin density	
C_1	-0.19	C_1	0.41
C_2	+0.40	C_2	1.03
O	-0.33	O	0.34
N	-0.64		
H_1	+0.41		
H_2	+0.26		

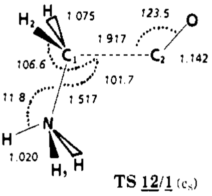
$\measuredangle H_1NC_1C_2$ 59.5°
$\measuredangle H_2C_1C_2N$ 117.9°



TS 11/12 (c_s)

Atomic charges		Spin density	
C_1	-0.25	N	0.71
C_2	+0.57	C_1	0.45
O	-0.30	C_2	0.43
N	-0.70	O	0.42
H	+0.37		
H_2	+0.28		

$\measuredangle H_1NC_1C_2$ 60.2°
$\measuredangle H_2C_1C_2N$ 112.1°



TS 12/1 (c_s)

Atomic charges		Spin density	
C_1	-0.17	C_1	1.10
C_2	+0.35	C_2	0.41
O	-0.27	O	0.24
N	-0.62		
H	+0.40		
H_2	+0.25		

$\measuredangle H_1NC_1C_2$ 59.5°
$\measuredangle H_2C_1C_2N$ 117.9°

and has often been referred to.[29] As the structures and energies of hydrogen-bridged species are very sensitive to basis set effects, an accurate calculation of this particular part of the potential energy surface would require a substantially larger basis set augmented by polarization and diffuse functions. This is for the time being impossible. Nevertheless, the present results suggest that the starting ion $CH_3CONH_2^{\bullet+}$ rearranges such that the departing molecular fragments remain electrostatically bound, thus enabling transfer of the hydrogen from the methyl group to the NH_2 function. We should mention that a direct 1,3-hydrogen migration $CH_3CONH_2^{\bullet+} \rightarrow CH_2C(O)NH_3^{\bullet+}$ would require 14.8 kcal/mol of energy above TS **10/11**.

Although far from being complete, the potential energy surface depicted in Figure 2 contains several notable features. For example, TS **10/11** represents the highest point in the isomerization/dissociation of $CH_3CONH_2^{\bullet+}$ *en route* to $CH_2NH_3^{\bullet+}$ and CO. Thus, hydrogen exchange between the methyl and amino hydrogen of $CH_3CONH_2^{\bullet+}$ must occur prior to the formation of **11** with intermediates and transition structures lower in energy than or comparable to that of TS **10/11**. With regard to the hydrogen scrambling the following results were obtained. While rotation of the CH_3–C(O) bond of **6** requires ca. 1 kcal/mol and the equilibration of the amino hydrogens in the course of reaction **6** $\rightleftarrows$ **9** is below TS **10/11**, a propeller-like rotation of the NH_3 moiety of **10** via a C_s symmetry transition structure (which would bring about *complete* scrambling) was calculated to be 3.1 kcal/mol higher in energy than TS **10/11**. As the 3-21G basis set used throughout for geometry optimizations does not reproduce the ionization energies of CH_2CO and NH_3 in the right order, it could well be that this deficiency may in particular effect loosely bound structures and may therefore account for the discrepancies. As the size of the system prevents us from using substantially larger basis sets, this particular problem cannot be solved unequivocally. On the other hand, it should be recalled that the hydrogen scrambling accompanying CO loss from $CH_3CONH_2^{\bullet+}$, while being extensive, is still far from being complete.

