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Gaseous HCN^+, HNC^+, and $HCNH^+$ Ions[1]

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Abstract: Two isomers of CHN^+ can be identified from their collisional activation mass spectra. Molecular HCN ions are predominantly the HCN^+ isomer, but decomposition of a wide variety of N-organic ions produces only the more stable HNC^+ isomer. Of the three possible isomers of CH_2N^+, only $HCNH^+$ is found to be produced by a variety of decomposition and ion–molecule reactions. Formation of these ions in the mass spectra of CH_3CN and CH_3NC is unusual in involving the neutral loss of CH_2 and CH, which apparently is due to the large stabilization resulting from the addition of one and two hydrogens to CN^+.

Molecular HCN is stable, while its isomer HNC has been observed only as a transient species.[2] In contrast, the HNC^+ ion is more stable than its HCN^+ isomer by 1.3 eV according to theoretical calculations,[3] and by 0.6 eV from charge exchange experiments.[4] In the latter ground-state formation of the isomers HCN^+ from HCN ionization and HNC^+ by unimolecular decomposition of CH_3NC^+ and $CH_3NH_2^+$ was assumed. We report here a further investigation utilizing collisional activation (CA) mass spectra[5] of the formation of these CHN^+ isomers over a range of energies from a variety of precursors. Because the isobaric $C_2H_3^+$ (m/z 27) ions commonly occur in mass spectra from background as well as fragmentation, this study utilized a CA instrument capable of high resolution separation of such interfering ions.[6]

The reported[4] formation of HNC^+ from CH_3NC is of particular interest because this must involve the loss of CH_2:, a neutral loss that is highly unusual in mass spectra.[7] Our initial examination of the mass spectrum of CH_3NC not only confirmed the formation of CHN^+ (2% of base peak), but also showed a more abundant CH_2N^+ peak (3%) formed by the even more surprising loss of CH. Further, we find that CH_3CN^+ also shows similar losses of CH as well as CH_2. CH_2N^+ ions have attracted substantial interest with reference to their role in the interstellar formation of HCN and HNC. Although H_2CN^+ has been suggested as the stable isomeric structure,[8] theoretical calculations by Schaefer[9] predict that the linear $HCNH^+$ is the most stable isomer, with CNH_2^+ and H_2CN^+ being 2.0 and 3.1 eV, respectively, less stable.

Experimental Section

The tandem CA mass spectrometer[6] used has a high-resolution Hitachi RMH-2 as MS-I. Ions formed by 70-eV electrons or by chemical ionization (CI) are accelerated by 10 keV, separated by MS-I, and made to undergo collisions with a helium molecular beam; the resulting CA product ions are separated by an electrostatic analyzer used as MS-II. The helium flow rate was increased until the precursor ion abundance was reduced to 40% of its original value; at an equivalent pressure, the abundance of a precursor ion such as $C_7H_7^+$ would be reduced to $\sim$10% of its original value. Spectra were computer averages of $\sim$20 scans; the data for CH_2N^+ from CH_3NC and CH_3CN are averages of $\geq$5 such runs. Confirmatory data were also measured on a reverse-geometry RMU-7 double-focusing mass spectrometer[10] using 8-keV precursor ions, but only representative CA data for CHN^+, corrected for $C_2H_3^+$ interference, are reported.

The RMH-2-separated precursor CHN^+ ions (m/z 27.0109) contained less than 2% $C_2H_3^+$ ions (27.0235) based on m/z 25 in the CA spectrum. Measuring the CA spectra of CH_2N^+ (m/z 28.0187) required MS-I separation of $H^{13}CN^+$ (28.0143), which differs by 1/6400, as well as of N_2^+ (28.0061) and CO^+ (27.9949). Care had to be taken to avoid drift of MS-1 off the CH_2N^+ peak during the multiple scanning of its CA spectrum; $H^{13}CN^+$ contamination increases $[m/z\ 14^+]/[12^+]$. The $CHDN^+$ precursor ion was separated from $CD^{15}N$, $^{13}CDN^+$, $C^{13}CD_2^+$, and $C_2HD_2^+$.

Protonation used to prepare precursor ions for reported CA spectra was done with H_2O as the CI reagent gas. Self-protonation of HCN gave the same CA spectrum of CH_2N^+ within experimental error.

