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Absolute Heat of Formation and Singlet−Triplet Splitting for HCCN

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The absolute heat of formation at 298 K for ground-state triplet cyanocarbene, HCCN, has been determined from a measurement of the chloride dissociation energy of $ClCHCN^-$. Analysis of the energy-resolved collision-induced dissociation cross section as a function of center-of-mass collision energy in a flowing afterglow triple quadrupole instrument gives a chloride dissociation enthalpy of 43.7 ± 2.5 kcal/mol. Proton-transfer bracketing experiments were used to determine a gas-phase acidity, ΔH_{acid}, of 357.7 ± 2.0 kcal/mol for $ClCH_2CN$. The heat of formation at 298 K for $ClCH_2CN$ was determined from collision-induced dissociation of a series of protonated nitriles to be 25.5 ± 3.8 kcal/mol. The chloride ion dissociation enthalpy and the heat of formation and gas-phase acidity of $ClCH_2CN$ are combined in a simple thermochemical cycle to give an absolute heat of formation for HCCN of 115.6 ± 5.0 kcal/mol. High level theoretical calculations were performed in support of the experimental study at the G2 (**I**), CBS-Q (**II**), CBS-APNO (**III**), B3LYP/6-31G* (**IV**), and B3LYP/6-311++G** (**V**) levels of theory. The compound methods, **I**−**III**, give predictions for the acidity and heat of formation of $ClCH_2CN$ and for the heat of formation of the triplet ground state and first excited singlet state of HCCN that are in good agreement with experiment. The density functional theory predictions (**IV**,**V)** for these quantities are fair at best. The heat of formation of ^{3}HCCN is used to derive additional thermodynamic quantities including a C−H bond dissociation enthalpy in CH_2CN of 107.3 ± 5.4 kcal/mol and a singlet−triplet splitting for HCCN of 11.1 ± 5.8 kcal/mol.

Introduction

Cyanocarbene (HCCN) is an important interstellar molecule that is thought to be an intermediate in the formation of larger polynitriles.[1,2] The triplet ground state of HCCN has been verified by matrix ESR studies. In their initial papers, Bernheim and co-workers reported zero-field splitting parameters, $D = 0.849\ \mathrm{cm}^{-1}$ and $E = 0\ \mathrm{cm}^{-1}$, consistent with a linear allene-like form for the triplet carbene,[3] whereas early theoretical studies concluded that the bent form of the carbene was more stable than the linear form.[4] The disagreement over the actual structure of HCCN continued for years with theory predicting a bent structure[5−8] and experiments suggesting a linear geometry.[9−11] In the 1990s, Curl and co-workers seem to have settled the argument by proposing a "quasi"-linear structure based on measurements of the ν_5 bending vibrational frequency.[12,13]

Despite the interest in the structure of the ground state of HCCN, the thermochemical properties of cyanocarbene and its isomers are not known experimentally, although theoretical calculations have been reported. In conjunction with a neutralization/reionization mass spectrometry study of HCCN, HNCC, and HCNC, Schwarz and co-workers have mapped out the potential energy surfaces for the cationic, neutral, and anionic $[H,C_2,N]$ molecules.[14] The best theoretical prediction of the thermochemistry for HCCN is from Francisco,[15] who calculated the heat of formation for the triplet ground state and the first excited singlet state using G2 theory to be 114 ± 2 and 126.5 ± 2 kcal/mol, respectively.

Negative ion photoelectron spectroscopy (NIPES) is often a very powerful method for the investigation of the thermochemical properties of organic reactive intermediates, including biradicals and carbenes,[16] and has been used extensively for the investigation of the heats of formation and singlet−triplet splittings in these species. The gas-phase reactivity of the radical anion of HCCN has been examined by Grabowski and Melly,[17] whereas $HCCN^-$ and its isomer $HCNC^-$ have been studied by Nibbering and co-workers.[18] Therefore, these ions are stable and could be examined by using NIPES. Ellison and co-workers have recently described the photoelectron spectrum of the $HCCN^-$ ion and the $HCNC^-$ isomer, wherein they investigate the relative energies of the singlet and triplet states of the carbenes.[19] However, direct determination of the singlet−triplet energy from the photoelectron spectrum of $HCCN^-$ is challenging because of the large geometry difference between the ion and the triplet carbene, and because triplet HCCN is a "floppy" molecule that is not well described using harmonic oscillator and rigid rotor approximations. On the other hand, the transition from the ion to the *singlet* state of HCCN is nearly vertical, such that a very accurate electron binding energy of 2.518 ± 0.008 eV is obtained for the singlet state.[19] The heat of formation of the $HCCN^-$ ion can be calculated to be 68.7 ± 3.7 kcal/mol from the measured proton affinity, 374 ± 3 kcal/mol, reported by Grabowski and Melly[17] and Matimba et al.,[18] and the heat of formation of CH_2CN.[20,21] From this result and the measured electron binding energy, the heat of formation of the *excited-state* singlet carbene is found to be 126.7 ± 3.7 kcal/mol. Nimlos et al.[19] have also assigned an electron affinity of 2.014 ± 0.010 eV for the triplet state, implying a heat of formation of 115.1 ± 3.7 kcal/mol and a singlet−triplet splitting of 11.6 kcal/mol, which is in good agreement with theoretical

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predictions. However, determination of the electron affinities of triplet carbenes is notoriously challenging,[22,23] and an independent measure of the triplet heat of formation is desired to confirm the photoelectron assignment.

