Experimental Enthalpy of Formation of Isonitrile from Collision-Induced Dissociation Threshold Energy Measurements

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The enthalpy of formation of HNC is determined using collision-induced dissociation threshold measurements with protonated nitriles. The average value obtained using five different nitrile precursors is 49.7 ± 2.9 kcal/mol, which agrees with the previously reported experimental value after accounting for revisions in the proton affinity scale. While the main dissociation pathway for all ions is found to be simple cleavage, the protonated propionitrile and acrylonitrile ions also dissociate by formation of $HCNH^+$ formed by intramolecular proton transfer.

Hydrogen isocyande (HNC) is a reactive molecule that has been extensively studied both experimentally and computationally. Although this isomer of hydrogen cyanide (HCN) was first isolated at 4 K in an Ar matrix,[1] the gas phase molecule was actually identified[2,3] in dense interstellar clouds before it was observed in the laboratory. The assignment of the interstellar line U90.7 at 90663.59 MHz was eventually confirmed by Brown and co-workers,[4] who measured the microwave spectrum of HNC generated in a heated sample of HCN. Subsequently, the structure of HNC has been characterized using a combination of spectroscopic approaches.[5]

Because of its small size, HNC has been examined at very high levels of theory. Many of the computational studies carried out have investigated the rearrangement of HCN to HNC.[6−10] At the highest levels of theory examined (multireference CI, coupled cluster),[7,11−13] HNC is found to be 14−15 kcal/mol higher in energy than HCN. The barrier for the isomerization has also been examined and is calculated to be ca. 45 kcal/mol.[6−10]

Despite the theoretical interest in the isomerization of HCN to HNC, the energy required for the reaction has not been established experimentally. Maki and Sams calculated an energy difference of 10.3 ± 1.1 kcal/mol on the basis of the intensities of absorption bands in high-resolution IR experiments.[14] At the same time, Ellison and co-workers estimated a lower limit of 17 kcal/mol (6000 cm^{-1}) on the basis of chemiluminescence observed in proton transfer reactions.[15] In 1982, Pau and Hehre[16] determined the proton affinity of HNC by measuring the energy to abstract D^+ from $DCNH^+$ ion in an ICR mass spectrometer. They observed D^+ in the reaction of $DCNH^+$ with ethanethiol and stronger bases, but not for the reaction with propionaldehyde or weaker bases. They concluded that the proton affinity of HNC was between those of propionaldehyde and ethanethiol and assigned a value 14.8 ± 2 kcal/mol higher than that of HCN on the basis of the available reference data at the time. This leads to an enthalpy of formation for HNC of 47.1 ± 2 kcal/mol. Both values are in excellent agreement with theoretical predictions, which give $\Delta H_{f,298}(HNC) = 46-47$ kcal/mol. However, the proton affinity scale has undergone significant revision in recent years, such that the currently recommended proton affinities of propionaldehyde and ethanethiol (187.9 and 188.7 kcal/mol, respectively)[17] are higher than that of HCN by 17.5 and 18.3 kcal/mol, respectively. This means that the proton affinity and, subsequently, the enthalpy of formation of HNC are higher than those of HCN by ca. 18 kcal/mol, ∼ 3 kcal/mol larger than the value originally assigned by Pau and Hehre. More importantly, the reassessed enthalpy of formation of HNC is 3 kcal/mol higher than the values calculated at the highest levels of theory. Given that these levels of theory should be capable of giving relative proton affinities of HNC and HCN that are accurate to within at least ± 2 kcal/mol, the discrepancy with experiment is surprising.

This paper reports an experimental enthalpy of formation of HNC as determined using collision-induced dissociation (CID) threshold measurements for the reaction shown in eq 1

$$RCNH^+ \rightarrow R^+ + CNH \tag{1}$$

The advantage of this approach is that it is possible to utilize systems with different values of R, with each providing a separate measure of the enthalpy of formation of HNC. The systems examined in this work include acetonitrile, propionitrile, pivalonitrile, acrylonitrile, and benzonitrile (R = CH_3, C_2H_5, t-C_4H_9, C_2H_3, and C_6H_5, respectively). The enthalpy of formation of HNC derived in this work is 17.4 ± 2.9 kcal/mol higher than that of HCN, in agreement with what is obtained using the results of Pau and Hehre and the revised proton affinity scale.

