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Gaseous $[H_2, C, N]^+$ and $[H_3, C, N]^{+\cdot}$ Ions. Generation, Heat of Formation, and Dissociation Characteristics of $[H_2CN]^+$, $[HCNH]^+$, $[CNH_2]^+$, $[H_2CNH]^{+\cdot}$, and $[HCNH_2]^{+\cdot}$

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Abstract: The ions $[H_2CN]^+$, $[HCNH]^+$, $[CNH_2]^+$, $[H_2CNH]^{+\cdot}$, and $[HCNH_2]^{+\cdot}$ have been generated in the gas phase and identified by means of their unimolecular and collisionally induced dissociation characteristics. Two heats of formation were determined: $\Delta H_f°[CNH_2]^+ = 265 \pm 9$ kcal mol^{-1} and $\Delta H_f°[HCNH_2]^{+\cdot} = 258 \pm 1$ kcal mol^{-1}. The energy barrier for the reaction $[HCNH_2]^{+\cdot} \rightarrow [H_2CNH]^{+}$ was estimated to be greater than 59 kcal mol^{-1} and that for $[HCNH]^+ + H^\cdot \rightarrow [HCNH_2]^{+\cdot} = 35 \pm 2$ kcal mol^{-1}.

The ionized oxycarbenes $[COH]^+$, $[HCOH]^{+\cdot}$, and $[CH_3COH]^{+\cdot}$ were predicted by ab initio molecular orbital calculations to lie in a potential well separated by a large energy barrier from their isomers of conventional structure, $[H^+CO]$,[1] $[H_2CO]^{+\cdot}$,[2] and $[CH_3CHO]^{+\cdot}$.[3] These ions should therefore be observable in gas-phase ion chemistry. Subsequent events have verified these predictions;[4–7] in addition, the ionized oxycarbenes $[C(OH)_2]^{+\cdot}$,[7] $[CH_3OCOH]^{+\cdot}$,[6] and $[C_6H_5COH]^{+\cdot}$[8] have been identified by experiment. Heats of formation ($\Delta H_f°$) for all these ions lie above those of their isomers of conventional structure by 5–25 kcal mol^{-1}.

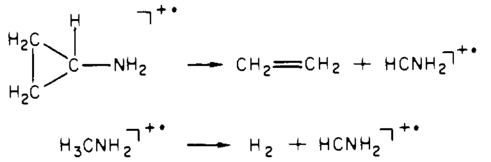
In this paper we describe the identification of three nitrogen containing analogues of the above, namely $[H_2CN]^+$, $[CNH_2]^+$, and $[HCNH_2]^{+\cdot}$, and compare their properties with those of the conventional isomers $[HCNH]^+$[9] and $[CH_2NH]^{+\cdot}$. $[H_2, C, N]^+$ isomers are of interest in interstellar chemistry where $[HCNH]^+$ is believed to play a central role in the formation of organic molecules.[10]

Results and Discussion

Aminomethylene Cation $[HCNH_2]^{+\cdot}$ and Its Isomer, Ionized Formaldimine $[H_2CNH]^{+\cdot}$. These ions together with the third isomer, $[H_3CN]^{+\cdot}$, the methylnitrenium cation, have been considered in recent ab initio molecular orbital calculations by Frish et al.[11] The latter ion was found to rearrange without an activation energy to the $[H_2CNH]^{+\cdot}$ cation, a stable species whose $\Delta H_f°$ was calculated to lie 6.2 kcal mol^{-1} above that of $[HCNH_2]^{+\cdot}$. The barrier to interconversion between these stable ions has not been reported.

By analogy with the behavior of their oxy counterparts,[5,7] the dissociative ionization of cyclopropylamine and methylamine[12] would be expected to yield $[HCNH_2]^{+\cdot}$, by loss of C_2H_4 and H_2, respectively. Although $[H_2CNH]^{+\cdot}$ can be generated by direct ionization of the transient neutral molecule,[13] it is more conveniently produced via a 2 + 2 cycloreversion reaction in azetidine molecular ions (see below).