In recent years, Squires and co-workers have shown that heats of formation for ground-state carbenes[24−27] and other reactive intermediates[28−31] can be obtained using energy-resolved collision-induced dissociation. For example, the threshold enthalpy for collision-induced halide loss from a suitably chosen α-halocarbanion (ΔH_T, eq 1) can be combined with auxiliary thermochemical quantities according to eq 2 to derive a heat of formation for the carbene. In addition to ΔH_T, determination of the

$$RCHX^- \rightarrow RCH + X^- \qquad (1)$$

heat of formation of the carbene by using eq 2 requires the gas-phase acidities (ΔH_{acid}) and heats

$$\Delta H_{f,298}(RCH) = \Delta H_T + \Delta H_{acid}(RCH_2X) + \Delta H_{f,298}(RCH_2X) - \Delta H_{acid}(HX) - \Delta H_{f,298}(HX) \qquad (2)$$

of formation of RCH_2X and HCl. This approach has been shown to give reliable heats of formation for ground-state singlet carbenes and biradicals, for which the dissociation from a singlet carbanion is spin allowed.[24,26,28] Ground-state triplets have also been examined. For example, Poutsma et al.[25] measured the heats of formation of methylene (CH_2), vinylcarbene ($CH_2{=}CH{-}CH$), and phenylcarbene, (C_6H_5CH) by using three different halocarbanion precursors, RCH_2X, where X = Cl, Br, and I. Dissociation energies were measured for each halocarbanion, from which three independent values for the apparent heat of formation for the carbenes could be obtained. In the cases examined,[25] good agreement was observed among the apparent heats of formation obtained from the three different precursors, which was interpreted to mean that the halocarbanions dissociate in the adiabatic limit to form the ground-state triplet carbenes. Therefore, the energy-resolved CID approach can be applied to the determination of the heats of formation of triplet carbenes as well. In this work, we applied the CID approach described above to the determination of the heat of formation of cyanocarbene. We obtained a heat of formation that is in good agreement with that predicted by MO calculations. Moreover, by combination of the heat of formation for the triplet state with the measured heat of formation of the singlet from Ellison and co-workers,[19] the singlet−triplet splitting in the carbene was obtained. Last, we describe an experimental determination of the heat of formation of chloroacetonitrile, needed for the calculation of the heat formation of the carbene.

Experimental Section

All experiments were performed on a flowing afterglow-triple quadrupole instrument.[32] The pressure, flow rate and flow velocity of the helium buffer gas were P_{He}= 0.400 Torr, F_{He} = 190 STP cm^3/s, and υ_{He} = 9600 cm/s. For negative ion experiments, hydroxide was created by electron impact ionization on a mixture of N_2O and CH_4 in the ion source region of the instrument located in the upstream end of the flow tube. The chlorocyanomethyl anion, $ClCHCN^-$, was produced by the proton-transfer reaction of OH^- with $ClCH_2CN$ vapors added through a downstream inlet in the flow tube. For the positive ion experiments, protonated nitrile cations were produced by chemical ionization with H_3O^+ acting as the protonating agent.

A small fraction of the ions are gently extracted though a small orifice in a nosecone into the triple quadrupole region of the instrument for either single-stage or tandem mass spectrometric analysis. Collision-induced dissociation is carried out using mass-selected ions in the gastight, r.f.,-only quadrupole (Q2) with either Ne, Ar, or Xe serving as the target gas. The axial kinetic energy of the ions in the laboratory frame is determined by the Q2 rod offset voltage, with the absolute energy scale determined by retarding potential analysis. The pressure in the collision cell is measured with an absolute pressure transducer. Product ions and un-reacted parent ions are extracted into the third quadrupole for mass analysis and are detected with an electron multiplier operating in single-ion counting mode.

The gas-phase acidity of $ClCH_2CN$ was obtained from bracketing experiments. $ClCH_2CN$ was allowed to react with a series of reference base anions of known proton affinity. Observation of products corresponding to proton transfer indicates that this reaction is exothermic and therefore that the acidity of $ClCH_2CN$ is greater than that of the conjugate acid of the reference base. The reverse reaction in which $ClCHCN^-$ is reacted with a series of reference acids is also carried out. The results of these two sets of experiments are used to determine the gas-phase acidity of $ClCH_2CN$ (see below).

Energy Threshold Experiments. Details of the procedures used for data collection and analysis of the energy-resolved CID experiments have been presented elsewhere.[25,28,32,33] In the present experiments, the yield of product ion is monitored as a function of the axial kinetic energy of the reactant ion, E_{lab}, which was calibrated by a retarding potential analysis with the Q2 pole offset voltage serving as the retarding potential. An appearance curve is generated by plotting the CID cross section versus collision energy in the center-of-mass frame, $E_{CM} = E_{lab}(m/(m + M))$, where m and M are the masses of the neutral target gas and the reactant ion, respectively. Absolute cross sections were calculated in the thin target limit from $\sigma_p = I_p/INl$, where I_p and I are the intensities of the product and reactant ions, N is the number density of the target gas and l is the effective path length.[32]

The threshold for collision-induced dissociation is derived by fitting the appearance curves with a model function that explicitly takes into account the contribution of the reactant ion internal energy.[34−36] In this expression, E_0 is the desired energy threshold, σ_0 is a

$$\sigma = \sigma_0 \sum_{i=1}^{3n-6} \frac{g_i P_D(E,E_i\tau)[E + E_i - E_0]^n}{E} \qquad (3)$$

scaling factor, n is an adjustable parameter and i denotes rovibrational states having energy E_i and population g_i ($\Sigma g_i = 1$). The rovibrational energy distributions of the reactant ions were obtained from rotational constants and scaled vibrational frequencies obtained from either semiempirical[37] or ab initio molecular orbital calculations.[38] The P_D term is the probability that an ion having internal energy ($E + E_i$) will dissociate within the experimental time window, τ (ca. 30 μs),[32] and is estimated from RRKM calculations of the reactant ion decay rate as a function of internal energy.[39,40] Properties of the dissociation transition states required for the RRKM analyses are generated using the procedures described by Armentrout and co-workers,[41] wherein a product-like structure is assumed. The appearance curves were fit by varying E_0, n, and σ_0 in an iterative manner so as to minimize deviations from the model function and the data in the steeply rising portion of the curve using the

TABLE 1: Acid/Base Bracketing Results for $ClCH_2CN$[a]

HB	ΔG_{acid}[b]	forward	reverse
$CH_3(C{=}O)C_6H_5$	354.5 ± 2.0	yes	no
$CH_3CH_2(C{=}O)C_6H_5$	353.9 ± 2.0	yes	no
$H(C{=}O)NH_2$	352.8 ± 2.0	yes	no
pyrrole	350.9 ± 2.0	slow	yes
$CHCl_3$	349.9 ± 2.0	no	yes
$(TMS)_2NH$	349.0 ± 2.0	yes	yes
indene	346.7 ± 2.0	no	yes
$p\text{-}NO_2{-}C_6H_4CH_3$	345.3 ± 2.0	no	yes

[a] Forward: $ClCH_2CN + B^- \rightarrow ClCHCN^- + HB$ Reverse: $ClCHCN^- + HB \rightarrow ClCH_2CN + B^-$. [b] Acidity values taken from ref 52.

