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Bond Strengths of Ethylene and Acetylene

Kent M. Ervin,[†] Scott Gronert,[‡] S. E. Barlow,[‡] Mary K. Gilles,[†] Alex G. Harrison,[‡,§] Veronica M. Bierbaum,[*,†] Charles H. DePuy,[*,‡] W. C. Lineberger,[*,†] and G. Barney Ellison[*,†]

Contribution from the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215, and the Joint Institute for Laboratory Astrophysics, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado 80309-0440.
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Abstract: Negative ion photoelectron spectroscopy and gas-phase proton transfer kinetics were employed to determine the CH bond dissociation energies of acetylene, ethylene, and vinyl radical: $D_0(\mathrm{HCC{-}H}) = 131.3 \pm 0.7$ kcal mol^{-1}, $D_0(\mathrm{CH_2CH{-}H}) = 109.7 \pm 0.8$ kcal mol^{-1}, and $D_0(\mathrm{CH_2C{-}H}) = 81.0 \pm 3.5$ kcal mol^{-1}. The strengths of each of the other CH and CC bonds in acetylene and ethylene and their fragments were derived. The energy required to isomerize acetylene to vinylidene was also determined: $\mathrm{HC{\equiv}CH \rightarrow H_2C{=}C}$: $\Delta H_{\mathrm{isom},0} = 47.4 \pm 4.0$ kcal mol^{-1}. As part of this study, proton transfer kinetics in a flowing afterglow/selected-ion flow tube apparatus were used to refine the acidities of ethylene, acetylene, and vinyl. The gas-phase acidity of acetylene was tied to the precisely known values for hydrogen fluoride, $\Delta G_{\mathrm{acid},298}(\mathrm{HF}) = 365.6 \pm 0.2$ kcal mol^{-1}, and water, $\Delta G_{\mathrm{acid},298}(\mathrm{H_2O}) = 383.9 \pm 0.3$ kcal mol^{-1}, yielding $\Delta G_{\mathrm{acid},298}(\mathrm{HCC{-}H}) = 369.8 \pm 0.6$ kcal mol^{-1}. The gas-phase acidity equilibria of acetylene with isopropyl alcohol and *tert*-butyl alcohol were also measured. Combined with relative acidities from the literature, these measurements yielded improved acidities for the alcohols, $\Delta G_{\mathrm{acid},298}((\mathrm{CH_3})_2\mathrm{CHO{-}H}) = 370.1 \pm 0.6$ kcal mol^{-1}, $\Delta G_{\mathrm{acid},298}((\mathrm{CH_3})_3\mathrm{CO{-}H}) = 369.3 \pm 0.6$ kcal mol^{-1}, $\Delta G_{\mathrm{acid},298}(\mathrm{C_2H_5O{-}H}) = 372.0 \pm 0.6$ kcal mol^{-1}, and $\Delta G_{\mathrm{acid},298}(\mathrm{CH_3O{-}H}) = 375.1 \pm 0.6$ kcal mol^{-1}. The gas-phase acidity of ethylene was measured relative to ammonia, $\Delta G_{\mathrm{acid},298}(\mathrm{NH_3}) = 396.5 \pm 0.4$ kcal mol^{-1}, giving $\Delta G_{\mathrm{acid},298}(\mathrm{C_2H_4}) = 401.0 \pm 0.5$ kcal mol^{-1}. The gas-phase acidity of vinyl radical was bracketed, 375.1 ± 0.6 kcal mol^{-1} $\leq \Delta G_{\mathrm{acid},298}(\mathrm{CH_2C{-}H}) \leq 380.4 \pm 0.3$ kcal mol^{-1}. The electron affinities of ethynyl, vinyl, and vinylidene radicals were determined by photoelectron spectroscopy: $\mathrm{EA(HCC)} = 2.969 \pm 0.010$ eV, $\mathrm{EA(CH_2CH)} = 0.667 \pm 0.024$ eV, and $\mathrm{EA(CH_2C)} = 0.490 \pm 0.006$ eV.

One of the most important properties of a molecule is the strength of each of the bonds.[1] However, there are few molecules larger than triatomics for which *all* of the sequential bond dissociation energies are known; examples include methane,[2] silane,[3a] germane,[3b] ammonia,[3c] phosphine,[3c] and arsine.[3c] The first CH bond dissociation energies of acetylene[4–7] and ethylene,[8–11] among the smallest stable hydrocarbon molecules, are the subject of conflicting experimental measurements. In this paper, we use gas-phase ion chemistry and photoelectron spectroscopy to establish each of the bond strengths of $\mathrm{HC{\equiv}CH}$ and $\mathrm{CH_2{=}CH_2}$. We report the energies required to dissociate these simple hydrocarbons into all possible fragments.

Modern ion chemistry and spectroscopy provide a powerful avenue by which bond strengths can be determined. Our method uses the thermochemical cycle[12,13] represented by eq 1–4.

$$\begin{array}{llll}
\mathrm{R^-} & \rightarrow \mathrm{R + e^-} & \mathrm{EA(R)} & (1) \\
\mathrm{RH} & \rightarrow \mathrm{R^- + H^+} & \Delta H_{\mathrm{acid}}(\mathrm{RH}) & (2) \\
\mathrm{H^+ + e^-} & \rightarrow \mathrm{H} & -\mathrm{IP(H)} & (3) \\
\hline
\mathrm{RH} & \rightarrow \mathrm{R + H} & D(\mathrm{R{-}H}) & (4)
\end{array}$$

Negative ion photoelectron spectroscopy is employed to measure the radical electron affinity, EA(R), which is the enthalpy change for process 1, and proton transfer kinetics are used to determine the hydrocarbon gas-phase acidity, $\Delta H_{\mathrm{acid}}(\mathrm{RH})$, which is the enthalpy change for process 2. These values can be combined with the precisely known ionization potential of the hydrogen atom,[14] IP(H), according to eq 5 to extract the homolytic bond dissociation

$$D(\mathrm{R{-}H}) = \mathrm{EA(R)} + \Delta H_{\mathrm{acid}}(\mathrm{RH}) - \mathrm{IP(H)} \qquad (5)$$

energy, $D(\mathrm{R{-}H})$. The bond dissociation energy[15] is defined as the enthalpy change for reaction 4.

We have determined the gas-phase acidities of $\mathrm{CH_2{=}CH_2}$, $\mathrm{CH_2{=}CH}$, $\mathrm{HC{\equiv}CH}$, and $\mathrm{C_2H}$ by proton transfer kinetics in a flow tube reactor. Separate photoelectron spectroscopy experiments provide electron affinities for $\mathrm{CH_2{=}CH}$, $\mathrm{CH_2{=}C}$, and $\mathrm{C_2H}$. These values are used in eq 5 to determine the hydrocarbon bond strengths $D(\mathrm{CH_2CH{-}H})$, $D(\mathrm{H_2CC{-}H})$, and $D(\mathrm{HCC{-}H})$. Together with established heats of formation for related species, these experimental values enable us to derive all of the other bond dissociation energies in acetylene and ethylene.

Electron Affinity Measurements

Negative ion photoelectron spectroscopy[16] was used to measure the electron affinities of the vinyl,[17,18] vinylidene,[19] and ethynyl[20]

[†] Joint Institute for Laboratory Astrophysics and Department of Chemistry and Biochemistry.

[‡] Department of Chemistry and Biochemistry.

[§] Permanent address: Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario M5S 1A1, Canada.

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radicals. In this experiment a mass-selected beam of organic anions (R^-) was intersected by a continuous, fixed-frequency argon ion laser beam. The anions were photodetached according to eq 6.

$$R^- + \hbar\omega_0 \rightarrow R + e^-(KE) \qquad (6)$$

Electrostatic energy analysis was used to measure the kinetic energy (KE) of the photodetached electrons with 5–20-meV resolution. From the kinetic energy of the (0,0) vibrational origin transition in the photoelectron spectrum, we extract the electron affinity of the organic radical, $EA(R) = \hbar\omega_0 - KE_{origin}$.

Vinyl anions were formed in a dc discharge ion source by the reaction $F^- + (CH_2{=}CH)_4Si \rightarrow (CH_2{=}CH)_3SiF + CH_2{=}CH^-$ (100 pA),[17] or in a microwave discharge flowing afterglow source from $CH_2{=}CHCOOH$ (5 pA).[18] Vinylidene and acetylide anions (100 pA) were produced in the flowing afterglow by the reactions $O^- + CH_2{=}CH_2 \rightarrow CH_2{=}C^- + H_2O$ and $O^- + HCCH \rightarrow C_2H^- + OH$, respectively. The laser wavelength was 488.0 nm ($\hbar\omega_0 = 2.540$ eV)[17] or 351.1 nm ($\hbar\omega_0 = 3.531$ eV)[18] for the studies on the $CH_2{=}CH^-$ ion and 351.1 nm for $CH_2{=}C^-$ and C_2H^-. In each case, the vibrational origin in the photoelectron spectrum was unambiguously assigned.[17,19,20] The photoelectron spectra and origin assignments are shown in Figure 1. The energies of the origin transitions yield the following electron affinities: $EA(CH_2CH) = 0.667 \pm 0.024$ eV, $EA(CH_2C) = 0.490 \pm 0.006$ eV, and $EA(C_2H) = 2.969 \pm 0.010$ eV.

The photoelectron spectra exhibit vibrational hot bands which can be used to estimate the vibrational temperatures of the ions. Based on Franck–Condon analyses, the vibrational temperatures were typically 300–500 K. In the case of C_2H^-, however, elevated populations of the excited CC stretch mode (1800 cm^{-1}) were found, up to 15% depending on source conditions. It was found that these vibrationally excited anions could be efficiently removed from the beam by adding an excess of HCCH in the reaction with O^-, or by adding a quencher such as propylene or isobutane to the helium in the flow tube.

Gas-Phase Acidity Measurements

Proton Transfer Kinetics. The gas-phase acidities of HCCH, C_2H_4, CH_2CH, and C_2H were determined from kinetics measurements of proton transfer reactions using a tandem flowing afterglow/selected-ion flow tube (FA/SIFT) instrument.[21] Anions were produced in an electron impact flowing afterglow ion source, extracted, and passed through a quadrupole mass filter to select a single ion species for study. These mass-selected ions were then injected into a flow tube reactor ($P_{He} \approx 0.5$ Torr). The anions (R^-) were allowed to undergo 10^4 or more collisions with the helium buffer gas before introduction of an acid HA at a downstream inlet into the flow tube. Reactant and product ion intensities from proton transfer,

$$R^- + HA \rightleftharpoons RH + A^- \qquad (7)$$

were measured in a second quadrupole mass filter following the flow tube. Reaction rates were determined by monitoring the depletion of reactant ions as a function of reaction time. Neutral reagent flow rates were determined from the pressure change as a function of time in a calibrated volume system. All measurements were made at a flow tube temperature[22] of 300 ± 2 K. Product branching ratios were also measured, using calibrated corrections for the mass discrimination of the detection system.