The partial collisional activation (CA) mass spectra of the isomeric ions generated as described above are shown in Figure 1. Peaks at m/z 26, 27, and 28 have been omitted because their relative abundances are closely similar and therefore not structure characteristic. The CA mass spectrum of ionized formaldimine, $[H_2CNH]^{+\cdot}$ (Figure 1a), clearly reflects its structure; cf. the intense peaks at m/z 14 ($[CH_2]^{+\cdot}$) and m/z 15 ($[NH]^+$). The Appearance Energy (AE) of the m/z 29 ions generated from azetidine was measured by using energy selected electrons (see Experimental Section), AE = 10.46 ± 0.05 eV, leading to $\Delta H_f°[H_2CNH]^{+\cdot} = 252$ kcal mol^{-1} ($\Delta H_f°$(azetidine) = 23.5 kcal mol^{-1},[14] $\Delta H_f°$ (ethylene) = 12.5 kcal mol^{-1} [15]). The identical CA mass spectra of the m/z 29 ions generated from cyclopropylamine and methylamine are strikingly different from that of $[H_2CNH]^{+\cdot}$ (Figure 1b); m/z 13 ($[CH]^+$) and m/z 16 ($[NH_2]^+$) are now predominant, in keeping with the proposed structure $[HCNH_2]^{+\cdot}$.



Note also that the ion $[HCNH_2]^{+\cdot}$ displays a characteristically narrow collisional ionization peak at m/z 14.5, $[HCNH_2]^{2+}$. We suggest that the above CA mass spectrum (Figure 1b) is that derived from *pure* $[HCNH_2]^{+\cdot}$ ions because the heat of formation of the ion was measured to be 6 kcal mol^{-1} *higher* than that of $[H_2CNH]^{+\cdot}$, AE (m/z 29) = 11.00 ± 0.05 eV, $\Delta H_f°$(cyclopropylamine) = 17.5 kcal mol^{-1},[14] leading to $\Delta H_f°[HCNH_2]^{+\cdot} = 258$ kcal mol^{-1}. This experimental heat of formation is greater than the value obtained from ab initio molecular orbital calculations[11] by ca. 12 kcal mol^{-1} (as illustrated in Figure 3).

The ions $[H_2CNH]^{+\cdot}$ and $[HCNH_2]^{+\cdot}$ undergo only one reaction in the μs time frame, viz. the loss of $H^\cdot$. The metastable

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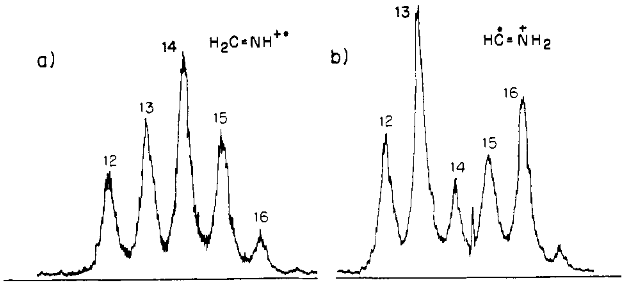

Figure 1. Partial collisional activation mass spectra of (a) $[H_2CNH]^{+\cdot}$ and (b) $[HCNH_2]^{+\cdot}$ ions.

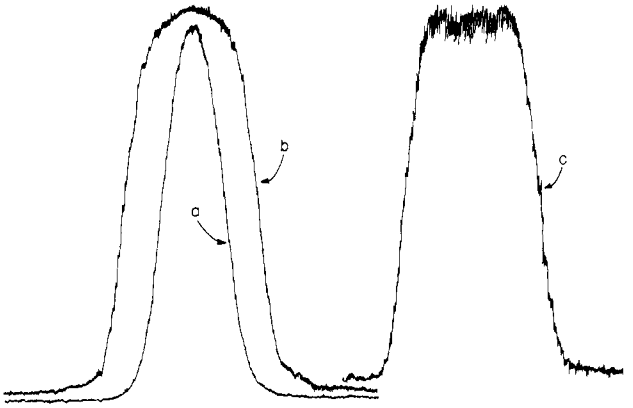

Figure 2. Metastable peak shapes for the reactions: (a) $[H_2CNH]^{+\cdot} \rightarrow [HCNH]^+ + H^\cdot$ (b) $[HCNH_2]^{+\cdot} \rightarrow [H_2, C, N]^+ + H^\cdot$ (c) $[DCNH_2]^{+\cdot} \rightarrow [DCNH]^+ + H^\cdot$.

peaks for this reaction are shown in Figure 2. Loss of $H^\cdot$ from $[H_2CNH]^{+\cdot}$ ions is characterized by a narrow simple Gaussian[16] type peak ($T_{0.5}$ = 65 meV); $[HCNH_2]^{+\cdot}$ ions on the other hand display a much broader peak ($T_{0.5}$ = 250 meV) which does not have the dished summit[17] expected from its shape and thus may well consist of two components. The fragmentation behavior of $[DCNH_2]^{+\cdot}$ ions derived from $[D_3CNH_2]^{+\cdot}$ lends support for this suggestion; these ions lose both $H^\cdot$ and $D^\cdot$ in a (peak height) ratio of ca. 15:1 and with markedly different kinetic energy releases, $T_{0.5}$ ($H^\cdot$ loss) = 285 meV (see also Figure 2; note change of peak shape), $T_{0.5}$ ($D^\cdot$ loss) = 65 meV.