CRUNCH program as developed by Ervin, Armentrout and co-workers.[36,41,42] During the fit, the trial functions are convoluted with a Doppler broadening function,[43] which accounts for thermal motion of the target, as well as the kinetic energy of the reactant, approximated by a Gaussian function with full width at half-maximum of 1.5 eV, lab. Threshold energies derived from the fitting correspond to 0 K bond dissociation energies. The 298 K dissociation enthalpies are obtained by standard thermodynamic transformations.

Gas purities were as follows: He (99.995%), Ar(99.955%), Ne (99%), N_2O(99.99%), CH_4 (99%), NF_3 (98%). All liquid reagents were obtained commercially and used as supplied except for degassing prior to use.

Computational Details. Ab initio molecular orbital and density functional theory calculations for singlet and triplet HCCN, singlet and triplet CH_2, CH_4, CH_3CN, $ClCH_2CN$, and $ClCHCN^-$ were performed using the Gaussian 98W suite of programs.[38] Optimized geometries and harmonic vibrational frequencies were calculated using several different levels of theory. Predictions for the heats of formation for triplet and singlet HCCN were obtained from two different approaches. The first was through the calculation of atomization energies using the G2 theoretical method of Pople (method **I**)[44] and the CBS-Q (**II**)[45] and CBS-APNO (**III**)[46] methods of Petersson. The second approach was to use the isodesmic reaction shown in eq 4

$$^{x}CH_2 + CH_3CN \rightarrow {}^{x}HCCN + CH_4 \qquad (4)$$

The 298 K enthalpy of reaction 4 was evaluated with methods **I**−**III**, and also with the hybrid DFT methods B3LYP/6-31G* (**IV**) and B3LYP/6-311++G** (**V**).[47,48] The calculated enthalpy of reaction 4 is then combined with the experimental heats of formation at 298 K for acteonitrile, methane and singlet or triplet methylene (Table 3) to give a prediction for the heat of formation at 298 K for HCCN. All optimized structures were verified to be minima from the absence of negative eigenvalues in the Hessian matrix. Thermodynamic information was obtained from scaled vibrational frequencies with scaling factors taken from Scott and Radom.[49]

Results and Discussion

In this section, we describe the determination of the heat of formation of HCCN from energy-resolved CID threshold measurements. The CID experiments with chlorocyanomethyl anion are described first, followed by a description of gas-phase acidity bracketing results. The last datum required to determine the heat of formation of the carbene is the heat of formation of chloroacetonitrile ($ClCH_2CN$). An experimental determination of that quantity from energy-resolved CID of the protonated nitrile is also provided.

The chlorocyanomethyl anion ($ClCHCN^-$) was generated by proton transfer between OH^- and $ClCH_2CN$ in the flow reactor. In addition to the desired carbanion, a high yield of Cl^- was also observed, presumably due to nucleophilic substitution. Collision-induced dissociation of $ClCHCN^-$ with Ar and Ne target over the range 0−10 eV (center-of-mass) gives Cl^- as the only observed ionic product. Measured cross sections as a function of collision energy are shown in Figure 1. The maximum cross section for the dissociations with Ar collision gas are 1−2 Å^2 near 5 eV (c.m.). The energy-resolved cross sections were fit with the model function shown in eq 3. Although RRKM effects were included in the fit, they do not have a significant effect on the modeled dissociation energy due to the small size of the reactant ion, and the relatively low threshold for dissociation. The average threshold energy for collision-induced chloride loss from $ClCHCN^-$ from replicate measurements was determined to be 1.84 ± 0.11 eV, where the uncertainty includes the standard deviation of the data, and a 0.15 eV (lab) uncertainty in the absolute energy scale. This value corresponds to a 298 K enthalpy of dissociation of 43.7 ± 2.5 kcal/mol.

The acidity of $ClCH_2CN$ was determined from acid−base bracketing experiments. Moderately basic anions such as acetophenone enolate and pyrrolide deprotonate $ClCH_2CN$, while anions such as deprotonated *p*-nitrotoluene and CCl_3^- are not sufficiently basic to remove a proton. The results of the acid−base bracketing reactions are listed in Table 1. In addition to the "forward" reactions of $ClCH_2CN$ with reference bases, "reverse" bracketing experiments in which $ClCHCN^-$ is allowed to react with reference acids were also carried out. The results of these experiments are also shown in Table 1. Of particular relevance is that $ClCHCN^-$ is observed to deprotonate $(TMS)_2NH$, and that $(TMS)_2N^-$ deprotonates $ClCH_2CN$. The fact that the reaction is reversible indicates that the gas-phase acidity of $ClCH_2CN$ is nearly the same as that of $(TMS)_2NH$. From the results listed in Table 1, the gas-phase acidity for $ClCH_2CN$ is concluded to be between that of $CHCl_3$ and pyrrole, and a value of $\Delta G_{acid} = 350.0 \pm 2.0$ kcal/mol is assigned. The quantity ΔH_{acid} can be obtained from ΔG_{acid} by the addition of a $T\Delta S_{acid}$ term. The entropies of $ClCH_2CN$ and $ClCHCN^-$ were estimated from the molecular constants obtained from calculations at the B3LYP/6-311++G** level of theory to be 68.3 and 68.2 eu, respectively, which, when combined with the entropy of a proton

TABLE 2: Thermochemical Data Used to Calculate $\Delta H_{f,298}(ClCH_2CN)$[a]

R =	CH_3	C_2H_5	C_2H_3	C_6H_5	$t\text{-}C_4H_9$
$DH_{298}(R^+{-}CNH)$[b]	5.11 ± 0.10	3.28 ± 0.05	3.98 ± 0.05	4.03 ± 0.04	2.07 ± 0.06
PA(RCN)	186.2	189.8	187.5	194.0	193.8
$\Delta H_{f,298}(RCN)$	17.7 ± 0.1	12.3	43.0	52.3	−0.79
$\Delta H_{f,298}(R^+)$	261.8 ± 0.1	215.6 ± 0.5	261.8 ± 3.0	265.5 ± 3.0	169.9 ± 0.9
$\Delta H_{f,298}(ClCH_2CN)$[c]	27.9 ± 4.0	24.5 ± 3.7	25.8 ± 4.7	26.1 ± 4.8	23.7 ± 3.8

[a] Values in kcal/mol unless otherwise noted; all data as reported in ref 52. [b] In eV. [c] Calculated using eq 6 with PA($ClCH_2CN$) = 178.2 ± 1.0 kcal/mol and $\Delta H_{f,298}(CH_2Cl^+) = 230.6 \pm 2.3$ kcal/mol.