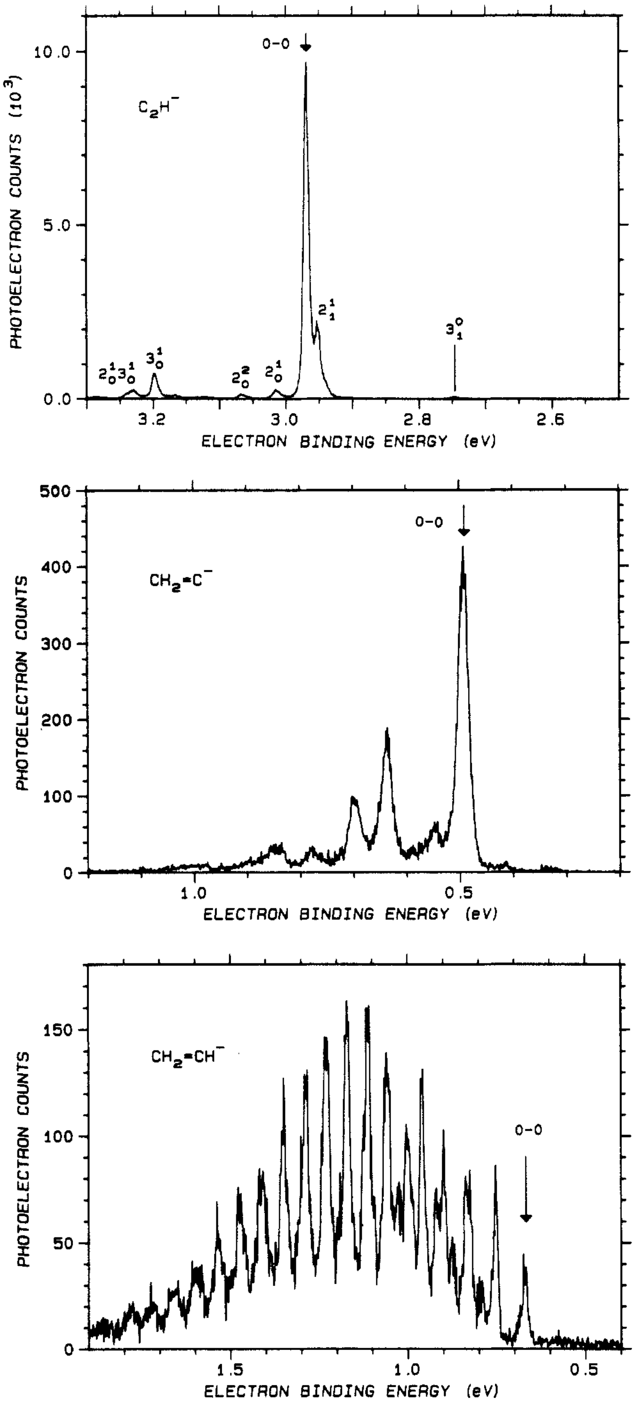

Figure 1. Photoelectron spectra at 351.1 nm of C_2H^- (top), H_2CC^- (middle), and CH_2CH^- (bottom). Photoelectron counts are plotted as a function of the electron binding energy, which is the photon energy minus the measured electron kinetic energy. Arrows mark the assigned vibrational origin transitions. In the spectrum of C_2H^-, transitions of the ν_2 bend and ν_3 CC stretch vibrations are labeled.

Thermochemical Derivations. Provided that the rates measured for the forward and reverse directions of eq 7 correspond to the same elementary reaction, we can obtain the equilibrium constant from $K_{eq} = k_7/k_{-7}$. The relation $\Delta G_{rxn} = -RT \ln K_{eq}$ then yields the gas-phase acidity for RH relative to HA. Absolute gas-phase acidities were obtained from independently known gas-phase acidities for HA according to $\Delta G_{acid}(RH) = \Delta G_{acid}(HA) - \Delta G_{rxn}$. Where measurement of only the forward direction of reaction 7 was possible, the gas-phase acidity of RH was bracketed between acids HA of known acidity.

Experimental free energies of acidity were converted to enthalpies using $\Delta H_{acid} = \Delta G_{acid} + T\Delta S_{acid}$. Entropy data were taken in most cases from the JANAF Tables.[14] Values for species not

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Table I. Calculated Entropies and Enthalpies

species	$H_{298} - H_0$[a] (kcal mol^{-1})	S_{298}[b] (cal mol^{-1} K^{-1})	vib freq (cm^{-1})	rotational constants (cm^{-1})	ref
C_2H $\tilde{X}$ $^2\Sigma^+$	2.5	50.9	3600, 1840, 370 (2)	1.46	48
C_2H^- $\tilde{X}$ $^1\Sigma^+$	2.4	48.8	3200, 1800, 500 (2)	1.39	20, 49
CH_2C $\tilde{X}$ $^1A_1$	2.7	53.2	3025, 1635, 1165 835, 3050, 320	9.62, 1.32, 1.16	19
CH_2C^- $\tilde{X}$ $^2B_2$	2.5	53.6	2770, 1485, 1305 2765, 900, 765	9.72, 1.20, 1.07	19
CH_2CH $\tilde{X}$ $^2A'$	2.5	55.8[c]	3265, 3190, 3115, 1670, 1445, 1185, 920, 825, 785	7.49, 1.07, 0.93	17
CH_2CH^- $\tilde{X}$ $^1A'$	2.5	54.5	2970, 2730, 2690, 1500, 1380, 1190, 1070, 900, 840	6.29, 1.08, 0.92	17
NH_2^- $\tilde{X}$ $^1A_1$	2.4	45.2	3122, 1463, 3191	22.75, 13.11, 8.34	*d*
HCCH $\tilde{X}$ $^1\Sigma_g^+$	2.4				*e*

[a] $H_{298} - H_0 = \int_0^{298} C_p(T)\,dT$, ±0.1 kcal mol^{-1}. [b] ±0.5 cal mol^{-1} K^{-1}. [c] An experimental value of 55.9 ± 2.6 cal mol^{-1} K^{-1} has been reported (ref 11). [d] Tack, L. M.; Rosenbaum, N. H.; Owrutsky, J. C.; Saykally, R. J. *J. Chem. Phys.* **1986**, *85*, 4222. Botschwina, P. *J. Mol. Spectrosc.* **1986**, *117*, 173. [e] Data for acetylene in JANAF, 3rd ed.,[14] other than at 298 K, are erroneous, apparently having been calculated for $2C + 2H_2 \rightarrow HCCH$. The value listed here was recalculated using JANAF molecular constants.

included in the compilation, or based on obsolete molecular parameters, were calculated using the assumptions and formulas given in JANAF.[14] These values are listed in Table I along with the molecular constants used in the calculations. The hydrocarbon radicals and ions studied in this work are sufficiently well-characterized that the estimated uncertainties in S_{298} are no greater than ±0.5 cal mol^{-1} K^{-1}.

Because ionization potentials and electron affinities are strictly changes of enthalpy at 0 K, while the gas-phase acidities were measured at room temperature,[22] eq 5 is more properly written in the form

$$D_{298}(\mathrm{R{-}H}) = \Delta H_{\mathrm{acid,298}}(\mathrm{RH}) + \mathrm{EA}_0(\mathrm{R}) - \mathrm{IP}_0(\mathrm{H}) + \int_0^{298} \Delta C_p(T)\,dT \quad (8)$$

where the correction for integrated heat capacities[23] is given by

$$\int_0^{298} \Delta C_p(T)\,dT = \int_0^{298} \{C_p(T)[\mathrm{R}] - C_p(T)[\mathrm{R}^-] + C_p(T)[\mathrm{H}] - C_p(T)[\mathrm{H}^+]\}\,dT \quad (9)$$

This heat capacity correction is normally less than 0.5 kcal mol^{-1} since the structures and vibrational frequencies of the ions and neutrals are similar. The correction is commonly neglected (i.e., the approximation $\int_0^{298} \Delta C_p(T)\,dT = 0$ as adopted by Lias et al.[13]), but in this work we explicitly applied eq 9 in order to extract accurate values for D_{298}(R–H). Integrated heat capacities were taken from JANAF[14] or calculated and listed in Table I; the estimated uncertainties are within ±0.1 kcal mol^{-1}. Because H and H$^+$ have identical integrated heat capacities,[23] IP$_{298}$(H) and IP$_0$(H) are the same (313.587 ± 0.002 kcal mol^{-1}).[14] Corrections of $\Delta H_{\mathrm{acid,298}}$ to $\Delta H_{\mathrm{acid,0}}$ analogous to eq 9 were made to obtain D_0(R–H). Absolute gas-phase acidities for acids (e.g., HF, H_2O, and NH_3) used to anchor the measured relative gas-phase acidities were derived from experimental bond energies and electron affinities using the equations

$$\Delta H_{\mathrm{acid,0}}(\mathrm{RH}) = D_0(\mathrm{R{-}H}) - \mathrm{EA}_0(\mathrm{R}) + \mathrm{IP}_0(\mathrm{H}) \quad (10a)$$

$$\Delta G_{\mathrm{acid,298}}(\mathrm{RH}) = \Delta H_{\mathrm{acid,0}}(\mathrm{RH}) + \int_0^{298} \Delta C_{p,\mathrm{acid}}(T)\,dT - T\Delta S_{\mathrm{acid,298}} \quad (10b)$$

where the heat capacity term corrects $\Delta H_{\mathrm{acid,0}}$(RH) to $\Delta H_{\mathrm{acid,298}}$(RH).

Table II. Proton Transfer Reactions

reaction	k_{exp} (cm^3 s^{-1})[a]	k_{ADO} (cm^3 s^{-1})[b]	ΔG_{rxn} (kcal mol^{-1})
(11) $F^- + HCCH \rightleftarrows HF + C_2H^-$			+4.27 ± 0.20
k_{11}	(1.0 ± 0.3) × 10^{-12}	1.3 × 10^{-9}	
k_{-11}	(1.3 ± 0.2) × 10^{-9}	2.3 × 10^{-9}	
(12) i-PrO$^-$ + HCCH ⇌ i-PrOH + C_2H^-			−0.29 ± 0.13
k_{12}	(8.5 ± 1.3) × 10^{-10}[c]	1.0 × 10^{-9}	
k_{-12}	(5.2 ± 0.8) × 10^{-10}[c]	2.2 × 10^{-9}	
(13) t-BuO$^-$ + HCCH ⇌ t-BuOH + C_2H^-			+0.48 ± 0.13
k_{13}	(4.4 ± 0.7) × 10^{-10}[c]	1.0 × 10^{-9}	
k_{-13}	(9.8 ± 1.5) × 10^{-10}[c]	2.2 × 10^{-9}	
(14) $NH_2^- + C_2H_4 \rightleftarrows CH_2CH^- + NH_3$			+4.54 ± 0.24
k_{14}	(2.7 ± 1.0) × 10^{-13}	1.5 × 10^{-9}	
k_{-14}	(5.5 ± 0.9) × 10^{-10}	2.0 × 10^{-9}	
(15) $CH_2{=}C^- + H_2O \rightarrow CH_2{=}CH + OH^-$			≥3.5
k_{15}	≤4 × 10^{-12}	2.2 × 10^{-9}	
k_{-15}		1.4 × 10^{-9}	
(16) $CH_2{=}C^- + CH_3OH \rightarrow CH_2{=}CH + CH_3O^-$			≤0.0
k_{16}	1.2 × 10^{-9}[d]	2.0 × 10^{-9}	

[a] Systematic errors give an additional ±10% uncertainty in rates; however, these errors cancel in the determination of ΔG_{rxn}. [b] Collision rate calculated by ADO theory (ref 36). [c] These rate constants represent total reaction including a small clustering contribution which essentially cancels in the equilibrium constant. [d] Reference 37.