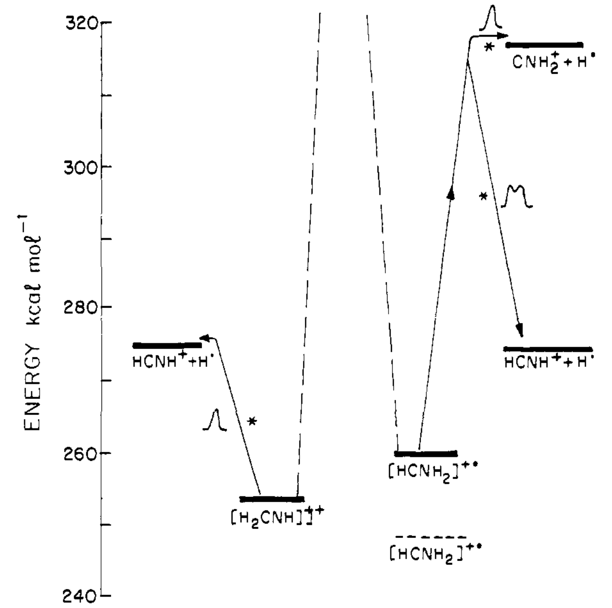

Figure 3. Energy diagram for isomeric $[H_3, C, N]^{+\cdot}$ ions. (Broken horizontal line is from ab initio calculations[11]).

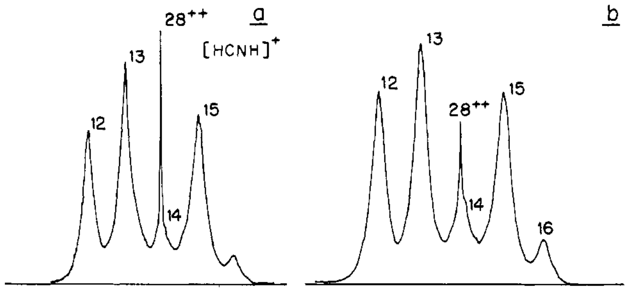

Figure 4. Partial collisional activation mass spectra of $[H_2, C, N]^+$ ions. See text for discussion.

The AE values for these two metastable peaks were measured by using a comparative method[18] and were found to be the same within experimental error (AE) ($H^\cdot$ loss) = 13.8 ± 0.1 eV, AE ($D^\cdot$ loss) = 14.0 ± 0.4 eV). For $H^\cdot$ atom loss this leads to an apparent $\Delta H_f°$ for $[DCNH]^+$ of 261 kcal mol^{-1} ($\Delta H_f°(D_3CNH_2)$ = −5.5 kcal mol^{-1},[14] $\Delta H_f°(H^\cdot)$ = 52 kcal mol^{-1},[15]), far above the well-established value,[19] 226 kcal mol^{-1}, for $[HCNH]^+$. We propose that ions of structure $[DCNH]^+$ are formed in the $H^\cdot$ atom loss but with a substantial barrier (35 ± 2 kcal mol^{-1}) for the reverse reaction. For $D^\cdot$ atom loss the AE value leads to an apparent heat of formation of the daughter ion of 265 ± 9 kcal mol^{-1}. Considering the relatively small amount of kinetic energy released during this fragmentation and the CA characteristics of $[H_2, C, N]^+$ ions, which are described below, we propose that this reaction generates $[CNH_2]^+$ ions, near the thermochemical threshold, by direct bond cleavage. The potential energy diagram shown in Figure 3 summarizes our proposals: the barrier for the interconversion between $[HCNH_2]^{+\cdot}$ and $[H_2CNH]^{+\cdot}$ is *at least* 59 kcal mol^{-1} above that of $[HCNH_2]^{+\cdot}$ (because $\Delta H_f°[CNH_2]^+$ is 39 ± 9 kcal mol^{-1} greater than $\Delta H_f°[HCNH]^+$). The latter value is in good agreement with the most recent theoretical calculations, which predict an energy difference of ca. 40 kcal mol^{-1}.[20]

The system $[H_2CNH]^{+\cdot}/[HCNH_2]^{+\cdot}$ has a behavior which closely parallels that of the isoelectronic oxygen system $[H_2CO]^{+\cdot}/[HCOH]^{+\cdot}$.[7] Note that although $[HCNH_2]^{+\cdot}$ and $[HCOH]^{+\cdot}$ are thermodynamically less stable than their counterparts of conventional structure, they nevertheless inhabit deeper potential wells. The exothermic reactions $[H^+CO] + H^\cdot \rightarrow [HCOH]^{+\cdot}$ and $[HCNH]^+ + H^\cdot \rightarrow [HCNH_2]^{+\cdot}$ have considerable barriers (25 and 38 kcal mol^{-1}, respectively), whereas the exothermic reactions leading to $[H_2CO]^{+\cdot}$ and $[H_2CNH]^{+\cdot}$ have no or small barriers.[7] An interpretation of these differences in terms of the electron density in the reactant ions is given elsewhere.[8]

The identification of the appreciable energy barriers for these simple reactions of small cations is of importance when the role of such processes is to be considered in interstellar chemistry.