Experimental Section

The experiments described here were carried out using a flowing afterglow triple-quadrupole apparatus that has been described previously,[18] and only a brief description is provided here. A chemical ionization agent, CH_5^+, is generated by electron ionization of methane added at the electron impact source and is carried through the flowing afterglow by the helium buffer (P[He] = 0.400 Torr, flow[He] = 200 std cc/s). Protonated nitrile ions are prepared in the flowing afterglow by proton transfer from CH_5^+ to the appropriate nitrile introduced downstream from the ion source. The ions produced in the flowing afterglow are thermalized to ambient temperature by ca. 10^5 collisions with He before they exit the flowing afterglow. The results obtained do not depend on the position

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at which the ions are formed, suggesting that thermalization of the ions is rapid for these systems.

Ions are sampled through a 1 mm orifice in a nose cone into a differentially pumped chamber containing a triple-quadrupole analyzer. The ions with the desired mass-to-charge ratio are selected using the first quadrupole and injected into the second quadrupole (Q2), which is a gastight collision cell, where they undergo CID. Absolute cross sections, σ_p, are calculated using the relationship $\sigma_p = I_p/INl$, where I_p and I are the intensities of the product and the reactant, respectively, N is the number density of the target, and l is the path length for the reaction. The effective path length for the collision cell is measured to be 24 ± 4 cm on the basis of calibration experiments with the reaction $Ar^+ + D_2 \rightarrow ArD^+ + D$, which has a well-established reaction cross section.[19] Although absolute cross sections have estimated uncertainties of ±50%, relative cross sections are considered more reliable (±20%). The CID collision energy in the center-of-mass frame (E_{CM}) is calculated using $E_{CM} = E_{lab}(m/(m + M))$, where m and M are the mass of the target and the ion, respectively, and E_{lab} is the energy in the lab frame, which corresponds to the Q2 rod offset. Cross sections are measured at different pressures and linearly extrapolated to $p = 0$ before analysis.

Data Analysis

Cross sections as a function of energy are modeled using eq 2,[19−21] where E is the translational energy, E_i is the internal energy of the reactant ion, E_0 is the 0 K dissociation energy, σ_o is a scaling factor, and n is an adjustable parameter.

$$\sigma(E) = \sigma_o \sum_i g_i (E + E_i - E_0)^n / E \qquad (2)$$

The cross section is the sum over the ion internal energy distributions, E_i, weighted by the relative populations, g_i, where the internal energy distributions are obtained using vibrational frequencies and rotational constants calculated at the Becke 3LYP/6-31+G* level of theory. The calculated frequencies are scaled by 0.965 to account for anharmonicity. Fitting is carried out by varying the parameters σ_o, n, and E_0 to minimize the deviation between the cross sections in the steeply rising region just above the threshold. All analysis is carried out using the CRUNCH program written by Armentrout and co-workers.

Included into the fit, in addition to the internal energy, are the dissociation lifetimes of the ion, which are calculated using an RRKM approach.[22] The dissociation probability of the ion is determined from the rovibrational levels available to the energized molecule (after collision) and the transition state for the dissociation, with the rotational constants and vibrational frequencies of the energized molecule assumed to be the same as those in the reactant ion. In the calculation, the internal energy of the energized molecule is assumed to be distributed statistically over all the rovibrational degrees of freedom, and the vibrations and rotations are allowed to couple with the dissociation coordinate.[22]

An important consideration in the RRKM analysis is the structure of the transition state. The simple bond dissociation reactions examined in this work occur without a reverse energy barrier[23] and are therefore expected to have loose, product-like transition states. The transition states for the dissociations in this work correspond to the "phase space limit," which is an orbiting transition state consisting of the dissociation products. As described by Rodgers et al.,[22] the transition state for the dissociation must properly correlate the degrees of freedom in the energized molecule with those in the product. For example, the energized molecule, which is assumed to have a structure similar to that of the reactant ion, has three translational, three rotational, and three N-6 vibrational degrees of freedom. However, the products $R^+ + HNC$ have six translational, five rotational (because HNC is linear), and three N-11 vibrational degrees of freedom, of which one is the reaction coordinate. In the transition state model developed by Armentrout and co-workers,[22] the remaining translational degrees of freedom created in the dissociation are treated as rotations of the ionic and neutral fragments within the transition state, which are in turn calculated using the B3LYP/6-31+G* rotational constants of the products.