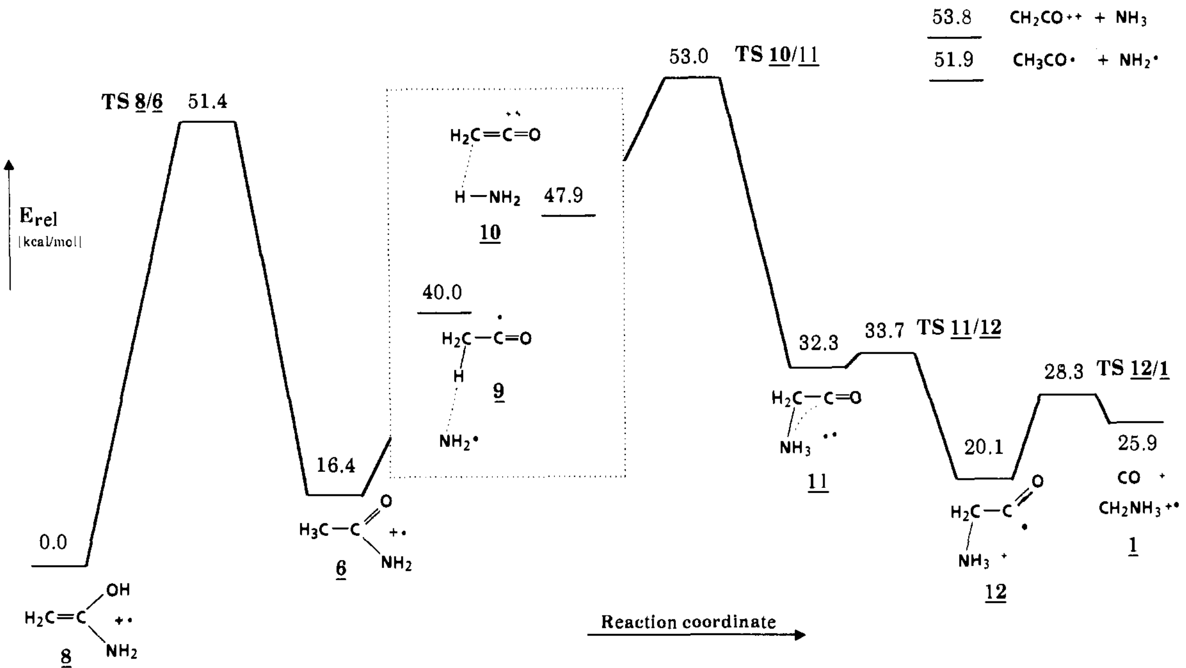


Figure 2. Reaction pathways of the potential energy surface of some $C_2H_5NO^{\bullet+}$ species, calculated at MP3/6-31G(d)//3-21G + ZPE (energies are given in kcal/mol relative to $CH_2{=}C(OH)NH_2^{\bullet+}$, **8**). For the part set in square brackets, see text.

The FTICR experiments of ND_3 with $CH_2{=}C{=}O^{\bullet+}$ clearly demonstrate that the product formed is pure $CH_2ND_3^{\bullet+}$. Thus, we must conclude that the interaction of ammonia with $CH_2{=}C{=}O^{\bullet+}$ commences at a region of the potential energy surface of the $CNH_5^{\bullet+}$ system energetically *below* TS **10/11**. We suppose that the interaction occurs in the region between TS **10/11** and the intermediates **11** and **12**.

We also note from Figure 2 two further interesting points: (i) The energy to generate $CH_2CO^{\bullet+}/NH_3$ from any possible intermediate involved along the isomerization of $CH_3CONH_2^{\bullet+}$ is *higher* than TS **10/11**. In particular, direct dissociation of the complex **10** to generate $CH_2CO^{\bullet+}$ and NH_3 is prevented by a barrier due to an avoided crossing. Comparing the relative energies of the dissociation products $CH_2CO/NH_3^{\bullet+}$ (62.6 kcal/mol) and $CH_2CO^{\bullet+}/NH_3$ (53.8 kcal/mol), the transition structure for the reaction **10** → $CH_2CO^{\bullet+}/NH_3$ is likely to be located within that energy range. As a perturbational treatment of the correlation effects is not adequately suited for a proper description, we refrained from locating this particular reaction path. Thus, in line with the experimental findings, the dissociation of $CH_3CONH_2^{\bullet+}$ to $CH_2CO^{\bullet+}/NH_3$ is of minor importance in comparison to the formation of $CH_2NH_3^{\bullet+}/CO$. Moreover, the fact that $CH_2CO^{\bullet+}/NH_3$ are separated by a barrier from forming **10** may well explain that in the ion/molecule reaction of $CH_2CO^{\bullet+}$ with NH_3 via intermediate **11** CO is expelled. Formation of **11** in contrast to **10** is continuously exothermic. (ii) We have also explored several pathways by which the global minimum on the $C_2H_5NO^{\bullet+}$ system, i.e., the enol of acetamide ($CH_2{=}C(OH)NH_2^{\bullet+}$, **8**), may rearrange to eventually eliminate CO. The energetically most feasible pathway corresponds to a 1,3-hydrogen migration of the hydroxyl hydrogen across the formal C=C double bond to transform **8** directly to **6**. Other pathways, like combinations of subsequent 1,2- respective 1,3-hydrogen migrations, are much higher in energy than TS **8/6**.[40] For the direct 1,3-hydrogen migration **8** → **6** we calculate at our best level of theory a barrier of 51.4 kcal/mol (above **8**). Thus, **6** once generated from **8** contains excess internal energy with the consequence that the kinetic energy release associated with loss of CO should be the larger when **8** is used as a precursor.[41] This prediction is in perfect agreement with the experimental observation (Table II): CO loss from **8** has a kinetic energy release of $T_{0.5}$ = 231 meV, while that for CO loss from **6** has a value of $T_{0.5}$ = 200 meV. Moreover, the $T_{0.5}$ data suggest that, as mentioned above, TS **10/11** should actually be lower in energy than TS **8/6**. A comparison of the MP2 and MP3 data (Table IV) for the two transition structures in question reveals that for TS **8/6** the MP convergence is much better than that for TS **10/11**; thus, it is highly likely that at a much higher level of theory the latter will be lowered in energy such that TS **10/11** < TS **8/6**.