TABLE 3: Measured and Supplemental Thermochemistry[a]

thermochemical property	value	reference
	gas phase acidities	
$ClCH_2CN$	357.7 ± 2.0	this work
HCl	333.4 ± 0.1	52
CH_3CN	372.9 ± 2.1	52
CH_2CN	374 ± 3	17,18
	bond dissociation enthalpies	
$NCCH-Cl^-$	43.7 ± 2.5	this work
$NCCH_2-H$	94.8 ± 2.1	20,21
$^3NCCH-H$	107.3 ± 5.4	this work
$^1NCCH-H$	118.0 ± 3.7	19
	heats of formation	
$ClCH_2CN$	25.5 ± 3.8	this work
HCl	−22.0 ± 0.02	52
CH_3CN	17.7 ± 0.1	52
CH_2CN	60.4 ± 2.1	20
^3HCCN	115.6 ± 5.0	this work
^1HCCN	126.7 ± 3.0	19
$^3CH_2$	92.9 ± 0.6	b
$1CH_2$	101.8 ± 0.5	c
CH_4	−17.8 ± 0.4	52
CH_3CN	17.7 ± 0.1	52
	electron affinities (eV)	
CH_2CN	1.544 ± 0.013	19
^3HCCN	2.05 ± 0.27	this work

[a] Values in kcal/mol, unless otherwise specified. [b] Leopold, D. G.; Murray, K. K.; Stevens-Miller, A. E.; Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849. [c] Lengel, R. K.; Zare, R. N. *J. A. Chem. Soc.* **1978**, *100*, 7495.

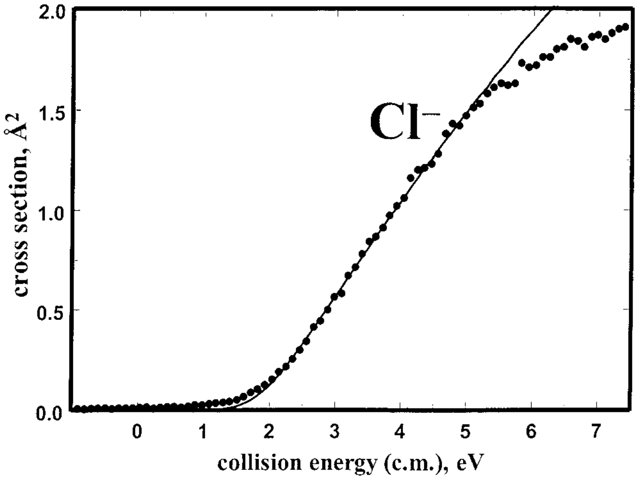

Figure 1. Cross sections for the formation of Cl^- upon collision-induced dissociation of $ClCHCN^-$ with argon target as a function of the center-of-mass collision energy. The solid line is the fully convoluted fit to the data as described in the text.

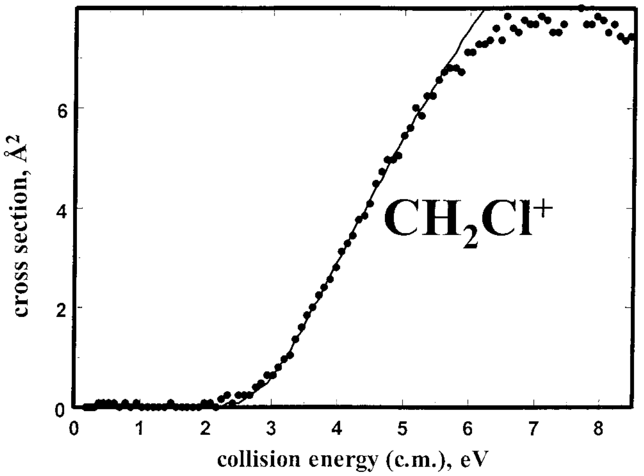

Figure 2. Cross sections for the formation of CH_2Cl^+ upon collision-induced dissociation of $ClCH_2CNH^+$ with argon target as a function of the center-of-mass collision energy. The solid line is the fully convoluted fit to the data as described in the text.

(26 eu) gives ΔS_{acid} = 25.9 eu. The resulting value of $\Delta H_{acid}(ClCH_2CN)$ is therefore 357.7 ± 2.0 kcal/mol.

To use eq 2 to determine the heat of formation of HCCN, a value for the heat of formation for $ClCH_2CN$ is needed. This quantity was determined from collision-induced dissociation experiments with protonated nitrile ions. Collision-induced dissociation of protonated chloroacetonitrile carried out in Q2 with Ar collision gas gives CH_2Cl^+ as the only product at low collision energies, resulting from loss of HNC (eq 5). At high energies, loss of chlorine atom (forming CH_2CNH^+) is also observed, but the cross section for this channel is about half of that for chloromethyl cation formation at 12 eV. Cross sections for formation of CH_2Cl^+ and CH_2CNH^+ as a function of energy are shown in Figure 2. The threshold energy for HCN loss from $ClCH_2CNH^+$ obtained by

$$\text{Cl-CH}_2\text{CNH}^+ \rightarrow \text{ClCH}_2^+ + \text{HNC} \tag{5}$$

modeling the data using eq 3 is determined to be 2.91 ± 0.11 eV, which corresponds to a 298 enthalpy of dissociation, $DH_{298}(ClCH_2^+\text{-}CNH)$ of 68.4 ± 2.4 kcal/mol. The heat of formation of $ClCH_2CN$ is obtained by comparing the dissociation enthalpy measured for the reaction shown in eq 5 with those of other protonated nitriles for which the heat of formation of the initial reactant is known (eq 6)

$$\text{RC}{\equiv}\text{NH}^+ + \text{ClCH}_2^+ \rightarrow \text{ClCH}_2\text{C}{\equiv}\text{NH}^+ + \text{R}^+ \tag{6}$$