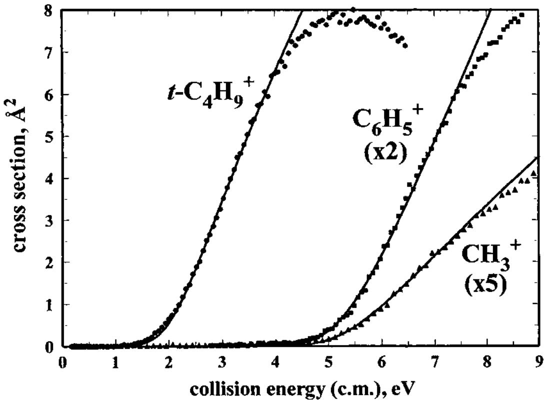


Figure 1. Cross sections for the formation of CH_3^+ (▲), t-$C_4H_9^+$ (●), and $C_6H_5^+$ (■) upon dissociation of CH_3CNH^+, t-$C_4H_9CNH^+$, and C_6H_5-CNH^+, respectively, as a function of the center-of-mass collision energy. The solid lines are the optimized fits to the data.

The transition state for the dissociation is characterized by the activation entropy, $\Delta S^\ddagger$, calculated using eq 3, where $Q^\ddagger$ and Q are the partition functions of the transition state and the activated complex, respectively, and $E^\ddagger$ and E are the corresponding average vibrational energies. By convention, the activation entropy is calculated at 1000 K. Loose transition states, such as those employed in this work, have activation entropies greater than zero.

$$\Delta S^\ddagger = k_B \ln Q^\ddagger/Q + (E_v{}^\ddagger - E_v)/T \qquad (3)$$

Dissociation thresholds obtained as described above are the 0 K dissociation energies. These are converted to the 298 K enthalpies, ΔH_{298}, using the difference in the integrated heat capacities of the products and reactants.

Results and Discussion

The key thermochemical data needed to determine the enthalpy of formation of isonitrile in this study are the enthalpies for the dissociation of the protonated nitriles (eq 1). Dissociation enthalpies for protonated acetonitrile, propionitrile, pivalonitrile, acrylonitrile, and benzonitrile (R = CH_3−, C_2H_5−, t-C_4H_9, C_2H_3−, and C_6H_5−, respectively) were obtained from energy-resolved collision-induced dissociation (CID) cross sections. The cross sections obtained for CH_3^+, $C_6H_5^+$, and t-$C_4H_9^+$ formation from protonated acetonitrile, benzonitrile, and pivalonitrile, respectively are shown in Figure 1. For the dissociation of $RCNH^+$, where R = CH_3− and C_6H_5−, simple dissociation to form R^+ is the only product channel observed. In the dissociation of t-$C_4H_9CNH^+$, the $C_3H_5^+$ and $C_2H_5^+$ cations are observed at energies higher than 10 eV and result from fragmentation of the *tert*-butyl cation.

For protonated propionitrile and acrylonitrile (R = C_2H_5− and C_2H_3−), a second low energy dissociation channel is

TABLE 1: Thermochemical Data Used to Calculate $\Delta H_{F,298}$(HNC)[a]

R =	CH_3	C_2H_5	C_2H_3	C_6H_5	t-C_4H_9
$DH_{298}(R^+{-}CNH)$[b]	5.11 ± 0.10	3.28 ± 0.05	3.98 ± 0.05	4.03 ± 0.04	2.07 ± 0.06
n[c]	1.4 ± 0.1	1.4 ± 0.1	1.4 ± 0.1	1.5 ± 0.1	1.5 ± 0.1
$\Delta S^{\ddagger}_{1000}$[d]	17.8	16.8	19.7	18.5	26.9
PA(RCN)[e]	186.2	189.8	187.5	194.0	193.8
$\Delta H_{f,298}$(RCN)[f]	17.7 ± 0.1[g]	12.3	43.0	52.3	−0.79
$\Delta H_{f,298}(R^+)$[h]	261.8 ± 0.1	215.6 ± 0.5	261.8 ± 3.0	265.5 ± 3.0	169.9 ± 0.9
$\Delta H_{f,298}$(HNC)[i]	53.2 ± 2.7	48.2 ± 2.3	51.1 ± 3.7	51.4 ± 4.0	49.0 ± 2.5

