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: $D_g^0(\text{HCC}^-) = 131.3 \pm 0.7 \text{ kcal mol}^{-1}$, $D_g^0(\text{CH}_2\text{C}^-) = 109.7 \pm 0.8 \text{ kcal mol}^{-1}$, and $D_g^0(\text{CH}_3\text{C}^-) = 81.0 \pm 3.5 \text{ kcal mol}^{-1}$. 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: $\text{HC}==\text{CH} \to \text{H}==\text{C}-\text{C}$. $\Delta H_{\text{endo}} = 47.4 \pm 4.0 \text{ kcal mol}^{-1}$. As part of this study, proton transfer kinetics in a flowing afterglow/selected-ion flow tube apparatus was 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, $AG^0_{\text{acid}}(\text{HF})$. In acetylene and ethylene and their fragments were derived. The energy required to isomerize acetylene to vinylidene was also determined: $\text{HC}==\text{CH} \to \text{H}==\text{C}-\text{C}$. $\Delta H_{\text{endo}} = 47.4 \pm 4.0 \text{ kcal mol}^{-1}$. As part of this study, proton transfer kinetics in a flowing afterglow/selected-ion flow tube apparatus was 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, $AG^0_{\text{acid}}(\text{HF})$. The gas-phase acidity of ethylene was measured relative to ammonia, $AG^0_{\text{acid}}(\text{NH}_3)$. The gas-phase acidity of vinyl was measured relative to ammonia, $AG^0_{\text{acid}}(\text{CH}_2=\text{CH}_2)$. The gas-phase acidity of vinyl radical was bracketed, $375.1 \pm 0.6 \text{ kcal mol}^{-1} \leq \Delta G_{\text{acid}}^0(\text{CH}_2=\text{CH}_2) \leq 380.4 \pm 0.3 \text{ kcal mol}^{-1}$. The electron affinities of ethynyl, vinyl, and vinylidene radicals were determined by photoelectron spectroscopy: $EA(\text{HCC}) = 2.969 \pm 0.010 \text{ eV}$, $EA(\text{CH}_2=\text{CH}) = 0.677 \pm 0.024 \text{ eV}$, and $EA(\text{CH}_2=\text{C}) = 0.490 \pm 0.006 \text{ eV}$.

One of the most important properties of a molecule is the strength of each of the bonds. However, there are few molecules larger than triatomics for which all of the sequential bond dissociation energies are known; examples include methane, silane, germane, ammonia, phosphine, and arsine. The first CH bond dissociation energies of acetylene and ethylene, 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 $\text{HC}==\text{CH}$ and $\text{CH}_2==\text{CH}_2$. 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.

\[
\begin{align*}
R^- &\rightarrow R + e^- \quad \text{EA}(R) \quad (1) \\
\text{RH} &\rightarrow R^- + \text{H}^+ \quad \Delta H_{\text{endo}}(\text{RH}) \quad (2) \\
\text{H}^+ + e^- &\rightarrow \text{H} \quad \text{IP}(\text{H}) \quad (3) \\
\text{RH} &\rightarrow R + \text{H} \quad D(R-H) \quad (4)
\end{align*}
\]

Negative ion photoelectron spectroscopy is employed to measure the radical electron affinity, $\text{EA}(R)$, which is the enthalpy change for process 1, and proton transfer kinetics are used to determine the hydrocarbon gas-phase acidity, $\Delta H_{\text{endo}}(\text{RH})$, which is the enthalpy change for process 2. These values can be combined with the precisely known ionization potential of the hydrogen atom, $\text{IP}(\text{H})$, according to eq 3 to extract the homolytic bond dissociation $D(R-H) = \text{EA}(R) + \Delta H_{\text{endo}}(\text{RH}) - \text{IP}(\text{H})$ energy, $D(R-H)$. The bond dissociation energy\(^5\) is defined as the enthalpy change for reaction 4.

We have determined the gas-phase acidities of $\text{CH}_2==\text{CH}^-$, $\text{CH}_3==\text{CH}^-$, $\text{HC}==\text{CH}^-$, and $\text{C}_2\text{H}^-$ by proton transfer kinetics in a flow tube reactor. Separate photoelectron spectroscopy experi-
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) = h\omega_0 - KE_{eq}. Vinyl anions were formed in a dc discharge ion source, extracted, and passed through a quadrupole mass filter following the reaction \( F^+ + (CH_2=CH)_2SiF \rightarrow (CH_2=CH)_2SiF + CH_2=CH\) (100 pA), or in a microwave discharge flowing afterglow source from \( CH_2=CHCOOH \) (5 pA). 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 \( (h\omega_0 = 2.540 \text{ eV}) \) or 351.1 nm \( (h\omega_0 = 3.531 \text{ eV}) \) for the studies on the \( CH_2=CH^- \) ion and 351.1 nm for \( CH_2=C^- \) and \( CH^- \). In each case, the vibrational origin in the photoelectron spectrum was unambiguously assigned. The photoelectron spectra and origin assignments are shown in Figure 1. The energies of the origin transitions yield the following electron affinities: \( EA(CH_2=CH)^- = 0.667 \pm 0.024 \text{ eV}, EA(CH_2C)^- = 0.490 \pm 0.006 \text{ eV}, \) and \( EA(CH)^- = 2.969 \pm 0.010 \text{ eV}. \) 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 \( (1800 \text{ cm}^{-1}) \) 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. Anions were produced in an electron impact flowing afterglow source, extracted, and then injected into a flow tube reactor \( (P_{He} = 0.5 \text{ Torr}) \). 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, \( R^- + HA \rightarrow RH + A^- \) 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 of 300 ± 2 K. Product branching ratios were also measured, using calibrated corrections for the mass discrimination of the detection system.

\[ R^- + h\omega_0 \rightarrow R + e^-(KE) \quad (6) \]

\[ R^- + HA \rightarrow RH + A^- \quad (7) \]

22) The differences between enthalpies or free energies at the experimental temperature of 300 ± 2 K and at the standard-state temperature of 298.15 K are generally within ±0.02 kcal mol⁻¹, and can be neglected.