The enthalpy change for this reaction is the difference between the dissociation enthalpies for $ClCH_2CNH^+$ and $RCNH^+$ ($\delta DH_{298}(RCNH^+,ClCH_2CNH^+)$), which can be used to calculate the heat of formation of $ClCH_2CN$ according to eq 7, where δPA is the difference in proton affinities between $ClCH_2CN$ and the reference, and $\delta\Delta H_{f,298}(R^+,CH_2Cl^+)$ is the difference in the heats of formation of the cation products

$$\Delta H_{f,298}(\text{ClCH}_2\text{CN}) = \delta\text{PA}(\text{ClCH}_2\text{CN,RCN}) - \delta D\text{H}(\text{ClCH}_2\text{CNH}^+\text{,RCNH}^+) + \delta\Delta H_{f,298}(\text{CH}_2\text{Cl}^+\text{,R}^+) + \Delta H_{f,298}(\text{RCN}) \tag{7}$$

The advantage of the relative approach outlined in eq 6 is that it is possible to use multiple references, each providing an independent measure of the heat of formation of $ClCH_2CN$. In this study, five nitriles were employed, with R = CH_3-, C_2H_5-, *t*-C_4H_9-, C_2H_3-, and C_6H_5-. Moreover, systematic errors introduced during the threshold measurement will tend to cancel, reducing the overall uncertainty. Last, the dissociation energies for the protonated reference nitriles have been measured previously using the same instrument[31] and therefore are readily available.

The differences in the dissociation enthalpies of the protonated reference nitriles used in this work are summarized in Table 2. Also included in Table 2 are the proton affinities and heats of formation of the reference nitriles, and the heats of formation of the product cations, R^+. The chloroacetonitrile heats of formation derived using these data along with PA($ClCH_2CN$) = 178.2 ± 1.0 kcal/mol and $\Delta H_{f,298}(CH_2Cl^+)$ = 230.6 ± 2.3

TABLE 4: Calculated Values for 298 K Heats of Formation for Singlet and Triplet HCCN, and Singlet−Triplet Splitting from Atomization and Isodesmic Approaches[a]

	G2 (**I**)	CBS-Q (**II**)	CBS-APNO (**III**)	B3LYP/6-31G* (**IV**)	B3LYP/6-311++G** (**V**)
$\Delta H_{\text{atom}}(^3\text{HCCN})^b$	388.1	392.3	392.1		
$\Delta H_{\text{atom}}(^1\text{HCCN})^b$	380.6	381.3	379.0		
$\Delta H_{\text{f,298}}(^3\text{HCCN})$	119.5	115.3	115.6		
$\Delta H_{\text{f,298}}(^1\text{HCCN})$	127.1	126.3	128.6		
$\Delta H_{\text{Singlet-Triplet}}$	7.6	11.0	13.0		
$\Delta H_{\text{eq 3}}(^3\text{HCCN})^c$	−12.6	−14.5	−15.4	−21.7	−20.1
$\Delta H_{\text{eq 3}}(^1\text{HCCN})^c$	−11.7	−11.5	−11.3	−18.3	−15.7
$\Delta H_{\text{f,298}}\ (^3\text{HCCN})$	115.9	114.0	113.1	106.8	108.4
$\Delta H_{\text{f,298}}\ (^1\text{HCCN})$	125.8	126.0	126.2	119.2	121.8
$\Delta H_{\text{Singlet-Triplet}}$	9.9	11.9	13.1	12.4	13.4

[a] Values in kcal/mol. [b] Calculated atomization enthalpy for the carbene. [c] Calculated enthalpy for the isodesmic reaction shown in eq 4.

kcal/mol[50−52] are shown at the bottom of Table 2. A weighted average of these data gives $\Delta H_{\text{f,298}}(\text{ClCH}_2\text{CN}) = 25.5 \pm 3.8$ kcal/mol.

Combining the acidity and heat of formation of ClCH_2CN, the threshold enthalpy for collision-induced chloride loss from ClCHCN^-, and other supplemental thermochemistry from Table 3 gives a heat of formation for HCCN of 115.6 ± 5.0 kcal/mol. Considering that all the α-halocarbanions examined previously have been found to undergo adiabatic dissociation, even in cases where the dissociations are spin forbidden,[25] the measured enthalpy is assigned as the heat of formation of the *triplet* carbene, ^{3}HCCN. This value can be combined with the measured heat of formation of the singlet of 126.7 ± 3.0 to give a derived singlet−triplet splitting for HCCN of 11.1 ± 5.8 kcal/mol.

Computational Results. Computational predictions for the experimentally measured quantities described above were obtained from ab initio and hybrid density functional calculations. Cartesian coordinates, vibrational frequencies and derived enthalpies at 298 K for ^{3}HCCN, ^{1}HCCN, $^3\text{CH}_2$, $^1\text{CH}_2$, CH_4, CH_3CN, ClCH_2CN, and ClCHCN^- obtained using methods **I**−**V** are available as Supporting Information (Tables S1−S3). Some of these species have been studied previously using a variety of theoretical methods. In most cases, only the total electronic energy and occasionally zero-point corrections were reported in the original papers. In addition, vibrational frequencies were usually not listed and as such it was impossible for us to adjust the 0 K energies to 298 K enthalpies. We have used the 0 K energies from the literature (see references Table S1) and have adjusted these to 298 K enthalpies by standard thermodynamic transformations using scaled vibrational frequencies.[49]

Heat of Formation of ^{1}HCCN and ^{3}HCCN and S−T Splitting. The heats of formation for singlet and triplet HCCN were determined by using both molecular orbital (**I**−**III**) and hybrid density functional (**IV**,**V**) approaches. For the triplet carbene, unrestricted methods, rather than restricted-open shell methods, were utilized. Spin contamination is more of a problem in the molecular orbital approaches than for B3LYP. The expectation values of $<S^2>$ for ^{3}HCCN were 2.273, 2.264, 2.384, 2.057, and 2.054 for methods **I**−**V** respectively. Francisco does not address spin contamination in his G2 study, and his work focused more on the structure and spectroscopy of HCCN than on its energetics.[15] Spin contamination values for triplet methylene are much smaller, < 2.017, for all methods investigated.