[a] Values in kcal/mol unless otherwise noted. [b] In eV; this work. [c] From the cross section model, eq 2. [d] Activation entropy for the dissociation, calculated using eq 3, in eu. [e] Taken from ref 17; uncertainties assumed to be ± 2 kcal/mol. [f] Values taken from ref 32 and have an uncertainty of ± 1 kcal/mol unless otherwise noted. [g] Reference 33. [h] Reference 26. [i] Calculated using eq 6.

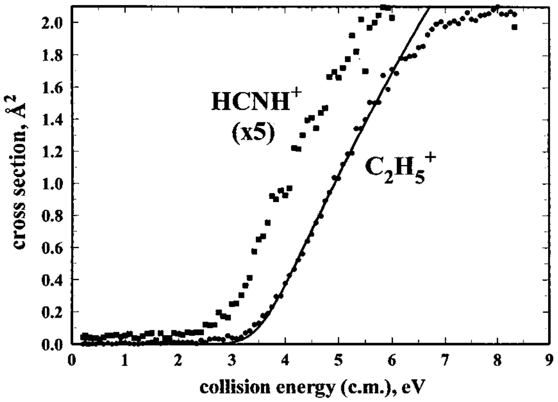


Figure 2. Cross sections for the formation of $C_2H_5^+$ (●) and $HCNH^+$ (■) upon dissociation of $C_2H_5CNH^+$ as a function of center-of-mass collision energy. The solid line is the optimized fit to the data.

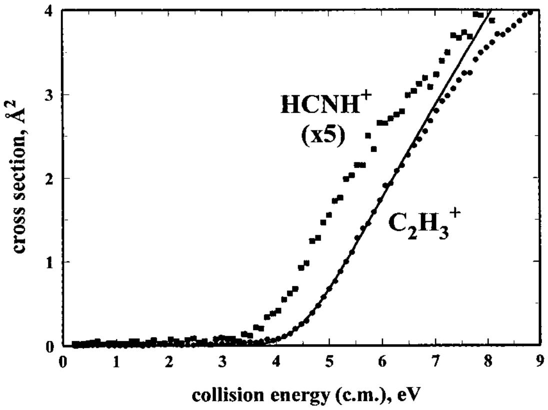
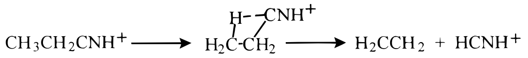
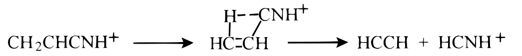


Figure 3. Cross sections for the formation of C_2H_3+ (●) and $HCNH^+$ (■) upon dissociation of $C_2H_3CNH^+$ as a function of center-of-mass collision energy. The solid line is the optimized fit to the data.

observed in addition to formation of R^+, corresponding to formation of m/z 28 (Figures 2 and 3, respectively). The apparent onsets for the m/z 28 ions are slightly lower than those for formation of R^+, although the maximum cross sections are about 1/5 as high. To identify the m/z 28 ion, CID was carried using $RCND^+$, which was generated via proton transfer using D_3O^+. In this case, the mass of the ion shifts to m/z 29, corresponding to $HCND^+$. Therefore, the m/z 28 ion results from proton transfer from R^+ to HNC during the dissociation to give $HCNH^+$ and ethylene or acetylene (eqs 4 and 5). These reaction channels



$$CH_3CH_2CNH^+ \longrightarrow \overset{H--CNH^+}{H_2C\text{-}CH_2} \longrightarrow H_2CCH_2 + HCNH^+ \quad (4)$$



$$CH_2CHCNH^+ \longrightarrow \overset{H--CNH^+}{HC{=}CH} \longrightarrow HCCH + HCNH^+ \quad (5)$$

are discussed in more detail below. Upon dissociation of $C_2H_5CNH^+$, the vinyl cation and CH_2CNH^+ are also observed at high energies, resulting from subsequent fragmentation of the ethyl cation and loss of methyl radical, respectively.