Acetylene. The gas-phase acidity of acetylene was determined relative to the acidity of HF, reaction 11 (Table II). Commercial acetylene (Matheson 99.6%) is dissolved in acetone, which can readily react with fluoride by proton transfer; thus for these experiments, acetylene was purified by passage through a dry ice/isopropyl alcohol trap. The complete removal of acetone was confirmed by the absence of a $CH_3COCH_2^-$ peak in the mass spectrum when fluoride reacts with acetylene. For the reverse reaction, a mixture of hydrogen fluoride (9.8%) in helium was employed to allow safe handling and accurate flow determinations. In this case, flow rates were measured with a mass flowmeter, calibrated for helium and corrected for the hydrogen fluoride contribution. Because of the proclivity of HF to react and adsorb on surfaces, it was necessary to allow several minutes for HF flows to attain steady state before reproducible rate constants could be determined.

Observed rate constants for reaction 11 are presented in Table II. In the endothermic reaction of F$^-$ with acetylene, proton transfer accounted for only (25 ± 6)% of the observed total depletion rate of k = (3.9 ± 0.3) × 10^{-12} cm^3 s^{-1}, while adduct formation accounted for the rest. We take the proton transfer rate as the total depletion rate times the fraction due to proton transfer, giving k_{11} = (1.0 ± 0.3) × 10^{-12} cm^3 s^{-1}. This treatment assumes that the F$^-$(HCCH) clusters would decompose back to reactants (the energetically favorable channel) in the great majority of cases in the absence of a stabilizing third-body collision.

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[23] We adopt the "stationary electron" or "ion" convention (ref 13), for which the heat capacity of the electron is zero. To obtain heats of formation of *anions* at 298 K in the "thermal electron" convention (ref 14), in which electrons are treated as an ideal gas, it is necessary to subtract 1.481 kcal mol^{-1} from the values given in this work. Similarly, one must add the same amount to EA$_{298}$. There is no difference between the two conventions at 0 K.

Table III. Gas-Phase Acidity Scale (kcal mol^{-1})

Acid	Absolute acidity (D − EA + IP)[a]		Relative acidity (equilibria)[b]		Absolute acidity (equilibria)[c]
	$\Delta G_{acid,298}$	Ref.	$\delta\Delta G_{acid,298}$	Ref.	$\Delta G_{acid,298}$
H_2O	383.9 ± 0.3	27			–
			9.0 ± 0.2	28	
CH_3OH	374.9 ± 0.7	29			375.1 ± 0.6
			3.1 ± 0.2	26	
EtOH	371.5 ± 1.4	29			372.0 ± 0.6
			2.0 ± 0.2	26	
iso-PrOH	369.5 ± 1.3	29			370.1 ± 0.6
			0.8 ± 0.2	26	
			0.29 ± 0.13	*d*	
HCCH	–				369.8 ± 0.6
			0.48 ± 0.13	*d*	
tert-BuOH	368.1 ± 1.7	29			369.3 ± 0.6
			4.27 ± 0.20	*d*	
HF	365.6 ± 0.2	24			–

[a] Absolute acidity calculated by eq 10 from literature values of bond energies and electron affinities. [b] Relative acidities obtained from proton transfer equilibrium measurements. [c] Recommended gas-phase acidities from relative equilibrium measurements are weighted averages anchored to the precise D − EA + IP values for HF and H_2O. [d] Values measured in this work are given in boldface type.

Using the known gas-phase acidity of HF,[24,25] $\Delta G_{acid,298}(HF)$ = 365.6 ± 0.2 kcal mol^{-1}, and the experimental value of $\Delta G_{rxn}(11)$ from Table II, we obtain $\Delta G_{acid,298}(HCCH)$ = 369.9 ± 0.3 kcal mol^{-1}.

Additional experiments were performed to measure the proton transfer equilibria of acetylene with isopropyl alcohol and *tert*-butyl alcohol, reactions 12 and 13 (Table II). The measured rates and derived relative acidities are shown in Table II. These measurements placed the acidity of acetylene between the two alcohols, in agreement with ion cyclotron resonance (ICR) equilibrium experiments.[26] In the reaction of acetylide ion with isopropyl alcohol (eq −12, Table II), tests were made to ensure that the C_2H^- reactant ions were vibrationally relaxed. This slightly endothermic reaction proceeds with an efficiency of 24% and thus might be expected to be sensitive to vibrational excitation. Addition of 10 mTorr of isobutane as a quencher to the helium buffer gas in the flow tube causes negligible change in the reaction rate coefficient, strongly suggesting that no vibrationally excited C_2H^- was initially present.

We can further anchor the gas-phase acidity of acetylene to the precise absolute value for water ($\Delta G_{acid,298}(H_2O)$ = 383.9 ± 0.3 kcal mol^{-1})[27] as a secondary calibrant. For this purpose, we use literature equilibrium values for the relative gas-phase acidities of the alcohols and water. The relative gas-phase acidities of methanol, ethanol, isopropyl alcohol, and *tert*-butyl alcohol have been measured by ICR equilibria,[13,26] and methanol has been tied to water by high-pressure mass spectrometric equilibrium measurements.[28] These values form a thermochemical ladder as depicted in Table III, which also presents absolute acidities for HF, H_2O, and the alcohols calculated from bond energies and electron affinities using eq 10. In Figure 2 we compare relative acidities measured in kinetics experiments with absolute acidities derived from literature[24,27,29] bond energies and electron affinities. This plot, which compares two independent experimental determinations of the same quantities, shows an excellent correlation. The difference in the acidities of H_2O and HF obtained from summing the equilibrium measurements for the individual steps shown in Table III, $\delta\Delta G_{acid,298}$ = 18.7 ± 0.5 kcal mol^{-1}, is in excellent agreement with that obtained from the absolute values based on bond energies and electron affinities, $\Delta G_{acid,298}(H_2O) - \Delta G_{acid,298}(HF)$ = 18.3 ± 0.4 kcal mol^{-1}. A linear regression fit to the data in Figure 2 (with each value weighted by the square reciprocal of the uncertainty) yields a slope of 0.98, compared to the true value of unity.[30] This good agreement lends confidence to the relative acidities of HCCH and the alcohols.

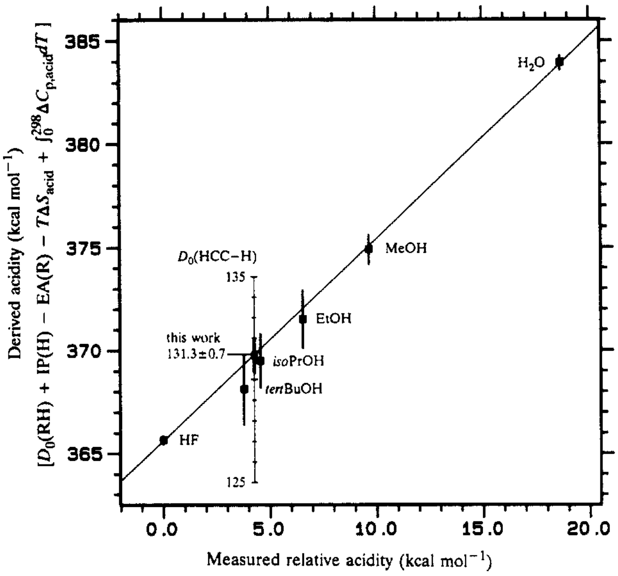

Figure 2. Comparison between relative gas-phase acidities (abscissa), $\delta\Delta G_{acid,298}$ for $A^- + BH \rightleftarrows AH + B^-$, obtained from ion kinetics measurements, and absolute gas-phase acidities (ordinate), $\Delta G_{acid,298}$ for AH $\rightleftarrows A^- + H^+$, calculated from experimental bond dissociation energies and electron affinities using eq 10. Numerical values are taken from Table III. The zero on the relative scale is arbitrarily placed at the value for HF. The solid line is a weighted linear regression fit to the data; the slope is 0.98 compared to the theoretical slope of unity. At the experimental relative acidity for HCCH (4.27 ± 0.20 kcal mol^{-1} above HF), a small ladder has been drawn showing the D − EA + IP values of the absolute gas-phase acidity of acetylene which would be obtained for various values of D_0(HCC–H) together with our value for EA(C_2H). The bond energy obtained in this work, D_0(HCC–H) = 131.3 ± 0.7 kcal mol^{-1}, is indicated by a circle.

Using the equilibrium acidities relative to H_2O, we obtain an estimate of $\Delta G_{acid,298}(HCCH)$ = 369.5 ± 0.5 kcal mol^{-1}, compared to the more direct measurement based on the equilibrium with

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(24) $\Delta G_{acid,298}(HF)$ = 365.6 ± 0.2 kcal mol^{-1} is calculated (eq 10) from D_0(HF) = 135.33 ± 0.17 kcal mol^{-1} (ref 25), EA(F) = 3.401 190 ± 0.000 004 eV (Blondel, C.; Cacciani, P.; Delsart, C.; Trainham, R. *Phys. Rev. A* **1989**, *40*, 3698), $\Delta S_{acid,298}(HF)$ = 19.30 ± 0.01 cal K^{-1} mol^{-1} (ref 14), and $\Delta H_{acid,298}(HF) - \Delta H_{acid,0}(HF)$ = 0.9 ± 0.1 kcal mol^{-1} (ref 14).

(25) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(26) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046.

(27) $\Delta G_{acid,0}(H_2O)$ = 383.9 ± 0.3 kcal mol^{-1} is calculated (eq 10) from D_0(HO–H) = 117.9 ± 0.3 kcal mol^{-1} (ref 14), EA(OH) = 42.146 kcal mol^{-1} (Schulz, P. A.; Mead, R. D.; Jones, P. L.; Lineberger, W. C. *J. Chem. Phys.* **1982**, *77*, 1153), $\Delta S_{acid,298}(H_2O)$ = 22.1 ± 0.2 cal K^{-1} mol^{-1} (ref 14), and $\Delta H_{acid,298}(H_2O) - \Delta H_{acid,0}(H_2O)$ = 1.2 ± 0.1 kcal mol^{-1} (ref 14).

(28) Meot-Ner, M.; Sieck, L. W. *J. Phys. Chem.* **1986**, *90*, 6687.