Appearance energies, measured by the vanishing current method, were of poor accuracy because of the low ion abundance at high resolution. The CN^+ data also tailed badly.

Methyl isocyanide was synthesized by a standard literature procedure,[11] and the other compounds were obtained commercially.

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Table I. Collisional Activation Spectra of $C(H,D)N^+$ Ions

	m/z					
compd	12	13	14	15	16	26
HCN	2.7	2.7	1.5	0.4		100
a	2.7	3.0	1.4	0.5		*b*
20 eV[a,c]	2.7	3.2	1.4	0.5		*b*
DCN	4.0		7.2		0.9	100
CH_3NC	3.7	1.9	1.9	1.5		100
a	3.7	1.5	1.5	1.3		*b*
CH_3NH_2[a]	3.7	1.2	1.3	1.4		*b*
$HCONH_2$[a]	3.7	1.3	1.4	1.6		*b*
CH_3CN	3.6	2.0	1.5	1.2		100
$HCON(CH_3)_2$	3.7	1.7	1.5	1.3		100
pyridine	3.9	2.3	1.6	1.1		100
benzonitrile	3.7	2.2	1.9	0.9		100

[a] Data from RMU-7; other data on the tandem/RMH-2 instrument. [b] RMU-7 determination of $[12^+]/[26^+]$ inaccurate, so $[12^+]$ value of tandem instrument assumed. [c] Ionizing electron energy 70 eV unless otherwise specified.

Table II. Collisional Activation Spectra of $C(H,D)_2N^+$ Ions

	m/z									
compd	12	13	14	15	16	17	18	26	27	28
$HCN + H^+$	2.1	1.5	1.4	1.2	0.4			22	100	
$HCN + D^+$[a]	1.7	1.0	1.2	0.2	1.5	0.4		19	36	67
$CH_3CN + D^+$[a]	1.7	1.2	1.4	0.6	1.0	0.2		13	32	77
$DCN + H^+$[a]	1.3	0.4	2.3	0.8	0.2	0.2		17	42	62
$CD_3CN + H^+$[a]	1.6	0.5	2.3	1.1	0.8	0.3		20	40	62
$DCN + D^+$	1.8		3.8	0.8[b]	2.2		0.4	18		100
CH_3NC	2.1	1.6	1.6	1.3	0.4			24	100	
CH_3CN	1.9	1.5	1.7	1.3	0.3			21	100	

[a] Using $CHDN^+$ as the precursor ion. Abundances are normalized to the base $[CN^+] + [C(H,D)N^+] = 122$; $[CHDN^{2+}] = 0.8$. [b] CD_2N^{2+}.

Results and Discussion

In confirmation of the results obtained by charge exchange,[4] the CA spectra of CHN^+ ions from methyl isocyanide and methylamine are the same, and differ significantly from the spectrum of CHN^+ ions from HCN (Table I). These spectra are consistent with the structures HNC^+ and HCN^+, respectively, as the spectrum of the former shows more abundant HN^+ ions, and that of the latter has more abundant HC^+ ions. Assuming equivalent CA cross sections, $[HN^+]$ indicates that the molecular ions from HCN contain <30% of the HNC^+ isomer; however, the true value is probably much less than this, as HN^+ is probably formed from HCN^+ by rearrangement in the same way that HC^+ is formed from HNC^+. Also lowering the ionizing electron energy does not change the CA spectrum from HCN appreciably.

The HNC^+ isomer is clearly the more stable.[3,4] This is the only isomer observed (Table I) for CHN^+ ions formed by mass spectral fragmentation of CH_3NH_2, CH_3NC, CH_3CN, $HCONH_2$, $HCON(CH_3)_2$, pyridine, and benzonitrile. However, the energy barrier for the exothermic isomerization $HCN^+ \rightarrow HNC^+$ can only be determined qualitatively from these data. Although for HCN ionization the appearance energy of the lowest energy dissociation process (H loss) is 5.8 eV above the ionization energy,[12] the photoelectron spectrum[13] indicates that >90% of the molecular ions are formed with <0.5 eV internal energy, so that this is the highest minimum value which can be derived for the $HCN^+ \rightarrow HNC^+$ barrier from these data.