The apparent energy onsets for the dissociations differ significantly depending on the identity of R. The lowest energy onset is observed for formation of t-$C_4H_9^+$ from protonated pivalonitrile at ~2 eV, while the onset for $C_6H_5^+$ formation from protonated benzonitrile or CH_3^+ cation from CH_3CNH^+ is ca. 5 eV. The dissociation thresholds obtained by modeling the CID cross sections using eq 2 are listed in the first row in Table 1, and the fits to the data are shown in Figures 1−3. The corresponding values for n and $\Delta S^{\ddagger}_{1000}$ are also provided in Table 1. The uncertainties on the threshold energies include the standard deviation of the values from replicate measurements, a 0.15 eV (lab) contribution to account for the uncertainty of the energy scale,[24] and an uncertainty due to the choice of the transition state model. The uncertainty in the transition state model corresponds to the effect on the threshold if the activation entropy is changed by ±2 eu. The choice of the transition state has the largest effect on the threshold obtained for the larger systems with the highest onsets. For example, the transition state contribution to the uncertainty of the $C_6H_5CNH^+$ dissociation energy is 0.07 eV, while that for the dissociation energy of CH_3CNH^+ is only 0.02 eV.

The presence of a low energy, $HCNH^+$ loss, channel for $C_2H_5CNH^+$ and $C_2H_3CNH^+$ suggests that the dissociation onsets may be subject to competitive shifts.[25] Therefore, the cross sections for CID of these ions were modeled by assuming statistical partitioning of the R^+ and $HCNH^+$ products as described by Rodgers and Armentrout.[25] The transition states for $HCNH^+$ loss were calculated at the B3LYP/6-31+G* level of theory. Qualitative depictions of the transition states are shown in eqs 4 and 5. As expected, the transition states for $HCNH^+$ loss are significantly "tighter" than those for HNC loss. Whereas the activation entropies for HNC loss from $C_2H_5CNH^+$ and $C_2H_3CNH^+$ are calculated to be 16.8 and 19.8 eu, respectively, the activation entropies for $HCNH^+$ loss are 8.1 and 12.7 eu, respectively. The threshold energies obtained for HNC loss are listed in Table 1. The threshold energies for $HCNH^+$ loss obtained from the modeling are 2.92 eV for $C_2H_5CNH^+$ and 3.90 eV for $C_2H_3CNH^+$. Given that $HCNH^+$ loss is calculated to be endothermic by only 2.25 and 2.63 eV for these ions,[26,27] the threshold energies for $HCNH^+$ loss indicate significant barriers in excess of the reaction endothermicity. If the HNC loss channels are fit without including the $HCNH^+$ channel, threshold energies of 3.35 and 4.08 eV are obtained for $C_2H_5CNH^+$ and $C_2H_3CNH^+$, respectively, indicating competitive shifts of 0.07 and 0.10 eV, respectively.

The measured thresholds can be used to calculate the enthalpy of formation of HNC using the thermochemical cycle shown in eq 6, where PA(RCN) is the proton affinity.

$$\Delta H_{f,298}(\mathrm{HNC}) = D_{298}(\mathrm{R}^+{-}\mathrm{CNH}) - \mathrm{PA}(\mathrm{RCN}) + \Delta H_{f,298}(\mathrm{RCN}) - \Delta H_{f,298}(\mathrm{R}^+) + \Delta H_{f,298}(\mathrm{H}^+) \quad (6)$$

Proton affinities of the nitriles examined in this work have been obtained previously from equilibrium measurements.[28−31] The currently recommended values[17] are listed in Table 1. The enthalpies of formation of the neutral nitrile,[32,33] RCN, and the corresponding cation[26] are also listed, while the derived enthalpy of formation is shown in the last row.