$[H_2, C, N]^+$ Ions, $[HCNH]^+$, the Iminomethylene Cation, $[CNH_2]^+$, the Aminomethylidene Cation, and $[H_2CN]^+$, the Methylenenitrenium Cation. The three $[H_2, C, N]^+$ isomers are generally agreed to play an important role in the interstellar formation of HNC and HCN.[21] These ions have been the subject of theoretical calculations,[20,21] which predict that $[HCNH]^+$ is the isomer of lowest heat of formation: $[CNH_2]^+$ was found to lie 40 kcal mol^{-1},[21] higher in energy with a barrier to $[HCNH]^+$ of a further 36 kcal mol^{-1}. For the third isomer, $[H_2CN]^+$, no potential minimum corresponding to this configuration was found. Although only $[HCNH]^+$ ions could be positively identified in a CA study of McLafferty and McGilvery,[9] the predicted large barrier for the interconversion $[CNH_2]^+$ and $[HCNH]^{+\cdot}$ makes

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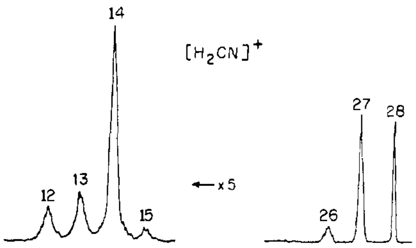

Figure 5. Collisional activation mass spectra of $[H_2CN]^+$ ions.

it likely that $[CNH_2]^+$ is experimentally observable. In the preceding section on $[HCNH_2]^{+\cdot}$ ions it was proposed that metastable $[DCNH_2]^{+\cdot}$ ions lose H$^\cdot$, to produce $[HCNH]^+$, and, albeit to a lesser extent, D$^\cdot$, to produce $[CNH_2]^+$. It may therefore be expected that $[H_2,C,N]^+$ ions derived from unlabeled $[H_3CNH_2]^{+\cdot}$ will consist of a mixture of both isomers. In Figure 4 are shown the partial CA mass spectra of $[H_2,C,N]^+$ ions derived from H_3CNH_2 and that of $[HCNH]^+$ ions generated by gas-phase protonation of HCN with H_3O^+.[9] The difference in the abundances of the singly charged ions are small, but reproducible; the ions generated from H_3CNH_2 display a more intense peak at m/z 16, $[NH_2]^+$, indicating the presence of $[CNH_2]^+$. A more striking feature, however, is the much lower abundance of the narrow charge-stripping peak at m/z 14 (m/z 28^{2+}). This may also be ascribed to the presence of $[CNH_2]^+$ if it can be shown that this isomer has a considerably lower collisional ionization cross section than $[HCNH]^+$. Following our argument in the preceding section, the labeled precursor D_3CNH_2 permits the separation of the two isomeric $[H_2,C,N]^+$ ions—$[CNH_2]^+$ ions remain at m/z 28 and $[HCNH]^+$ shifts to $[DCNH]^+$, m/z 29. However it was unfortunately not possible to obtain a CA mass spectrum of *pure* $[CNH_2]^+$ ions, because m/z 28 now also contains $[CDN]^{+\cdot}$ ions, of structure $[DNC]^{+\cdot}$;[9] m/z 12, 14, and 16 from the latter ion dominate the CA mass spectrum. There is, however, *no* detectable charge-stripping peak (which at even moderate resolution would be easily distinguishable when superimposed upon a singly charged m/z 14 signal). Weak peaks at m/z 13 and 15 must arise from $[CNH_2]^+$ ions.