CH_2N^+ Ions. The CH_2N^+ ions (Table II) formed by protonation of HCN (using H_2O or HCN) and by unimolecular dissociation of CH_3CN and CH_3NC all give the same CA mass spectrum within experimental error, indicating that they have a common structure. Of the three possible structures H_2CN^+, $HCNH^+$, and CNH_2^+, only one ($HCNH^+$) has hydrogen atoms which are nonequivalent. $CHDN^+$ ions were made in two ways, chemical ionization of HCN using D_2O as the reagent gas, and of DCN using H_2O as the reagent gas. Their CA spectra (Table II) are substantially different, supporting the structure $HC{\equiv}N^+H$, which has been predicted to be the most stable.[9] These CA spectra are also consistent with the expected structures $HCND^+$ and $DCNH^+$, respectively. The *m/z* 13 (CH^+) and 16 (DN^+) are larger in the presumed $HCND^+$ spectrum, and *m/z* 14 (CD^+ + N^+) and 15 (HN^+) are larger in the $DCNH^+$ spectrum. Chemical ionization of CD_3CN with H_2O as the reagent gas gives $CHDN^+$ fragment ions whose CA spectrum resembles that of $DCNH^+$, and chemical ionization of CH_3CN with D_2O gives $CHDN^+$ ions whose CA spectrum resembles the $HCND^+$ spectrum. The values of $([m/z\ 13^+] + [16^+])/([14^+] + [15^+])$ indicate the majority of $CH_3C{\equiv}N^+H'$ ions formed by the protonation of CH_3CN yield $HC{\equiv}N^+H'$ ions without H–H′ scrambling. Despite the mechanistic diversity of the reactions forming $HCNH^+$ from CH_3CN^+, CH_3NC^+, and CD_3CNH^+, and by chemical ionization, in none is there evidence for concomitant CNH_2^+ formation (such as an increased CA abundance of NH_2^+); CNH_2^+ is predicted[9] to be 2.0 eV less stable than $HCNH^+$, but to have a 1.3-eV isomerization barrier.

The CA spectra of $HCND^+$ and $DCNH^+$ also provide further evidence of the higher stability of HNC^+ vs. that of HCN^+. For $HCNH'^+$ the loss of H is ~15% greater than the loss of H′ after offsetting the isotope effects.

Losses of Neutral CH and CH_2. Peaks in electron ionization (EI) mass spectra due to the loss of CH_2 are unusual; for example, this accounts for a 2% peak in the mass spectrum of $(C_6H_5)_2PCH_2P(C_6H_5)_2$.[7] Confirming the EI spectral behavior of CH_3CN and CH_3NC reported above, their CA spectra show *m/z* 26, 27 and 28 abundances (total of *m/z* 12–40 = 100%) of 2.4, 2.4, and 3.8%, respectively, for CH_3CN^+, and 2.0, 2.4, and 3.4%, respectively, for CH_3NC^+. Further, the CA spectrum of $CD_3C{\equiv}N^+H$ shows abundances (total of *m/z* 12–44 = 100%) from losses of CD_2, CHD, and CD of 3.5, 2.7, and 1.8%, respectively.

Appearance energy determinations for CH_3CN and CH_3NC, respectively, gave CN^+, 20 and 20 eV; CHN^+, 15 and 15 eV; and CH_2N^+, 16 and 15 eV. (The photoelectron spectrum of CH_3CN, ionization energy 12.2 eV, shows almost no ion formation in the range 13.2–15.1 eV.)[13] Based on heats of formation,[14] the dissociation of CH_3CN^+ to lose CH_3, CH_2, and CH requires 6.9, 5.3, and 2.6 eV/mol, respectively, somewhat higher than indicated by the measured appearance energies. The favorable energies for the losses of CH_2 and CH vs. that of CH_3 more than offset the severe entropic requirements of the accompanying hydrogen rearrangements. This case is unusual because the addition of one or two hydrogens to CN^+ stabilizes it by 3.6 or 8.9 eV;[14] for comparison, the corresponding stabilizations for $C_2H_3^+$ are 0.5 and 2.2 eV.[12]

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