(29) Absolute gas-phase acidities of the alcohols are obtained using eq 10 with RO–H bond energies $D_{298}(CH_3O{-}H)$ = 104.1 ± 0.5 kcal mol^{-1}, $D_{298}(C_2H_5O{-}H)$ = 104.3 ± 1.0 kcal mol^{-1}, $D_{298}((CH_3)_2CHO{-}H)$ = 104.9 ± 1.0 kcal mol^{-1}, and $D_{298}((CH_3)_3O{-}H)$ = 105.2 ± 1.0 kcal mol^{-1} (Batt, L. *Int. Rev. Phys. Chem.* **1987**, *6*, 53; ref 38); alkoxy electron affinities EA(CH_3O) = 1.570 ± 0.022 eV, EA(C_2H_5O) = 1.726 ± 0.033 eV, EA($(CH_3)_2CHO$) = 1.839 ± 0.029 eV, and EA($(CH_3)_3O$) = $1.912^{+0.029}_{-0.054}$ eV (Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Phys. Chem.* **1982**, *86*, 4873); and $\Delta S_{acid,298}(ROH)$ = 22 ± 2 cal mol^{-1} K^{-1} (ref 26). The heat capacity corrections for the electron affinities are neglected.

(30) If instead of the ICR alcohol gas-phase acidities (ref 26) recommended by Lias et al. (ref 13), we used relative acidities from flowing afterglow experiments on the proton-transfer equilibria of C_2H^- with ethanol and methanol (Mackay, G. I.; Rakshit, A. B.; Bohme, D. K. *Can. J. Chem.* **1982**, *60*, 2594) in the ladder of Table III, then the resulting difference between the acidities of H_2O and HF would be $\delta\Delta G_{acid,298}$ = 18.0 ± 0.4 kcal mol^{-1} and the slope of the correlation in Figure 2 would be 1.02, i.e., in comparably good agreement with the absolute values.

HF, $\Delta G_{\mathrm{acid},298}(\mathrm{HCCH}) = 369.9 \pm 0.3$ kcal mol^{-1}. Using the correlation in Figure 2, which yields a weighted average of the two values, we obtain a final value of $\Delta G_{\mathrm{acid},298}(\mathrm{HCCH}) = 369.8 \pm 0.6$ kcal mol^{-1}, where the uncertainty is chosen conservatively to reflect the slight mismatch of the two anchoring points. Gas-phase acidities for the alcohols can be derived similarly. These alcohol acidities, listed in the final column of Table III, represent a quantitative improvement of the experimental gas-phase acidity scale between HF and H_2O. Previously discussed[13,28,31] discrepancies of 2 kcal mol^{-1} between the gas-phase acidity values for methanol and ethanol and the same acidities derived from experimental values of D(RO–H) and EA(RO), R = CH_3 and C_2H_5, have now been reduced to 0.2–0.5 kcal mol^{-1}, which is well within the experimental uncertainties.

Ethylene. We have measured the gas-phase acidity of ethylene relative to ammonia, reaction 14 (Table II). Research purity ethylene (≥99.99%) and electronic grade ammonia (99.995%) were employed. $C_2H_3^-$ was produced by first making $C_2H_3CO^-$ by reaction of acrolein ($CH_2{=}CHCHO$) with OH^- in the flowing afterglow source, and then injecting it into the flow tube with excess translational energy to eliminate CO by collision-induced dissociation. Because the reaction of NH_2^- with C_2H_4 is very slow, that reaction rate was measured in an argon buffer gas rather than in helium to reduce changes in the diffusive loss of ions due to the addition of large amounts of neutral reactant. The rate for reaction 14 has been reduced by 16% from the total reactant ion depletion rate to correct for contributions from clustering and from a trace reactive acetylene impurity to yield the proton transfer rate constant, $k_{14} = (2.7 \pm 1.0) \times 10^{-13}$ cm^3 s^{-1}.

The observed rate for reaction 14 is very small, near the lower limit of measurability in the FA/SIFT instrument. Fortunately, we were able to check this rate constant by comparing it to the reaction of NH_2^- with acetylene, using the known acetylene impurity in the ethylene reagent as an internal standard. Acetylene was present in the ethylene at a concentration of 14 ppm (Matheson Gas Products, Lot Analysis B5). In the reactions of NH_2^- with ethylene, we obtained a product spectrum in which the C_2H^- intensity was 10% of the CH_2CH^- signal. The known rate constant[32] for the reaction of NH_2^- with acetylene is 1.84×10^{-9} cm^3 s^{-1}. These values yield a rate constant for $NH_2^- + C_2H_4$ of $k_{14} = 2.6 \times 10^{-13}$ cm^3 s^{-1}, compared to the directly measured rate constant of $k_{14} = 2.7 \times 10^{-13}$ cm^3 s^{-1}. This excellent agreement lends credibility to this exceedingly small rate constant.

The reaction rates given in Table II yield $\Delta G_{\mathrm{rxn}}(14) = +4.54 \pm 0.24$ kcal mol^{-1}. From the gas-phase acidity of ammonia,[33] $\Delta G_{\mathrm{acid},298}(\mathrm{NH_3}) = 396.5 \pm 0.4$ kcal mol^{-1}, we obtain $\Delta G_{\mathrm{acid},298}(\mathrm{C_2H_4}) = 401.0 \pm 0.5$ kcal mol^{-1}. This yields $\Delta H_{\mathrm{acid},298}(\mathrm{C_2H_4}) = 409.4 \pm 0.6$ kcal mol^{-1}, in good agreement with a recent independent experimental value[34] of $\Delta H_{\mathrm{acid},298}(\mathrm{C_2H_4}) = 407 \pm 3$ kcal mol^{-1} obtained from threshold energies of endothermic reactions. An estimate[35] based on the product branching ratio in the reaction of OH^- with $CH_2CHSi(CH_3)_3$ gave $\Delta H_{\mathrm{acid},298}(\mathrm{C_2H_4}) = 407.5$ kcal mol^{-1}.

Vinyl. Because vinyl radical was not an available neutral reagent, the gas-phase acidity of C_2H_3 could not be determined by equilibrium measurements. Instead, we established $\Delta G_{\mathrm{acid},298}(\mathrm{CH_2CH})$ by bracketing the proton affinity of $CH_2{=}C^-$ between species of known acidity. Vinylidene radical anion, $CH_2{=}C^-$, was produced by injecting O^- into the flow tube followed by reaction with ethylene introduced just downstream of the injector. The reaction of $CH_2{=}C^-$ with ethylene is sufficiently slow that it did not interfere with this measurement. $CH_2{=}C^-$ did not react with water ($\Delta G_{\mathrm{acid},298}(\mathrm{H_2O}) = 383.9 \pm 0.3$ kcal mol^{-1}),[27] giving an upper limit of $k_{15} \leq 4 \times 10^{-12}$ cm^3 s^{-1}. Assuming the exoergic reverse reaction occurs upon every collision ($k_{-15} \approx k_{\mathrm{ADO}} = 1.4 \times 10^{-9}$ cm^3 s^{-1}),[36] we obtain $\Delta G_{\mathrm{rxn}}(15) \geq 3.5$ kcal mol^{-1}. The proton transfer of $CH_2{=}C^-$ with methanol [$\Delta G_{\mathrm{acid},298}(\mathrm{CH_3OH}) = 375.1 \pm 0.6$ kcal mol^{-1} (Table III)] was observed to be rapid, indicating that the reaction is exoergic or near thermoneutral, $\Delta G_{\mathrm{rxn}} \leq 0$. Guo and Grabowski[37] have used flowing afterglow techniques to measure a rate constant of $k_{16} = 1.2 \times 10^{-9}$ cm^3 s^{-1}, which corresponds to 60% of the collision rate. These observations bracket the gas-phase acidity of vinyl: 375.1 ± 0.6 kcal mol^{-1} $\leq \Delta G_{\mathrm{acid},298}(\mathrm{CH_2CH}) \leq 380.4 \pm 0.3$ kcal mol^{-1}. For convenience, we represent this result as $\Delta G_{\mathrm{acid},298}(\mathrm{CH_2CH}) = 377.6 \pm 3.1$ kcal mol^{-1}, which covers the outer bounds of the two limits. This result is essentially the same as that of Guo and Grabowski;[37] they report $\Delta H_{\mathrm{acid},298}(\mathrm{CH_2CH}) = 385 \pm 3$ kcal mol^{-1}, which yields $\Delta G_{\mathrm{acid},298}(\mathrm{CH_2CH}) = 377.8 \pm 3$ kcal mol^{-1}.

Ethynyl. C_2^- has a large hydrogen affinity and rapidly reacted with neutral reagents to form C_2H^- which then reacted further. Interference of this process prevented us from obtaining a firm bracket on the gas-phase acidity of C_2H. Product branching ratio measurements showed that C_2^- reacts with acetic acid [$\Delta G_{\mathrm{acid},298}(\mathrm{CH_3COOH}) = 341.5 \pm 1.9$ kcal mol^{-1}][13] by both proton transfer and H atom abstraction. There was no evidence of proton transfer with chloroform [$\Delta G_{\mathrm{acid},298}(\mathrm{HCCl_3}) = 349.2 \pm 6.0$ kcal mol^{-1}].[13] The latter result is not conclusive, however, because proton transfer might not successfully compete with the more exothermic atom abstraction channel. Consequently, our observations provide only a lower bound, $\Delta G_{\mathrm{acid},298}(\mathrm{C_2H}) > 341.5 \pm 1.9$ kcal mol^{-1}.

Discussion

Experimental electron affinities and gas-phase acidities are presented in Table IV. With these experimental results and auxiliary heats of formation[14,38-40] listed in Table V, we can complete several thermochemical cycles as shown in Table VI. We first employ eq 8 to determine experimental R–H bond dissociation energies for acetylene, ethylene, and vinyl (RH). Using these values and established heats of formation of C_2H_4, HCCH, and H, we can derive heats of formation for the corresponding organic radicals (R). We subsequently derive all of the other bond strengths of ethylene and acetylene, for which we require literature heats of formation of C, C_2, CH, and CH_2. Of these, only $\Delta H_f(\mathrm{C_2})$ appears to be subject to unresolved experimental discrepancies.[39]

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(31) Moylan, C. R.; Brauman, J. I. *J. Phys. Chem.* **1984**, *88*, 3175.

(32) Mackay, G. I.; Tanaka, K.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *24*, 125.

(33) $\Delta G_{\mathrm{acid},298}(\mathrm{NH_3}) = 396.5 \pm 0.4$ kcal mol^{-1} is calculated (eq 10) from $\mathrm{EA(NH_2)} = 0.771 \pm 0.006$ eV (Wickham-Jones, C. T.; Ervin, K. M.; Ellison, G. B.; Lineberger, W. C. *J. Chem. Phys.* **1989**, *91*, 2762), $D_0(\mathrm{NH_2{-}H}) = 106.7 \pm 0.3$ kcal mol^{-1} (Gibson, S. T.; Greene, J. P.; Berkowitz, J. *J. Chem. Phys.* **1985**, *83*, 4319. See also: Anderson, W. R. *J. Phys. Chem.* **1989**, *93*, 530), and $\Delta S_{\mathrm{acid},298}(\mathrm{NH_3}) = 25.0 \pm 1.0$ cal K^{-1} mol^{-1} and $\Delta H_{\mathrm{acid},298}(\mathrm{NH_3}) - \Delta H_{\mathrm{acid},0}(\mathrm{NH_3}) = 1.5 \pm 0.1$ kcal mol^{-1} (Table I and ref 14).