Although neutral products are not observed in this experiment, the measured enthalpy of formation is assigned to HNC. Given that RCN is protonated at the nitrogen, the formation of HNC is dynamically favored over HCN because it occurs via a loose transition state, whereas formation of HCN would occur through a tight transition state. The results for R = C_2H_5 and C_2H_3 provide experimental verification that the loss of (H,N,C) occurs by a loose transition state. Despite the fact that $HCNH^+$ is formed with a lower onset than loss of (H,N,C), the cross section for R^+ formation is ca. 5 times higher than that for $HCNH^+$ formation. For this to be the case, the transition state for loss of (H,N,C) must be "looser" than that for loss of $HCNH^+$. As described above, the transition state for the formation of $HCNH^+$ is calculated at the B3LYP/6-31+G* level of theory to have $\Delta S^{\ddagger}_{1000} = 8-12$ eu, much looser than expected for loss of HCN. The results also rule out the possibility that RCN is protonated on the nitrile carbon. If that was the case, then HCN could be formed via a loose transition state. However, the threshold energies obtained from the data are too high to correspond to formation of HCN through a loose transition state. Formation of HCN with low cross sections at low collision energies may contribute to some of the "tail" observed in Figures 1−3 , but, as described in the Experimental Section, these data are not included in the analysis. Last, the absence of (H,C,N) loss [as opposed to (D,C,N) loss] in the deuterium labeling experiments rules out formation of HCN by a proton exchange mechanism wherein the $HCNH^+$ protonates the incipient ethylene or acetylene.

The measured enthalpies of formation range from 48.2 to 53.2 kcal/mol, and agree within the quoted errors. The assigned uncertainties include (a) the uncertainties on the dissociation energies, (b) a ±2.0 kcal/mol contribution from the uncertainties of the proton affinities, and (c) the uncertainties for the neutral and cation enthalpies of formation. The final assigned value for the enthalpy of formation of HNC is obtained by using a weighted average, where the individual results are weighted by the standard deviation, the transition state error, and the uncertainty in the enthalpy of formation of the cation, R^+. This gives a final average that is weighted more heavily toward the values for systems having reproducible thresholds that are less affected by the choice of the transition state model, and those for which the reference thermochemistry is better established. The average value obtained from the five data sets is 49.7 ± 0.9 kcal/mol, where the uncertainty is the statistical combination of the weighting elements. The uncertainty is increased by the uncertainty of the enthalpy of formation in the neutral RCN, ±1 kcal/mol, and by the uncertainty in the energy scale. For the individual measurements, this is taken as 0.15 eV (lab). For the average, a conservative value of 0.07 eV (c.m.), which is the energy scale uncertainty for CH_3CNH^+, is applied. Last, the standard deviation of the five results is included to account for the scatter in the data.

After determining the uncertainty, the final assigned enthalpy of formation is $\Delta H_{f,298}(\mathrm{HNC}) = 49.7 \pm 2.9$ kcal/mol. Using this value along with the enthalpy of formation of $HNCH^+$ (227.6 ± 2.0 kcal/mol),[27] the proton affinity of HNC is calculated to be 187.8 ± 3.5 kcal/mol, or 17.4 ± 2.9 kcal/mol higher than that for HCN. This resulting difference in the PAs is in agreement with the range 17.5−18.3 kcal/mol established by the bracketing experiments of Pau and Hehre.[16] The enthalpy of formation of HNC obtained from this work is consistent with the lower limit suggested by Ellison and co-workers[15] and supports the conclusion obtained by considering the Pau and Hehre results in light of the revised proton affinity scale that the energy difference between HNC and HCN is slightly greater than the value predicted using high-level molecular orbital calculations.[7,11−13] However, the present results also agree, within error, with the theoretical values and therefore do not rule out the possibility that the bracketed proton affinity is too high. More experiments will be required to resolve the discrepancy.

Summary

Collision-induced dissociation threshold measurements have been used to determine the enthalpy of formation of hydrogen isonitrile, HNC. Five independent measurements led to $\Delta H_{f,298}$(HNC) = 49.7 ± 2.9 kcal/mol. This is 17.4 ± 2.9 kcal/mol higher than the enthalpy of formation of HCN, which agrees with the assignment of Pau and Hehre,[16] but is slightly higher than values obtained from high-level molecular orbital calculations.

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