Conclusions

The combined experimental/theoretical study reveals the following.

(i) Both decarbonylation of $CH_3CONH_2^{\bullet+}$ and ion/molecule reactions of ionized ketene with NH_3 generate $CH_2NH_3^{\bullet+}$. This ion can easily be characterized by its specific proton-transfer processes and its collision-induced reactions. The generation of $CH_3NH_2^{\bullet+}$ via a least-motion extrusion of CO does not seem to contribute significantly.[44]

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(40) Heinrich, N.; Schwarz, H., unpublished results.

(41) (a) Williams, D. H. *Acc. Chem. Res.* **1977**, *10*, 280. (b) Bowen, R. D.; Williams, D. H.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 451. (c) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169. (d) Reference 23b.

(42) As pointed out by a referee, the observation that the $CH_2D_3N^{\bullet+}$ ion, generated via ND_3 + $CH_2CO^{\bullet+}$, exclusively transfers a D^+ to ND_3 is in line with the expected distonic $CH_2NH_3^{\bullet+}$ ions but cannot, of course, exclude the $CH_2DND_2^{\bullet+}$ ion structure; this ion also is expected to transfer exclusively D^+ to ND_3. However, the experimental finding definitely excludes a reversible interconversion between **1** and **2** (and its isotopomers). Moreover, we do not see an easy route for specific formation of $CH_2DND_2^{\bullet+}$ via reaction of ND_3 with $CH_2CO^{\bullet+}$; the only conceivable pathway would be a $D^\bullet$ atom transfer from ND_3 to $CH_2CO^{\bullet+}$, followed in the complex by a S_N2 type reaction of $ND_2^\bullet$ upon the CH_2DCO^+ ion under expulsion of CO. However, we can expect then also to observe the ion CH_2DCO^+, as the reaction ND_3 + $CH_2CO^{\bullet+}$ → $ND_2^\bullet$ + CH_2DCO^+ is calculated to be *exo*thermic by 2.5 kcal/mol by using the heats of formation given in ref 34 and 35. Within the limit of detection we have *not* observed formation of CH_2DCO^+ and also *not* of CH_3CO^+ in the unlabeled case. We are, therefore, in favor of formation of the distonic ion $CH_2NH_3^{\bullet+}$ which cannot have more than 27.9 kcal/mol excess energy as the reaction NH_3 + $CH_2CO^{\bullet+}$ → $CH_2NH_3^{\bullet+}$ + CO is 27.9 kcal/mol exothermic according to the heats of formation data (ref 34). This energy is *not* sufficient to convert $CH_2NH_3^{\bullet+}$ into $CH_3NH_2^{\bullet+}$ as the barrier for this isomerization is 42 kcal/mol (ref 4).

(43) We should like to point out, as suggested by a referee, that the H/D scrambling might also occur in the reaction of $CH_2D_3N^{\bullet+}$ with CO. This possibility cannot be ruled out; however, as discussed in connection with the theoretical data (Figure 2), this possibility is less likely than H/D scrambling in the course of decarbonylation of $CD_3CONH_2^{\bullet+}$.

(ii) The two fundamentally different processes are linked by common intermediates, which are suggested to be hydrogen-bridged complexes.

(iii) The potential energy surface of the $C_2H_5NO^{\bullet+}$ system is such that the interactions of NH_3 with ionized ketene occur in a region of the potential surface which permits CO expulsion without any hydrogen scrambling. In contrast, starting from $CH_3CONH_2^{\bullet+}$ the isomerization involves intermediates which undergo hydrogen exchange between the CH_3CO and NH_2 groups.

(iv) The enol of ionized acetamide, i.e., $CH_2{=}C(OH)NH_2^{\bullet+}$, is separated by a significant barrier from $CH_3CONH_2^{\bullet+}$.