(34) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2517.

(35) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968.

(36) Collision rates are estimated by average dipole orientation (ADO) theory (Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Proc.* **1973**, *12*, 347) using tabulated polarizabilities and dipole moments (Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 66th ed.; CRC Press: Boca Raton, FL, 1985).

(37) Guo, Y.; Grabowski, J. J. *Int. J. Mass Spectrom. Ion Proc.*, in press.

(38) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(39) The heat of formation of C_2 as adopted by JANAF (ref 14) is derived from a spectroscopic extrapolation for the bond dissociation energy, $D_0(\mathrm{C_2}) = 49\,300 \pm 300$ cm^{-1} = 141.0 ± 0.9 kcal mol^{-1} (Messerle, G.; Krauss, L. *Z. Naturforsch.* **1967**, *22A*, 1744, 2015, 2023). Huber and Herzberg[25] cite $D_0(\mathrm{C_2}) = 6.21$ eV = 143.2 kcal mol^{-1}, giving preference to equilibrium measurements of the C_2 sublimation enthalpy from graphite. Equilibrium values [using $\Delta H_{f,0}(\mathrm{C})$ from Table V] include $D_0(\mathrm{C_2}) = 142.0 \pm 1.7$ kcal mol^{-1} (Drowart, J.; Burns, R. P.; DeMaria, G.; Inghram, M. G. *J. Chem. Phys.* **1959**, *31*, 1131), 145 ± 5 kcal mol^{-1} (Brewer, L.; Hicks, W. T.; Krikorian, O. H. *J. Chem. Phys.* **1962**, *36*, 182), 143.0 ± 1.6 kcal mol^{-1} (Kordis, J.; Gingerich, K. A. *J. Chem. Phys.* **1973**, *58*, 5058), 139.3 ± 0.6 kcal mol^{-1} (Zavitsanos, P. D.; Carlson, G. A. *J. Chem. Phys.* **1973**, *59*, 2966), and $>137 \pm 9$ kcal mol^{-1} [L'vov, B. V.; Novotny, I.; Pelieva, L. A. *J. Appl. Spectrosc.* (*Engl. Trans.*) **1980**, *32*, 553; *Zh. Prikl. Spektrosk.* **1980**, *32*, 965]. See also: Brewer, L.; Hagan, L. *High Temp. Sci.* **1979**, *11*, 233. Lacking a definitive determination, we provisionally use the Messerle and Krauss spectroscopic determination, but with error bars to include other values, $D_0(\mathrm{C_2}) = 141.0 \pm 2.5$ kcal mol^{-1}. This value affects our derived values for D(H–CC), $\Delta H_f(\mathrm{C_2^-})$, $D(\mathrm{H{-}C_2^-})$, and $\Delta H_{\mathrm{acid}}(\mathrm{C_2H})$ in Tables VI and IX.

(40) Helm, H.; Cosby, P. C.; Graff, M. M.; Moseley, J. T. *Phys. Rev. A* **1982**, *25*, 304. Brzozowski, J.; Bunker, P.; Elander, N.; Erman, P. *Astrophys. J.* **1976**, *207*, 414.

Table IV. Experimental Thermochemical Results (kcal mol^{-1})

Electron Affinities

species	photodetachment transition	this work		lit.[a]
		EA$_0$	EA$_{298}$[b]	EA$_0$
C_2H	$C_2H\ \tilde{X}\ ^2\Sigma^+ \leftarrow C_2H^-\ \tilde{X}\ ^1\Sigma^+$	68.5 ± 0.2	68.6 ± 0.3	67.8 ± 2.3
CH_2C	$CH_2C\ \tilde{X}\ ^1A_1 \leftarrow CH_2C^-\ \tilde{X}\ ^2B_2$	11.3 ± 0.2	11.5 ± 0.2	10.8 ± 0.5
CH_2CH	$CH_2CH\ \tilde{X}\ ^2A' \leftarrow CH_2CH^-\ \tilde{X}\ ^1A'$	15.4 ± 0.6	15.4 ± 0.6	18.4 ± 4.6
C_2	$C_2\ X\ ^1\Sigma_g^+ \leftarrow C_2^-\ X\ ^2\Sigma_g^+$	75.3 ± 0.5[c]	75.8 ± 0.5	78.2 ± 0.4

Gas-Phase Acidities

species	this work				lit.[a]
	$\Delta G_{acid,298}$	$\Delta S_{acid,298}$[d]	$\Delta H_{acid,298}$[e]	$\Delta H_{acid,0}$[b]	$\Delta G_{acid,298}$
HCCH	369.8 ± 0.6	26.8 ± 0.5[f]	377.8 ± 0.6	376.4 ± 0.6	368.5 ± 2.0
CH_2CH	377.6 ± 3.1[g]	23.9 ± 1.0[f]	384.7 ± 3.4	383.3 ± 3.4	378 ± 3[e,h]
C_2H_4	401.0 ± 0.5	28.1 ± 0.5[f]	409.4 ± 0.6	408.0 ± 0.6	399 ± 3[e,i]
C_2H	>341.5 ± 1.9	22.1 ± 1.0[f]	>348.1 ± 2.0	>347.0 ± 2.0	351.3 ± 1.7
CH_3OH	375.1 ± 0.6	22 ± 2[j]	381.7 ± 0.8		374.0 ± 2.0
C_2H_5OH	372.0 ± 0.6	22 ± 2[j]	378.6 ± 0.8		370.7 ± 2.0
i-PrOH	370.1 ± 0.6	22 ± 2[j]	376.7 ± 0.8		368.8 ± 2.0
tert-BuOH	369.3 ± 0.6	22 ± 2[j]	375.9 ± 0.8		368.1 ± 2.0

[a] Previously recommended values from the compilation of Lias et al. (ref 13), except as noted. [b] Calculated from 0 K or 298 K value using heat capacity data described in the text. [c] Reference 20. [d] In cal mol^{-1} K^{-1}. [e] Derived from $\Delta G_{acid} = \Delta H_{acid} - T\Delta S_{acid}$. [f] Calculated using entropy data described in text and Table I, cal mol^{-1} K^{-1}. [g] Bracketed value: 380.4 ± 0.3 kcal mol^{-1} $\geq \Delta G_{acid,298}(CH_2C{-}H) \geq$ 375.1 ± 0.6 kcal mol^{-1}. [h] Reference 37. [i] References 34 and 35. [j] Reference 26.

Table V. Auxiliary Heats of Formation (kcal mol^{-1})[a]

species	$\Delta H_{f,0}$	$\Delta H_{f,298}$	ref
C_2H_2	54.68 ± 0.17	54.55 ± 0.17	38
C_2H_4	14.58 ± 0.10	12.55 ± 0.10	38
H	51.6336 ± 0.0014	52.1030 ± 0.0014	14
C	170.0 ± 0.1	171.3 ± 0.1	14
C_2	199.0 ± 2.5	201.0 ± 2.5	*b*
CH	141.7 ± 0.4	142.6 ± 0.4	*c*
CH_2	92.8 ± 0.6	92.9 ± 0.6	2

[a] Thermal corrections between 0 K and 298 K calculated as required using heat capacity data described in text and Table I. [b] Derived from $D_0(C_2)$ (see ref 39) and ΔH_f(C). [c] Derived from D_0(CH) = 79.9 ± 0.4 kcal mol^{-1} (ref 40), ΔH_f(C), and ΔH_f(H).

Derived anion heats of formation, anion C–H bond dissociation energies, and gas-phase acidities are also presented in Table VI. The derived value of $\Delta H_{acid,298}(C_2H)$ = 355.6 ± 2.6 kcal mol^{-1} agrees with our experimental bound $\Delta H_{acid,298}(C_2H)$ > 348.1 ± 2.0 kcal mol^{-1}, and is consistent with the observed absence of proton transfer between C_2^- and chloroform [$\Delta H_{acid,298}(HCCl_3)$ = 357.1 ± 6.2 kcal mol^{-1}].[13]

Acetylene CH Bond Dissociation Energy. The experimental value of the CH bond dissociation energy in acetylene is controversial. Recent literature values are summarized in Table VII. Our value of D_0(HCC–H) = 131.3 ± 0.7 kcal mol^{-1} agrees with the previous value[4] based on eq 5, 130.4 ± 5 kcal mol^{-1}, but is more precise. Other recent independent measurements are clustered in two groups: those which agree with the present work, 131–133 kcal mol^{-1}, and those which favor a value of 127 kcal mol^{-1} or less.

Two direct experimental measurements of D_0(HCC–H) involve determination of the translational energy release in the photolysis of acetylene in a molecular beam. Wodtke and Lee[5] measured the velocity of the C_2H photofragment by time-of-flight with mass spectrometric detection, and obtained D_0(HCC–H) = 132 ± 2 kcal mol^{-1}, in good agreement with the present value. In a conceptually similar experiment, Wittig and co-workers[7] measured the velocity of the hydrogen atom fragment by Doppler multiphoton ionization spectroscopy, and found D_0(HCC–H) = 127 ± 1.5 kcal mol^{-1}. This discrepancy remains unresolved.

Spectroscopic methods can provide information about the bond dissociation energy of acetylene if predissociation can be identified. Acetylene fluorescence yields[41] showed a sharp cutoff above 132.9 ± 1.2 kcal mol^{-1}, which was attributed to the onset of the dissociative channel. Since there could be a barrier to dissociation, this value represents an upper bound. Field and co-workers[42] observed unimolecular lifetime decreases induced by a magnetic field, yielding an upper bound of ≤132.3 kcal mol^{-1}. In more recent work, Field and co-workers[6] observed decreases in fluorescence lifetimes induced by a Stark field, and assigned this to predissociation, giving a significantly lower upper limit, D_0(HCC–H) ≤ 126.647 ± 0.002 kcal mol^{-1}.

A bond energy based on the threshold for the photoionization process $HCCH + h\nu \rightarrow C_2H + H^+ + e^-$ using synchrotron radiation gave a value of D_0(HCC–H) = 132.6 ± 1.2 kcal mol^{-1}, strictly an upper limit.[43] Values[44] based on the appearance potential of C_2H^+ and the ionization potential of C_2H fall over a range of 124–135 kcal mol^{-1}, depending on the determination[44] of IP(C_2H). Bond energies based on pyrolysis kinetics[45,46] (118–124 kcal mol^{-1}) are significantly lower than any of the more recent experiments. A model[47] used to explain C_2H rotational distributions in the photodissociation of HCCH supports the higher bond energy value.

The present results are incompatible with the lower bond energies reported by the Wittig[7] and Field[6] groups. While certain effects could cause those experiments to be misleading (for example, multiphoton effects or acetylene hot bands in the Wittig experiment or an unknown fast nonradiative relaxation process in the Field experiment), we discuss here possible systematic errors in our experiments.