As mentioned above no relative minimum could be found on the potential surface of $[H_2, C, N]^+$ ions for the isomer $[H_2CN]^+$. However, should this ion exist in a potential well, the m/z 12–16 region of its CA mass spectrum ought to be readily distinguishable from those of its isomers. Note that the direct bond cleavage reaction $[H_2CN]^+ \rightarrow [CH_2]^{+\cdot} + N^\cdot$ is by far the *least* energy demanding fragmentation, and so an intense m/z 14 peak should be characteristics of $[H_2CN]^+$ ($\sum\Delta H_f^\circ$ $[CH_2]^{+\cdot} + N^\cdot = 446$ kcal mol^{-1},[15]); the next higher product enthalpies are for $[NH_2]^+$ + C and $[C]^+ + NH_2$ with both $\sum\Delta H_f^\circ = 475$ kcal mol^{-1}.[15]

No suitable precursor molecule could be found to generate $[H_2CN]^{+\cdot}$ ions by dissociation of positive ions. However, we observed that dissociative electron capture of H_3CNH_2 produces the negative ions $[H_4, C, N]^-$, $[H_2, C, N]^-$, $[CN]^-$, and $[NH_3]^-$. Of these, the $[H_2,C,N]^-$ ions contribute about 0.5% of the total ion current. The $[H_4, C, N]^-$ ions have been shown[22] to have the structure $[H_3CNH]^-$; a further 1,2-H_2 elimination would produce anions of structure $[H_2CN]^-$. Charge inversion of such ions by collision with He would then generate cations of the desired structure $[H_2CN]^+$. Charge inversion for kilovolt ions is a vertical process,[23] and provided the geometric differences between the anion and cation are not great, the instantaneously formed cations retain the structure of the anion. Autoejection[24] and autoionization[15] time scales decrease rapidly with increasing internal energy, and so superexcited negative ions have very short lifetimes, ca. 10^{-15}–10^{-16} s. Figure 5 shows the CA mass spectrum of the $[H_2, C, N]^+$ cations obtained by charge reversal of the mass selected $[CH_2N]^-$ anions. In contrast with the spectrum of $[HCNH]^+$ ions (Figure 4a) the m/z 12–16 region is dominated by the peak at m/z 14 $[CH_2]^{+\cdot}$. Essentially the same results were obtained by using D_3CNH_2 as the precursor molecule: the CA mass spectrum of the charge-reversed $[CD_2N]^-$ ions is dominated by m/z 16, $[CD_2]^{+\cdot}$.

Thus, the $[H_2, C, N]^+$ cations generated upon the charge-reversal are indeed $[H_2CN]^+$ ions. The observation that a sizeable fraction of the m/z $[28]^+$ ions can survive charge reversal, indicates that $[H_2CN]^+$ ions exist in a potential well.

Experimental Section

Collisonal activation (CA) mass spectra were recorded by using a VG-ZAB-2F mass spectrometer. A 100-μA electron beam of ionizing energy, ca. 60 eV, was used. Sample reservoir and ion source temperatures were ~150 °C. Collisional activation, charge-stripping, and charge reversal mass spectra were obtained by using helium as collision gas at a pressure of 4×10^{-7} torr as measured by an ion gauge situated near the diffusion pump located between the electric sector and the gas cell; the actual gas cell pressure is $\sim 4 \times 10^{-4}$ torr. The CA mass spectra were recorded under conditions of moderate mass resolution (ca. 3000) using the intermediate slit situated in front of the collision gas cell. In this way contributions from unwanted peaks do not contribute to the measured spectrum (e.g., $[C_2H_4]^{+\cdot}$, $[CO]^{+\cdot}$, $[N_2]^{+\cdot}$ as opposed to $[H_2, C, N]^+$). For comparitive puposes *all* CA mass spectra were recorded under identical resolution conditions. The reproducibility proved to be good, measurements being repeated over a period of months.

Metastable peak shapes were obtained on a Kratos AEI MS902-S mass spectrometer under conditions of good enegy resolution[16] (e.g., a main beam width of 2 V or less at an acceleration voltage of 7 kV). Appearance energies (except those measured on metastable peaks) were measured with an apparatus comprising an electrostatic electron monochromator with a quadruple mass analyzer and minicomputer data system.[25]

Metastable peak appearance energies were obtained on the AEI mass spectrometer using the metastable peak m/z $204^{+\cdot} \rightarrow m/z$ 77^+ in iodobenzene as the standard.[18] The dissociative electron capture experiments on H_3CNH_2 were performed at an indicated ion source pressure of ca. 3×10^{-5} torr; detailed conditions are given in ref 26. All compounds were of research grade and used without further purification.

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Registry No. $[HCNH_2]^{+\cdot}$, 89302-94-3; $[H_2CNH]^{+\cdot}$, 65130-65-6; $[HCNH]^+$, 38263-97-7; $[CNH_2]^+$, 86784-42-1; $[H_2CN]^+$, 53518-13-1; cyclopropylamine, 765-30-0; methylamine, 74-89-5.

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