Estimates for the heat of formation of ^{3}HCCN and ^{1}HCCN and the singlet−triplet energy difference are obtained from the total atomization enthalpy obtained from methods **I**,[44] **II**[45] and **III**[46] and are given in Table 4. The 298 K enthalpies for C, H, and N were obtained from standard thermodynamic transformations of the 0 K energies reported by Pople (**I**) and Petersson (**II**,**III**). Methods **I**−**III** give predictions for the 298 K heats of formation for ^{3}HCCN of 119.5, 115.3 and 115.6 kcal/mol, respectively, all of which are in agreement with our experimental determination of 115.6 ± 5.0 kcal/mol.

$$\text{HCCN} \rightarrow \text{H} + 2\text{C} + \text{N} \qquad (8)$$

A similar approach was used to give predictions for the heat of formation for ^{1}HCCN. The three compound methods give predictions for the heat of formation of ^{1}HCCN of 126.4, 127.9, and 128.1 kcal/mol for **I**−**III**, respectively. The agreement between the methods is somewhat better for the singlet than for the triplet, and all are in good agreement with the experimental value of 126.7 ± 3.0 kcal/mol.[19]

With predictions for the heats of formation of singlet and triplet in hand, we can make predictions for the singlet−triplet splitting for HCCN from the atomization approaches (Table 4). The G2 (**I**) theory prediction is the lowest at 7.6 kcal/mol. Because G2 under-stabilizes the triplet, this value is somewhat lower than the others, but is still within the experimental error limits. The CBS (**II**,**III)** methods give better predictions for the heats of formation for both the singlet and triplet carbene and therefore give more reliable predictions for the singlet−triplet splitting of 11.0 and 13.0 kcal/mol, respectively.

Estimates for the heats of formation for triplet and singlet HCCN were also obtained from isodesmic reaction shown in eq 4. The enthalpy of the hypothetical dihydrogen transfer reaction is calculated by using methods **I**−**V**. The results of these calculations are also shown in Table 4. The compound methods (**I**−**III)** give heats of formation of 115.9, 114.1, and 113.1 kcal/mol for ^{3}HCCN, all of which are in excellent agreement with the experimental determination. The hybrid DFT (**IV**,**V)** results of 106.8 and 108.4 are very low. Recently, the B3LYP functional combination has been used extensively for the calculation of molecular structures and energetic properties of carbenes,[25,53−58] biomolecules,[59−62] and molecules containing metals[63−65] and third- and fourth-row atoms.[66,67] In many cases, including some of our previous carbene work,[25] it has been shown to give results that are in reasonable agreement with experiment.[55,62,64] However, in some cases,[63] including the present study, B3LYP does not give satisfactory predictions for the absolute thermodynamic quantities of interest with either the minimal or extended basis sets.

Similar calculations were performed to give predictions for the heats of formation for ^{1}HCCN. Heats of formation of 125.8, 126.0, 126.2, 119.2, and 121.8 kcal/mol were obtained from methods **I**−**V**. As with the triplet, the compound methods (**I**−**III**) give excellent agreement with the experimental determination,[19] while the B3LYP methods (**IV**,**V**) give values that are

TABLE 5: Calculated Values for $\Delta H_{\mathrm{Acid}}(\mathrm{ClCH_2CN})$ and ΔH_f $(\mathrm{ClCH_2CN})^a$

	*G*2 (**I**)	CBS-Q (**II**)	B3LYP/ 6-31G* (**IV**)	B3LYP/ 6-311++G*** (**V**)
acidity	360.2	359.9	368.9	357.4
$\Delta H_{\mathrm{atom}}(\mathrm{ClCH_2CN})$	566.6	569.3		
$\Delta H_f(\mathrm{ClCH_2CN})$	22.2	19.5		

[a] Values in kcal/mol.

in fair agreement, at best, with the experimental heat of formation.

Predictions for the singlet−triplet splitting from the isodesmic approaches were also made with values ranging from 9.9 kcal mol (**I**) to 13.4 kcal/mol (**V**), all in excellent agreement with experiment. It is interesting to note that although B3LYP overstabilizes both the singlet and the triplet, the singlet−triplet splittings are in accord with the compound methods and experiment.

Gas-Phase Acidity and Heat of Formation for $\mathrm{ClCH_2CN}$. Predictions for the gas-phase acidity of $\mathrm{ClCH_2CN}$ were obtained using methods **I**, **II**, **IV**, and **V** and are given in Table 5. The compound methods (**I** and **II**) give predictions of 361.0 and 360.4 that are in reasonable agreement with the experimental value of 357.7 ± 2.0 kcal/mol. In some of our previous work, the gas-phase acidities of halomethanes were calculated using G2 theory.[26] The average deviation from the experimental acidities for $\mathrm{CH_2Cl_2}$, $\mathrm{CH_2ClF}$, and $\mathrm{CHCl_2F}$, was only 1.1 kcal/mol. In addition, Radom and co-workers have shown that G2 theory and CBS-Q give acidity values for $\mathrm{CH_3CN}$ that are within 2−3 kcal/mol of experiment.[68]

Whereas neither method **IV** nor **V** gave reliable predictions for the heats of formation singlet or triplet HCCN, method **V** gives a reasonable gas-phase acidity for $\mathrm{ClCH_2CN}$ of 357.4 kcal/mol. Method **IV** overestimates the acidity of $\mathrm{ClCH_2CN}$ by over 10 kcal/mol. This is not surprising, as diffuse functions are normally needed to properly treat anions.