The correct assignment of the origin transition in photoelectron spectra is always a matter of concern,[2] but for C_2H^- the assignment is unambiguous. The photodetachment is a vertical process with the (0,0) vibrational origin as the strongest peak, resolved from sequence bands of the bending vibration (Figure 1). The observed vibrational frequencies[20] of this electronic transition agree well with the experimental values[48] for $\tilde{X}\ ^2\Sigma^+$ C_2H, indicating that the

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(42) Chen, Y.-Q.; Jonas, D. M.; Hamilton, C. E.; Green, P. G.; Kinsey, J. L.; Field, R. W. *Ber. Bunsenges. Phys. Chem.* **1988**, *92*, 329.

(43) Shiromaru, H.; Achiba, Y.; Kimura, K.; Lee, Y. T. *J. Phys. Chem.* **1987**, *91*, 17.

(44) Appearance potential of C_2H^+ from acetylene: AP(C_2H^+) = 17.36 ± 0.01 eV (Dibeler, V. H.; Walker, J. A.; Rosenstock, H. M. *J. Chem. Phys.* **1973**, *59*, 2264); AP(C_2H^+) < 17.33 ± 0.05 eV (Norwood, K.; Ng, C. Y. *J. Chem. Phys.* **1989**, *91*, 2898); ionization potential: IP(C_2H) = 11.96 ± 0.05 eV (Okabe, H.; Dibeler, V. H. *J. Chem. Phys.* **1973**, *59*, 2430); IP(C_2H) = 11.51 ± 0.05 eV (Berkowitz, J. *Photoionization, Photodissociation, and Photoelectron Spectroscopy* Academic: New York, 1979; pp 285–290).

(45) Yampol'skii, Yu. P.; Zelentsov, V. V. *React. Kinet. Catal. Lett.* **1981**, *17*, 347.

(46) Frank, P.; Just, T. *Comb. Flame* **1980**, *30*, 231. Wu, C. H.; Singh, H. J.; Kern, R. D. *Int. J. Chem. Kinet.* **1987**, *19*, 975.

(47) Fletcher, T. R.; Leone, S. R. *J. Chem. Phys.* **1989**, *90*, 871.

Table VI. Hydrocarbon Thermochemistry (kcal mol^{-1})

quantity	value 0 K	value 298 K	derivation
Experimental C–H Bond Dissociation Energies			
D(HCC–H)	131.3 ± 0.7	132.8 ± 0.7	ΔH_{acid}(HCCH) + EA(C_2H) − IP(H)
D(CH_2CH–H)	109.7 ± 0.8	111.2 ± 0.8	ΔH_{acid}(C_2H_4) + EA(CH_2CH) − IP(H)
D(CH_2C–H)	81.0 ± 3.5	82.7 ± 3.5	ΔH_{acid}(CH_2CH) + EA(CH_2C) − IP(H)
Radical Heats of Formation			
ΔH_f(C_2H)	134.3 ± 0.7	135.3 ± 0.7	D(HCC–H) + ΔH_f(HCCH) − ΔH_f(H)
ΔH_f(CH_2CH)	72.7 ± 0.8	71.7 ± 0.8	D(CH_2CH–H) + ΔH_f(C_2H_4) − ΔH_f(H)
ΔH_f(CH_2C)	102.1 ± 4.0	102.2 ± 4.0	D(CH_2C–H) + ΔH_f(CH_2CH) − ΔH_f(H)
Derived C–H Bond Dissociation Energies			
D(H–HCCH)	33.6 ± 0.8	35.0 ± 0.8	ΔH_f(HCCH) + ΔH_f(H) − ΔH_f(CH_2CH)
D(H–HCC)	83.9 ± 4.2	85.1 ± 4.2	ΔH_f(C_2H) + ΔH_f(H) − ΔH_f(CH_2C)
D(H–CC)	116.3 ± 2.6	117.8 ± 2.6	ΔH_f(C_2) + ΔH_f(H) − ΔH_f(C_2H)
Derived C–C Bond Dissociation Energies			
D($CH_2{=}CH_2$)	171.0 ± 1.2	173.3 ± 1.2	2ΔH_f(CH_2) − ΔH_f(C_2H_4)
D($CH_2{=}CH$)	161.8 ± 1.1	163.8 ± 1.1	ΔH_f(CH_2) + ΔH_f(CH) − ΔH_f(CH_2CH)
D($CH_2{=}C$)	160.7 ± 4.2	162.0 ± 4.2	ΔH_f(CH_2) + ΔH_f(C) − ΔH_f(CH_2C)
D($HC{\equiv}C$)	177.4 ± 0.8	178.6 ± 0.8	ΔH_f(C) + ΔH_f(CH) − ΔH_f(C_2H)
D($HC{\equiv}CH$)	228.8 ± 0.7	230.6 ± 0.7	2ΔH_f(CH) − ΔH_f(HCCH)
Anion Heats of Formation			
ΔH_f(CH_2CH^-)	57.3 ± 0.6	56.3 ± 0.6	ΔH_f(CH_2CH) − EA(CH_2CH)
ΔH_f(CH_2C^-)	90.8 ± 4.0	90.7 ± 4.0	ΔH_f(CH_2C) − EA(CH_2C)
ΔH_f(C_2H^-)	65.8 ± 0.7	66.7 ± 0.7	ΔH_f(C_2H) − EA(C_2H)
ΔH_f(C_2^-)	123.7 ± 2.5	125.2 ± 2.5	ΔH_f(C_2) − EA(C_2)
Anion C–H Bond Dissociation Energies			
D(H–CCH_2^-)	85.1 ± 3.7	86.6 ± 3.7	ΔH_f(CH_2C^-) + ΔH_f(H) − ΔH_f(CH_2CH^-)
D(H–HCC^-)	26.7 ± 4.2	28.0 ± 4.2	ΔH_f(C_2H^-) + ΔH_f(H) − ΔH_f(CH_2C^-)
D(H–C_2^-)	109.5 ± 2.6	110.6 ± 2.6	ΔH_f(C_2^-) + ΔH_f(H) − ΔH_f(C_2H^-)
Gas-Phase Acidities			
ΔH_{acid}(CH_2C)	329.0 ± 4.2	330.1 ± 4.2	D(H–HCC) − EA(C_2H) + IP(H)
ΔH_{acid}(C_2H)	354.6 ± 2.6	355.6 ± 2.6	D(H–CC) − EA(C_2) + IP(H)

Table VII. CH Bond Dissociation Energy of Acetylene (kcal mol^{-1})[a]

D_0(HCC–H)	method	ref
131.3 ± 0.7	ΔH_{acid}(HCCH) + EA(C_2H) − IP(H)	this work
127 ± 1.5	HCCH + $h\nu \rightarrow C_2H$ + H (K.E.)	7
≤126.647 ± 0.002	Stark anticrossing spectroscopy	6
≤132.3 ± 0.004	Zeeman anticrossing spectroscopy	42
<132.9 ± 1.2	fluorescence yield cutoff	41
<132.6 ± 1.2	HCCH + $h\nu \rightarrow H^+ + C_2H + e^-$ threshold	43
124	acetylene pyrolysis kinetics	46
132 ± 2	HCCH + $h\nu \rightarrow C_2H$ (K.E.) + H	5
118	H + HCCH $\rightleftarrows C_2H + H_2$ kinetics	45
130.4 ± 5	ΔH_{acid}(HCCH) + EA(C_2H) − IP(H)	4
<123.8 ± 1.6	AP(C_2H^+) − IP(C_2H)	44
124.5 ± 1.2		
<134.2 ± 1.6		
134.9 ± 1.2		

[a] Literature values for ΔH_f(C_2H) converted to D(HCC–H) using auxiliary heats of formation given in Table V. Corrections from 298 K to 0 K calculated as required using heat capacity data described in the text, $D_{298} - D_0$ = 1.6 ± 0.1 kcal mol^{-1}.

$\tilde{A}\ ^2\Pi$ C_2H excited state cannot be implicated. Hot band frequencies agree with precise ab initio values[49] for $\tilde{X}\ ^1\Sigma$ C_2H^-. No electronically excited states of C_2H^- are expected or observed.

If for the sake of argument we accept Field's upper limit[6] for the acetylene bond energy, D_0(HCC–H) ≤ 126.65 kcal mol^{-1}, we can use eq 10 with the present value for EA(C_2H) to derive an alternate value for the gas-phase acidity of acetylene. Field's bond energy yields $\Delta G_{acid,298}$(HCCH) ≤ 365.15 kcal mol^{-1} versus our value of 369.8 ± 0.6 kcal mol^{-1}. Given that the gas-phase acidity of hydrogen fluoride[24] is $\Delta G_{acid,298}$(HF) = 365.6 ± 0.2 kcal mol^{-1}, a consequence of the lower bond energy would be that the F^- + HCCH proton transfer (reaction 11) would be exothermic by 0.45 kcal mol^{-1} or more, rather than 4.2 kcal mol^{-1} endothermic! An exothermic reaction is definitely at variance with the reaction rates we observe (Table II). In principle, the extremely slow rate for the forward reaction could be caused by an activation barrier (4–5 kcal mol^{-1}) rather than a reaction endothermicity. However, such a high barrier for a simple proton transfer process has not been observed previously.[31] The same barrier would also necessarily be present for the reverse reaction, but the fast rate of the reverse reaction (60% of the collision rate) contradicts this. A hypothetical scenario for giving a false fast rate for k_{-11} could involve the presence of C_2H^- in excited internal states under the conditions of the proton transfer experiments, but our quenching experiments with C_2H^- suggest that this is unlikely. Furthermore, to explain the observed rate for k_{-11} if the ground-state reaction indeed had a large barrier, an extraordinarily high population of >60% vibrationally excited C_2H^- would be necessary, and the vibrational energy would have to couple into the reaction coordinate in an atypically efficient way. Finally, an error of ≥4.7 kcal mol^{-1} in the gas-phase acidity of HCCH is incompatible with the proton transfer equilibria data taken as a whole (Table III and Figure 2), which show superb self-consistency between the relative acidities from equilibrium measurements and absolute acidities for HF and H_2O obtained from precisely known bond energies and electron affinities. Either Field's or Wittig's value for the bond dissociation energy would place the acetylene acidity far from the experimental acidity scale, as shown in Figure 2.