(v) In contrast to recent suggestions,[12,13] nucleophilic substitutions involving *radical cations* are very facile. There is no experimental evidence for their "forbiddeness".

Acknowledgment. Support of our work by the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Gesellschaft von Freunden der Technischen Universität Berlin, and Netherlands Organization for Pure Research (SOM/ZWO) is gratefully acknowledged. We are indebted to the Computer Center of TU Berlin for providing computer time. H.S. acknowledges helpful discussions with Profs. A. Pross and S. S. Shaik, Ben-Gurion University, Beersheba, Israel.

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(44) While the presence of even small amounts of ion **1** ($CH_2NH_3^{\bullet+}$) in a mixture of **1** and **2** ($CH_3NH_2^{\bullet+}$) could be detected by the presence of the charge-stripping signal (m/z 31^{2+}), it is more difficult to quantitatively determine the contribution of ion **2** to the spectrum assigned for **1**. However, a detailed comparison of the spectra shown in Figure 1 leaves no doubt that ion **2** contributes at best to a minor extent only. This conclusion is supported by an independent observation. The metastable peak for CO loss from $CH_3CONH_2^{\bullet+}$ is of composite nature with a broad component ($T_{0.5}$ = 200 meV) and a narrow one ($T_{0.5}$ = 5 meV). The latter contributes to ca. 2% of the total peak area, and we assign this peak to the extrusion reaction $CH_3CONH_2^{\bullet+} \rightarrow CO + CH_3NH_2^{\bullet+}$.

Magnetic-Field Effects in the Low-Temperature Polarized Emission and Absorption Spectra of Single-Crystal $[Ru(bpy)_3](PF_6)_2$

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Abstract: In this paper we report on the magnetic-field dependence of the broad-band emission spectra and the zero-phonon line emission and absorption of single-crystal $[Ru(bpy)_3](PF_6)_2$ at low temperatures. It is found that a magnetic field oriented with $\mathbf{H} \perp \mathbf{c}$ induces drastic effects, whereas $\mathbf{H} \| \mathbf{c}$ does not change the emission and absorption properties. At $T = 2$ K an increase of the total emission intensity by a factor of 6 is observed under the action of a magnetic field $H = 6$ T. The zero-phonon lines corresponding to the two lowest excited states exhibit a Zeeman effect, the energy separation growing from 7 cm^{-1} at zero field to 13 cm^{-1} at $H = 6$ T. Furthermore, the magnetic field changes the (temperature-dependent) ratio of the intensities of the zero-phonon emission lines by more than two orders of magnitude up to $H = 6$ T, the intensity of the lower energy line increasing while that of the higher energy line decreases. In absorption only the higher energy zero-phonon line is detectable in the absence of a magnetic field. Strong magnetic fields, however, induce the lower energy absorption line and cause the same Zeeman shift as in emission. The positions of the zero-phonon lines coincide in absorption and emission. All these experimental results are explained by magnetic-field-dependent mixing of the wave functions of the two lowest excited states. A simple perturbation calculation is presented to rationalize the experimental results.

The spectroscopic properties of the $[Ru(bpy)_3]^{2+}$ complex ion (with bpy = 2,2′-bipyridine) have been studied intensively during the past two decades. In their pioneering work Crosby and coworkers set up an energy level diagram consisting of a manifold of three closely spaced levels within an energy range of about 70 cm^{-1} with fairly different photophysical properties.[1-4] Subsequently a large number of spectroscopic and theoretical investigations were performed,[5-11] but until now it has not been possible to develop a consistent model of the electronic structure of the lowest excited states.

Considerable progress concerning the characterization of the lowest excited states has been made recently by the detection of the zero-phonon emission lines in crystalline $[Ru(bpy)_3](PF_6)_2$ and $[Ru(bpy)_3](ClO_4)_2$.[12-15] In these investigations it was possible to demonstrate that polarized emission spectroscopy on single crystals of the neat material is a powerful tool in determining the photophysical properties of the excited states. On the one hand this is due to a reduction of the inhomogeneous bandwidth to a value of about 2 cm^{-1}. On the other hand, group-theoretical assignments can be accomplished on the basis of polarized spectra and optical selection rules. As a consequence it could be shown that the two very lowest excited states, which are responsible for the low-temperature emission behavior of $[Ru(bpy)_3]^{2+}$, both transform as E' (in D_3'), at least for $[Ru(bpy)_3](PF_6)_2$, although they are separated by only 7 cm^{-1}. Moreover, it was demonstrated that the second coordination sphere (i.e., the counterion) influences

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