Predictions for the heat of formation of $\mathrm{ClCH_2CN}$ were obtained from the atomization energy method using methods **I** and **II** and are listed in Table 5. The CBS-Q prediction of 19.5 is ca. 2 kcal/mol lower than the G2 prediction of 22.2 kcal/mol, both of which are lower than the experimental value of 25.5 ± 3.7 kcal/mol. However, it has recently been shown that the experimental heat of formation of iodoacetonitrile is also 4−5 kcal/mol higher than that obtained from G2 calculations,[69] and so the discrepancy with theory found in this work is not unprecedented. It should be noted that both G2 and CBS-Q give predictions for the heat of formation of $\mathrm{CH_3CN}$,[68] ($\Delta H_f = 18.0$ and 18.7 kcal/mol for **I** and **II**) and $\mathrm{CH_3Cl}$,[44,45] ($\Delta H_f = -18.1$ and −19.1 kcal/mol for **I** and **II**) that are in excellent agreement with experiment (ΔH_f $(\mathrm{CH_3CN}) = 17.7$ kcal/mol; ΔH_f $(\mathrm{CH_3Cl}) = -20$ kcal/mol),[52] such that the origin of the discrepancy is likely due to an incomplete description of the halogen-cyano group interaction.

Derived Thermochemical Results. In this study, the heat of formation of $^3\mathrm{HCCN}$ has been found to be 115.6 ± 5.0 kcal/mol by using CID threshold measurements with chlorocyanomethyl anion. The experimental heat of formation of HCCN can be used to derive additional thermochemical properties, including the C−H bond dissociation enthalpy in cyanomethyl radical. The heat of formation of the cyanomethyl radical is 60.4 ± 2.1 kcal/mol, calculated by using the heat of formation of acetonitrile of 17 kcal/mol and a C−H BDE of 94.8 ± 2.1 kcal/mol (Table 3).[20,21] From the measured heat of formation of the triplet carbene determined in this work, the C−H BDE in cyanomethyl radical, the second C−H BDE in acetonitrile, is calculated to be 107.3 ± 5.4 kcal/mol.

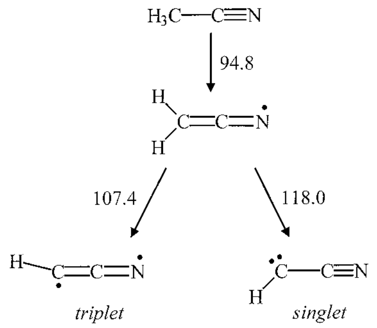

Figure 3. Experimentally determined C−H bond dissociation energies for the formation of singlet and triplet cyanocarbene from acetonitrile. Values are in kcal/mol.

It is instructive to compare the BDE for the formation of the triplet with that for formation of the singlet. The enthalpies for the C−H bond dissociation processes in acetonitrile are summarized in Figure 3. As noted in the preceding section, the C−H BDE in acetonitrile is 94.8 ± 2.1 kcal/mol, ~9 kcal/mol lower than that in methane. Of course, the difference in BDEs between methane and acetonitrile can be attributed to delocalization of the electron onto the nitrogen. The measured BDE for formation of the triplet carbene from cyanomethyl radical is 107.3 ± 5.4 kcal/mol, very similar to the C−H BDE in ketene, 105 ± 2 kcal/mol.[51] The similarity between the two BDEs is consistent with the valence bond structure of the cyanomethyl radical shown in Figure 3, wherein the system has a ketenyl-like structure with the unpaired electron more localized on the nitrogen.

The bond dissociation enthalpy for formation of the singlet state of cyanocarbene can be obtained from the heats of formation of $^1\mathrm{HCCN}$, $\mathrm{CH_2CN}$, and H to be 118.4 ± 3.7 kcal/mol, 11 kcal/mol higher than that for formation of the triplet. The difference between the two BDEs corresponds to the singlet−triplet splitting in HCCN, and can be understood by considering the structure of the singlet shown in Figure 3. The molecular orbital calculations indicate that the singlet, unlike the triplet, is strongly bent with the electrons localized on the divalent carbon. Therefore, to generate the singlet carbene, it is first necessary to break a ketene-like C−H bond in the cyanomethyl radical, which would be expected to require about 108 kcal/mol, as in the triplet. However, formation of the singlet also requires an additional 10 kcal/mol to account for the stabilization of the radical that is lost when the electrons are localized.

Because the heat of formation of the $\mathrm{HCCN^-}$ is known, the heat of formation of the triplet carbene measured in this work can be used to derive the electron affinity. The enthalpy difference between the heats of formation of the $\mathrm{HCCN^-}$ ion and the ground-state triplet carbene gives an electron affinity of 2.05 ± 0.27 eV. Ellison and co-workers estimate an electron affinity of 2.014 ± 0.010 eV[19] from the photoelectron spectrum of $\mathrm{HCCN^-}$, which agrees very well with our indirectly determined value.[19]

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Supporting Information Available: Cartesian coordinates, scaled vibrational frequencies, and enthalpies at 298 K for for ^{3}HCCN, ^{1}HCCN, $^3CH_2$, $^1CH_2$, CH_4, CH_3CN, $ClCH_2CN$, and $ClCHCN^-$ obtained using methods **I**−**V** (7 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Yung, Y. L.; Allen, M.; Pinto, J. P. *Astrophys. J. Suppl.* **1984**, *55*, 465.

(2) Yung, Y. *Icarus* **1987**, *72*, 468.

(3) Bernheim, R. A.; Kempf, R. J.; Reichembercher, E. F. *J. Magn. Reson.* **1970**, *3*, 5.

(4) Zandler, M. E.; Goddard, J. D.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1979**, *101*, 1072.

(5) Kim, K. S.; Schaefer, H. F., III; Radom, L.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 4148.

(6) Rice, J. E.; Schaefer, H. F., III *J. Chem. Phys.* **1987**, *86*, 7051.

(7) Deidi, E. T.; Schaefer, H. F., III *J. Chem. Phys.* **1992**, *96*, 4449.

(8) Aoki, K.; Fueno, H.; Ikuta, S. *Chem. Phys. Lett.* **1993**, *202*, 33.

(9) Dendramis, A.; Leroi, G. E. *J. Chem. Phys.* **1977**, *66*, 4334.

(10) Brown, F. X.; Saito, S.; Yamamoto, S. *J. Mol. Spectrosc.* **1990**, *143*, 203.

(11) Endo, Y.; Ohshima, Y. *J. Chem. Phys.* **1993**, *98*, 6618.

(12) Morter, C. L.; Farhat, S. K.; Curl, R. F. *Chem. Phys. Lett.* **1993**, *207*, 153.