Based on these considerations, the possibility that the present HCCH acidity is 4.7 kcal mol^{-1} or more in error is untenable. A further experimental test would be a direct measurement of the equilibrium constant for reaction 11. Interference of clustering reactions precludes this in the FA/SIFT apparatus, but it might be possible by pulsed high-pressure mass spectrometric techniques where higher temperatures may be used to suppress clustering.[28]

Ethylene Bond Dissociation Energy. Experimental values of the CH bond dissociation energy in ethylene from the recent literature are reviewed in Table VIII. Our value of D_0(CH_2-

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Table VIII. CH Bond Dissociation Energy of Ethylene (kcal mol^{-1})[a]

D_0(CH$_2$CH–H)	method	ref
109.7 ± 0.8	$\Delta H_{acid}(C_2H_4) + EA(C_2H_3) - IP(H)$	this work
103.7 ± 1.9	pyrolysis of $C_2H_4 + H_2$	52
≤108 ± 3	$C_2H_3Br + h\nu \rightarrow C_2H_3 + Br$ (K.E.)	8
103.8 ± 0.5	$F + C_2D_4 \rightarrow C_2D_3 + DF$ (K.E., $v = 4$)	8
111.3 ± 0.5	$F + C_2D_4 \rightarrow C_2D_3 + DF$ (K.E., $v = 3$)	8, *b*
105.3 ± 2.0	$C_2H_3I + h\nu \rightarrow C_2H_3 + I$ (K.E.)	50
105.0 ± 0.3	$C_2H_3 + HCl \rightleftarrows Cl + C_2H_4$ kinetics	11
104.3 ± 0.4	$Cl + C_2H_4 \rightleftarrows C_2H_3 + HCl$ kinetics	10
>106.8 ± 0.8	photoionization of C_2H_3	9
<116.7 ± 1.2	$C_2H_4 + h\nu \rightarrow H^+ + C_2H_3 + e^-$ threshold	43
101.5 ± 2	pyrolysis of 1,3-butadiene	53
110 ± 2	$CH_4^+ + C_2H_2 \rightarrow CH_3^+ + C_2H_3$ threshold	56
104 ± 1	appearance energies	55
100 – 104	pyrolysis of C_2H_4	54
109.6 ± 2.2	proton affinity of C_2H_3 (ICR)	57

[a] Literature values for ΔH_f(CH$_2$CH) converted to D(CH$_2$CH–H) using auxiliary heats of formation given in Table V. Corrections from 298 K to 0 K calculated as required using heat capacity data described in the text, $D_{298} - D_0 = 1.5 \pm 0.1$ kcal mol^{-1}. [b] See text.

CH–H) = 109.7 ± 0.8 kcal mol^{-1} is in agreement with a lower bound (>106.8 ± 0.8 kcal mol^{-1}) obtained recently from photoionization[9] of C_2H_3. Measurement of the kinetic energy release in the photodissociation[8] of C_2H_3Br yields an upper limit of 108 ± 3 kcal mol^{-1}, which also agrees with the present experiment within the uncertainty. In a similar experiment on the photodissociation of vinyl iodide,[50] an estimate of $D_0(C_2H_3{-}H) = 105.3 \pm 2$ kcal mol^{-1} was obtained. The product translational energy distribution[8] in the molecular beam reaction $F + C_2D_4 \rightarrow C_2D_3 + DF(v)$ yields 103.8 ± 0.5 kcal mol^{-1}, *if* the DF vibrational level is assigned to $v = 4$ as suggested by indirect evidence[51] from the HF product state distributions in the decomposition of C_2H_3F. However, an alternate assignment[8] to DF($v = 3$) yields 111.3 ± 0.5 kcal mol^{-1} and does not appear inconsistent.

Recent radical kinetics experiments[10,11] on the $Cl + C_2H_4 \rightleftarrows HCl + C_2H_3$ reaction give substantially lower values than found in the present work. Measurement[10] of the forward rate constant and the equilibrium constant for this reaction as a function of temperature (263–338 K) gives 104.3 ± 0.4 kcal mol^{-1}, while measurement[11] of the reverse rate constant (297–495 K) combined with the previous forward rate[10] gives 105.0 ± 0.3 kcal mol^{-1} (all values corrected to 0 K). Values obtained from pyrolysis kinetics[52-54] are also lower, 100–104 kcal mol^{-1}. Appearance energy measurements[55] give 104 ± 1 kcal mol^{-1}. Other positive ion techniques are in general agreement with the present work: 110 ± 2 kcal mol^{-1} from the kinetic energy threshold[56] of the endoergic reaction $CH_4^+ + C_2H_2 \rightarrow CH_3^+ + C_2H_3$, and 109.6 ± 2.2 kcal mol^{-1} obtained by ion cyclotron resonance bracketing experiments[57] on proton transfer from $C_2H_4^+$.

From this review one sees that there are essentially two groups of results, one in agreement with the present value near $D_0(C_2H_3{-}H) = 110$ kcal mol^{-1}, and the other a lower value of $D_0(C_2H_3{-}H) = 104$–105 kcal mol^{-1}. Rather than dwelling on possible errors in other experiments, we briefly discuss potential systematic difficulties in our measurements.

There are three interrelated values involved in our thermochemical cycle (eq 5): the C–H bond dissociation energy of ethylene, the gas-phase acidity of ethylene, and the electron affinity of the vinyl radical. Any two determine the other. Our gas-phase acidity and electron affinity values give a bond strength of 110 kcal mol^{-1}. If the bond dissociation energy were 105 kcal mol^{-1}, then one of our experiments would have to be in error by 5 kcal mol^{-1}. Assuming first that the gas-phase acidity measurement is correct, in order to obtain a bond dissociation energy for ethylene of 105 kcal mol^{-1}, the electron affinity of vinyl radical must be smaller by 5 kcal mol^{-1}; i.e., $EA(C_2H_3) \approx 0.46$ eV. This would place the origin in the photoelectron spectrum (Figure 1) about two quanta of the observed CCH bending vibrational progression to the right of the observed origin, outside of the possible error in the determination and in a region where no photodetachment is even observed. The origin assignment is also supported by vibrational frequency shifts observed for deuterated vinyl anions.[17] The structural identity of the ion as $CH_2{=}CH^-$ is supported by the agreement of the observed vibrational transition frequencies with theoretical values for vinyl radical.[17] Indeed, it is difficult to see what other structure the ion might have since the only plausible isomer, CH_3C^-, should by analogy with HC^- have totally different chemical and physical properties. If the vinyl anion were excited vibrationally, hot bands would appear to the right of the origin; misassignment of a hot band as the origin would therefore give an apparent electron affinity which is too low, an error in the wrong direction.

We were able to carry out an independent chemical check on the electron affinity of vinyl anion. If $EA(C_2H_3)$ were about 0.46 eV rather than the measured value of 0.67 eV, then some electron transfer from $C_2H_3^-$ to oxygen,[58] $EA(O_2) = 0.451 \pm 0.007$ eV, should be observable under our experimental conditions. We therefore injected $C_2H_3^-$ into our flow tube and added an excess of O_2. No O_2^- ions were produced, but HO_2^- (60%) and HCC^- (40%) product ions were formed with a rate constant of $k = 3.3 \times 10^{-10}$ cm^3 s^{-1} (reaction efficiency 43%). Our flow tube can also be operated with an electric drift field, which increases the kinetic energy of the ions relative to the neutrals.[21] As we gradually increased the kinetic energy of the vinyl anions, an O_2^- signal appeared and increased until it equalled the intensity of HO_2^- at approximately 0.18 eV (4 kcal mol^{-1}) center-of-mass kinetic energy. These observations are fully compatible with $EA(C_2H_3) = 0.67$ eV, but not with a value of 0.46 eV.

If we therefore accept the vinyl electron affinity measured in this work, postulating an ethylene bond energy of 105 kcal mol^{-1} requires a gas-phase acidity for ethylene of 396 kcal mol^{-1} rather than the 401 kcal mol^{-1} reported here. The acidities of ethylene and ammonia[33] would then be nearly the same; i.e., the reaction $NH_2^- + C_2H_4 \rightarrow NH_3 + C_2H_3^-$ (eq 14, Table II) would be nearly thermoneutral rather than 5 kcal mol^{-1} endothermic. Qualitative experiments show this cannot be true. Addition of a large excess of ethylene into a stream of NH_2^- in the SIFT produces only a trace of the vinyl anion. Addition of ethylene to ND_2^- produces NHD^- and NH_2^- by hydrogen/deuterium exchange faster than $C_2H_3^-$ is formed,[59] showing that there is no kinetic barrier to proton abstraction. In contrast, if a trace of ammonia is added to a stream of the vinyl anion in the SIFT, NH_2^- is immediately produced and the vinyl anion signal is rapidly depleted. A high population of vibrationally excited vinyl anions (28% above 2000 cm^{-1}) could conceivably give a false fast rate with ammonia, but these excited anions would have to survive a minimum of 3×10^4 collisions with the helium buffer gas, which is implausible. No evidence is seen for excited vinyl anions in other chemical reactions (e.g., with O_2) or in the photoelectron spectrum. Reactions of NH_2^- with impurities in the flow tube is ruled out by monitoring product ions; in any event, such reactions could only increase the apparent rate, giving an error in the wrong direction. A gas-phase acidity of 396 kcal mol^{-1} is therefore incompatible with our observations.

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(54) Ayranci, G.; Back, M. H. *Int. J. Chem. Kinet.* **1981**, *13*, 897.

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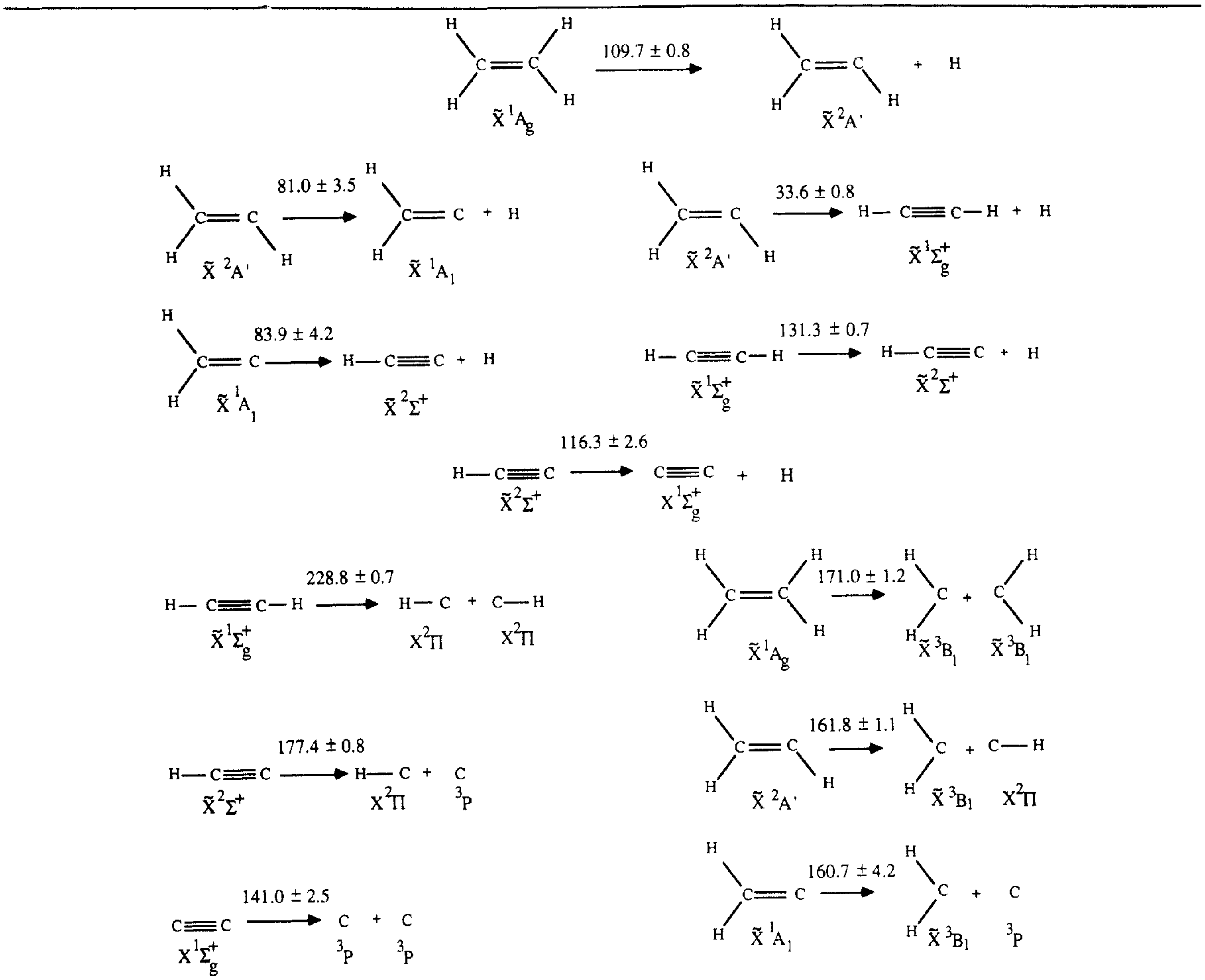
Table IX. Experimental Bond Dissociation Energies (D_0 in kcal mol^{-1})



In the case of acetylene, we were able to use additional proton transfer equilibrium measurements to tie acetylene's relative gas-phase acidity to secondary standards. Because of the sparsity of gas-phase acids weaker than NH_3, this is not presently feasible for ethylene. Nevertheless, a CH bond energy of 104–105 kcal mol^{-1} for ethylene is incompatible with our measurements of EA(C_2H_3) and $\Delta G_{acid}(C_2H_4)$.