(13) Han, J. X.; Hung, P. Y.; DeSain, J.; Jones, W. E.; Curl, R. F. *J. Mol. Spectrosc.* **1999**, *198*, 421.

(14) Goldberg, N.; Fiedler, A.; Schwarz, H. *J. Phys. Chem.* **1995**, *99*, 15327.

(15) Francisco, J. S. *Chem. Phys. Lett.* **1994**, *230*, 372.

(16) Wenthold, P. W.; Lineberger, W. C. *Acc. Chem. Res.* **1999**, *32*, 597−604.

(17) Grabowski, J. J.; Melly, S. J. *Int. J. Mass Spectrom. Ion Processes* **1987**, *81*, 147.

(18) Matimba, E. K.; Crabbendam, A. M.; Ingemann, S.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Processes* **1992**, *114*, 85.

(19) Nimlos, M. R.; Davico, G.; Schwartz, R.; Raymond, T.; Geise, C. M.; Wenthold, P. G.; Lineberger, W. C.; Blanksby, S. J.; Hadad, C. M.; Petersson, G. A.; Allen, M. D.; Ellison, G. B. *J. Mol. Spectrosc.*, submitted.

(20) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

(21) The heat of formation used for CH2CN in this work is ca. 2 kcal/mol higher than that recommended in the Berkowitz review (ref 20) because we have used a higher value for the heat of formation of acetonitrile (Table 3).

(22) Leopold, D. G.; Murray, K. M.; Stevens-Miller, A. E.; Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849.

(23) Schwartz, R. L.; Davico, G. E.; Ramond, T. M.; Lineberger, W. C. *J. Phys. Chem. A* **1999**, *103*, 8213.

(24) Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 5573.

(25) Poutsma, J. C.; Nash, J. J.; Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 4686.

(26) Poutsma, J. C.; Paulino, J. A.; Squires, R. R. *J. Phys. Chem.* **1997**, *101*, 5327.

(27) Liu, X.; Wenthold, P. G. *J. Phys. Chem. A.* **2001**, submitted.

(28) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6401.

(29) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 7378.

(30) Jensinger, R. A.; Squires, R. R. *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 745−757.

(31) Wenthold, P. G. *J. Phys. Chem. A* **2000**, *104*, 5612.

(32) Marinelli, P. J.; Paulino, J. A.; Sunderlin, L. S.; Wenthold, P. G.; Poutsma, J. C.; Squires, R. R. *Int. J. Mass Spectrom. Ion Processes* **1994**, *130*, 89.

(33) Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 2788.

(34) Chesnavich, W. J.; Bowers, M. T. *J. Phys. Chem.* **1985**, *83*, 900.

(35) Sunderlin, L. S.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Processes* **1989**, *94*, 149.

(36) Schultz, R. H.; Crellin, K. C.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 8590.

(37) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, N.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, version A.9; Gaussian, Inc: Pittsburgh, PA, 1998.

(39) Robinson, J. P.; Holbrook, K. A. Wiley-Interscience: New York, 1972.

(40) Forst, W. *Theory of Unimolecular Reactions*; Academic: New York, 1973.

(41) Rodgers, M. T.; Ervin, K. M.; Armentrout, P. B. *J. Chem. Phys.* **1997**, *106*, 4499.

(42) Ervin, K. M.; Armentrout, P. B. *J. Chem. Phys.* **1985**, *83*, 166.

(43) Chantry, P. J. *J. Chem. Phys.* **1971**, *55*, 2746.

(44) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(45) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598.

(46) Montgomery, J. A., Jr.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900.

(47) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(48) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785.

(49) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16 502.

(50) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493−532.

(51) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. *Neutral Thermochemical Data*, February 2000 ed.; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 20899, 2000.

(52) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Ion Energetics Data*; Mallard, W. G., Lindstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 20899 (http://webbook.nist.gov), 1999.

(53) Matzinger, S.; Bally, T.; Patterson, E. V.; MacMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535.

(54) Hu, C.-H. *Chem. Phys. Lett.* **1999**, *309*, 81.

(55) Das, D.; Whittenburg, S. L. *J. Mol. Structure (THEOCHEM)* **1999**, *492*, 175.

(56) Stracener, L. L.; Halter, R. J.; McMahon, R. J.; Castro, C.; Karney, W. L. *J. Org. Chem.* **2000**, *65*, 199.

(57) Geise, C. M.; Hadad, C. M. *J. Org. Chem.* **2000**, *65*, 8348.

(58) I., L.; Zhu, Z.; Tae, E. L.; Tippmann, E.; Hill, B. T.; Platz, M. S. *J. Am. Chem. Soc.* **2001**, *123*, 6061.

(59) Knapp-Mohammady, M.; Jalkanen, K. J.; Nardi, F.; Wade, R. C.; Suhai, S. *Chem. Phys.* **1999**, *240*, 63.

(60) Rulísek, L.; Zdenek, H. *J. Am. Chem. Soc.* **2000**, *122*, 10 428.

(61) Marino, T.; Russo, N.; Tocci, E.; Toscano, M. *J. Mass Spectrom.* **2001**, *36*, 301.

(62) Kuntz, A. F.; Boynton, A. W.; David, G. A.; Colyer, K. E.; Poutsma, J. C. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 72.

(63) Rodgers, M. T.; Stanley, J. R.; Amunugama, R. *J. Am. Chem. Soc.* **2000**, *122*, 10 969.

(64) Zhang, X. G.; Liyanage, R.; Armentrout, P. B. *J. Am. Chem. Soc.* **2001**, *123*, 5563.

(65) Calatayud, M.; Silvi, B.; Andres, J.; Beltran, A. *Chem. Phys. Lett.* **2001**, *333*, 493.

(66) Guillemin, J. C.; Decouzon, M.; Maria, P. C.; Gal, J. F.; Mo, O.; Yanez, M. *J. Phys. Chem. A* **1997**, *101*, 9525.

(67) Bozzelli, J. W.; Jung, D. *J. Phys. Chem. A* **2001**, *105*, 3941.

(68) Mayer, P. M.; Taylor, M. S.; Wong, M. W.; Radom, L. *J. Phys. Chem. A* **1998**, *102*, 7074.

(69) Lafleur, R. D.; Szatary, B.; Baer, T. *J. Phys. Chem. A* **2000**, *104*, 1450−1455.