Vinylidene–Acetylene Isomerization. Our value of $\Delta H_f(CH_2{=}C)$, combined with ΔH_f(HCCH), yields the enthalpy of the isomerization of acetylene to vinylidene:

$$H{-}C{\equiv}C{-}H \rightarrow H_2C{=}C: \qquad (17)$$

$\Delta H_{isom,0} = 47.4 \pm 4.0$ kcal mol^{-1}. Within the uncertainty, which represents the bracketed experimental range (not a standard deviation), this value is in agreement with an upper limit,[60] $\Delta H_{isom,0} \leq 44.4 \pm 0.3$ kcal mol^{-1}, obtained from a statistical analysis of spectra of highly vibrationally excited acetylene. The latter value implies that the gas-phase acidity of vinyl radical is actually at the lower end of the bracketed range obtained in this work. A recent RRKM analysis[61] of shock tube data yields $\Delta H_{isom,298} \leq 44 \pm 2$ kcal mol^{-1}, in good agreement.

Theoretical Bond Strengths. Ab initio studies of hydrocarbon radical energetics at various levels of theory are too numerous to review in detail here. The recent calculations of Curtiss and Pople,[62] including "higher level corrections" intended to yield ±2 kcal mol^{-1} accuracy, are noteworthy. They found D_0(HCC-H) = 133.5 kcal mol^{-1}, $D_0(CH_2CH\text{-}H)$ = 110.2 kcal mol^{-1}, and D_0(HCCH-H) = 32.8 kcal mol^{-1}. The excellent agreement with the present experimental values of 131.3 ± 0.7, 109.7 ± 0.8, and 33.6 ± 0.8 kcal mol^{-1}, respectively, is encouraging. Montgomery and Petersson[63] recently reported ab initio calculations, including extrapolations to the complete basis set limit, which gave D_0(HCC-H) = 131.54 ± 0.45 kcal mol^{-1}, in superb agreement with the present result. The bond dissociation energies in Table IX provide a challenge for theoretical methods in general that aim to predict bond strengths with chemical accuracy, particularly for the species with multiple bonds, which require extensive treatment of correlation effects.

Conclusions

The final results of our experimental studies are collected in Table IX. This summary shows the dissociation energies of $CH_2{=}CH_2$ and $HC{\equiv}CH$ into *all* possible fragments.

The acetylene and ethylene CH bond dissociation energies (Tables VII and VIII) are controversial. The magnitude of the discrepancies among various experimental determinations, up to 5 kcal mol^{-1} for values with cited precisions better than ±1 kcal mol^{-1}, indicates that some of the experiments have serious

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unexposed errors. Careful consideration of potential systematic errors in the experiments reported here have produced no "smoking guns", and we have confidence in our values, $D_0(\mathrm{HCC{-}H}) = 131.3 \pm 0.7$ kcal mol^{-1} and $D_0(\mathrm{C_2H_3{-}H}) = 109.7 \pm 0.8$ kcal mol^{-1}. These two primary results are based on completely independent measurements. The sources of the disagreements with other experiments remain to be discovered. In the meantime, those requiring the bond energies for critical applications should consider the range of values in Tables VII and VIII. We note that improved techniques over the last 5 years have narrowed the range of experimental bond dissociation energies for acetylene and ethylene from 10–25 kcal mol^{-1} to about 5 kcal mol^{-1}.

Despite unresolved discrepancies with other experiments, the general trends shown in Table IX are certain. A large variation is observed in the CH and CC bond dissociation energies for the various molecules and radicals. A theoretical analysis of the precise magnitudes of the bond strengths in Table IX is beyond the scope of this paper, but it is useful to make some general remarks on the observed trends.

Methane, ethylene, and acetylene represent the simplest set of hydrocarbons with sp^3, sp^2, and sp hybridized carbon atoms, respectively. As expected, the CH bond dissociation energies for these molecules increase with greater s character of the bonding orbital: $D_0(\mathrm{CH_3{-}H}) = 103.24 \pm 0.12$ kcal mol^{-1} (ref 14), $D_0(\mathrm{CH_2CH{-}H}) = 109.7 \pm 0.8$ kcal mol^{-1}, and $D_0(\mathrm{HCC{-}H}) = 131.3 \pm 0.7$ kcal mol^{-1}.

In the closed-shell molecules $\mathrm{CH_2{=}CH_2}$ and $\mathrm{HC{\equiv}CH}$, it is harder to break the first CH bond than subsequent CH bonds. For example, it costs 110 kcal mol^{-1} to produce the $\mathrm{CH_2{=}CH}$ radical from ethylene, but subsequent cleavage of the vinyl α-CH bond, eq 18, requires only 81 kcal mol^{-1}. The reduced CH bond

$$\mathrm{CH_2{=}CH^{\bullet}} \rightarrow \mathrm{H} + \mathrm{CH_2{=}C{:}} \qquad (18)$$

energy may be attributed to the singlet-coupling of the remaining electron pair, which stabilizes the singlet diradical vinylidene product, $\mathrm{CH_2{=}C{:}}$ ($\tilde{X}\ ^1A_1$). Removal of a CH bond from vinylidene, eq 19, uncouples the electron pair but the CC bond order

$$\mathrm{CH_2{=}C{:}} \rightarrow \mathrm{H} + \mathrm{HC{\equiv}C^{\bullet}} \qquad (19)$$

increases upon formation of ethynyl radical. We find $D_0(\mathrm{H{-}HCC}) = 84$ kcal mol^{-1}. In contrast, removal of the β-CH bond of vinyl, eq 20, requires merely 34 kcal mol^{-1} because it generates an

$$\mathrm{CH_2{=}CH^{\bullet}} \rightarrow \mathrm{H} + \mathrm{HC{\equiv}CH} \qquad (20)$$

additional CC π bond upon formation of acetylene, as well as because the CH bonds in acetylene are stronger due to the sp hybridization. It is important to emphasize that experimental bond dissociation energies result not only from the intrinsic "strength" of the bond being broken, but also from additional stabilization or destabilization of the dissociation products. Attributing these effects to changes in the strengths of either CC bonds or CH bonds, to changes in electronic configurations (e.g., electron pairing effects or rehybridization), to resonance energies, or to some combination, is arbitrary in the absence of precise theoretical definitions.

In conclusion, these experiments demonstrate the power of gas-phase ion spectroscopy and ion kinetics techniques to determine bond dissociation energies of a variety of hydrocarbon radicals. This work also substantially improves the precision of the experimental gas-phase acidity scale between HF and H_2O.

Acknowledgment. This paper is dedicated to Professor W. Doering, who in his Cope Award address (Dallas, April 1989) lamented the fact that there seemed to be waning interest in the thermochemistry of hydrocarbons. We thank J. J. Grabowski for providing his results on the acidity of $\mathrm{CH_2CH}$ before publication, and we are grateful to Thom Dunning and Emily Carter for discussions concerning theoretical studies. This work was supported by grants of the National Science Foundation to C.H.D. (CHE-8815459), to V.M.B. (CHE-8815446), and to W.C.L. (CHE-8819444 and PHY-8604504), and by a grant from the U.S. Department of Energy Chemical Physics program to G.B.E. (DE-FG02-87ER13695).

Mechanistic Aspects of Decarboxylation Reactions of Group 10 $(\mathrm{PCy_3})_2\mathrm{M(H)O_2CH}$ Derivatives

Donald J. Darensbourg,* Philip Wiegreffe, and Charles G. Riordan

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received December 1, 1989*

Abstract: Kinetic data for the $^{13}\mathrm{CO_2}$ exchange reactions of the *trans*-$(\mathrm{Cy_3P})_2\mathrm{M(H)O_2CH}$ (M = Ni, Pd) derivatives to afford the corresponding *trans*-$(\mathrm{Cy_3P})_2\mathrm{M(H)O_2{}^{13}CH}$ species are presented. These processes were found to exhibit a first-order dependence on the metal complex and to be independent of tricyclohexylphosphine or carbon dioxide concentrations. The activation parameters for the nickel complex were determined to be $\Delta H^* = 22.1\ (9)$ kcal·mol^{-1} and $\Delta S^* = -5\ (3)$ cal·mol^{-1}·deg^{-1}, whereas the analogous parameters for the palladium complex were found to be $\Delta H^* = 21\ (2)$ kcal·mol^{-1} and $\Delta S^* = 4\ (8)$ cal·mol^{-1}·deg^{-1}. The reaction pathways are proposed to proceed via rate-determining $\mathrm{CO_2}$ extrusion to provide the dihydride complexes, followed by rapid $^{13}\mathrm{CO_2}$ insertion into the M–H bond to yield the formate derivatives. Consistent with this proposal the carbon dioxide exchange rate is greater than 1200 times faster for the palladium derivative, where the $(\mathrm{Cy_3P})_2\mathrm{Pd(H)_2}$ intermediate is a stable species, than for its nickel analogue, where the corresponding dihydride complex is unknown. Kinetic parameters for the intramolecular C–H/Ni–D exchange process involving *trans*-$(\mathrm{Cy_3P})_2\mathrm{Ni(O_2CH)D}$ are indicative of a reaction pathway coincident with that defined for intermolecular $\mathrm{CO_2}$ exchange.

Introduction

It is of importance to mechanistically understand the C–H bond forming reaction accompanying the insertion of $\mathrm{CO_2}$ into transition-metal hydrides to afford metalloformates, since this is a quintessential process in carbon dioxide reductions. Although this carboxylation process or its counterpart in reverse, decarboxylation,

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