**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 \( v_2 \) bend and \( v_3 \) 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 \( K_{eq} = k_2/k_1 \). The relation \( \Delta G_{eq} = -RT \ln K_{eq} \) 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 \( \Delta G_{ad} (RH) = \Delta G_{ad} (HA) - \Delta G_{eq} \). 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 \( \Delta H_{ad} = \Delta G_{ad} + T \Delta S_{ad} \). Entropy data were taken in most cases from the JANAF Tables. Values for species not
Table I. Calculated Entropies and Enthalpies

<table>
<thead>
<tr>
<th>species</th>
<th>$H_{298}$ - $H_0^a$ (kcal mol$^{-1}$)</th>
<th>$S_{298}^b$ (cal mol$^{-1}$ K$^{-1}$)</th>
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<tr>
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<td>50.9</td>
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<td>C$_2$H$_4$</td>
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<td>48.8</td>
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<tr>
<td>H$_2$C=CH$_2$</td>
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<td>55.8$^c$</td>
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</tr>
<tr>
<td>HCHC</td>
<td>2.4</td>
<td>45.2</td>
</tr>
</tbody>
</table>

$^a$H$_{298}$ - $H_0 = \int H(T) dT$, $\pm 0.1$ kcal mol$^{-1}$. $^b$From JANAF.$^c$An experimental value of 55.9 $\pm$ 2.6 kcal mol$^{-1}$ K$^{-1}$ has been reported (ref 11).

Table II. Proton Transfer Reactions

<table>
<thead>
<tr>
<th>reaction</th>
<th>$k_{exp}$ (cm$^3$ s$^{-1}$)</th>
<th>$k_{1000}$ (cm$^3$ s$^{-1}$)</th>
<th>$\Delta G_{exp}$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(11) F$^-$ + HCCCH$^+ = HF$ + H$^+$</td>
<td>$2.2 \times 10^{-9}$</td>
<td>$2 \times 10^{-9}$</td>
<td>-4.54 $\pm$ 0.24</td>
</tr>
</tbody>
</table>

*Systematic errors give an additional $\pm 10\%$ uncertainty in rates; however, these errors cancel in the determination of $\Delta G_{exp}$. Collision rate calculated by ADO theory (ref 36). These rate constants represent total reaction including a small clustering contribution which essentially cancels in the equilibrium constant. Reference 37.

readily react with fluoride by proton transfer; thus for these experiments, acetylene was purified by passage through a dry ice/isopropanol alcohol trap. The complete removal of acetone was confirmed by the absence of CH$_3$COCH$_3$ peaks 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 possibility 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$^-$/acetylene, proton transfer accounted for only (25 $\pm$ 6)% of the observed total depletion rate of k = (3.8 $\pm$ 0.3) $\times$ 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 $k_1 = (1.0 \pm 0.3) \times 10^{-12}$ cm$^3$ s$^{-1}$. This treatment assumes that the F$^-$/HCCCH 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.
Bond Strengths

Relative acidities from relative equilibrium measurements are weighted averages of bond energies and electron affinities. Recommended gas-phase acidities from relative equilibrium measurements are shown in Table III. The zero on the relative scale is arbitrarily placed at the value of 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 HCCCH (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 Dₚ(HCC-H) together with our value for EA(CH₃). The bond energy obtained in this work, Dₚ(HCC-H) = 131.3 ± 0.7 kcal mol⁻¹, is indicated by a circle.

Using the known gas-phase acidity of HF, 24,25 \( \Delta G_{a,cid}^{0}(HF) = 365.6 \pm 0.2 \text{ kcal mol}^{-1} \), and the experimental value of \( \Delta G_{a,cid}^{0}(11) \) from Table II, we obtain \( \Delta G_{a,cid}^{0}(HCCH) = 369.9 \pm 0.3 \text{ kcal mol}^{-1} \).

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 The slight 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 (\( \Delta G_{a,cid}^{0}(H_2O) = 383.9 \pm 0.3 \text{ kcal mol}^{-1} \)) 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-buty 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, \( \Delta G_{a,cid}^{0} = 18.7 \pm 0.5 \text{ kcal mol}^{-1} \), is in excellent agreement with that obtained from the absolute values based on bond energies and electron affinities, \( \Delta G_{a,cid}^{0}(H_2O) - \Delta G_{a,cid}^{0}(HF) = 18.3 \pm 0.4 \text{ kcal mol}^{-1} \). A linear regression fit to the data in Figure 2 (with each value weighted by the square root of the uncertainty) yields a slope of 0.98, compared to the true value of unity. 20 This good agreement lends confidence to the relative acidities of HCCCH and the alcohols.

Using the equilibrium acidities relative to \( H_2O \), we obtain an estimate of \( \Delta G_{a,cid}^{0}(HCCH) = 369.5 \pm 0.5 \text{ kcal mol}^{-1} \), compared to the more direct measurement based on the equilibria with (24) \( \Delta G_{a,cid}^{0}(HF) = 365.6 \pm 0.2 \text{ kcal mol}^{-1} \) is calculated (eq 10) from Dₚ(HF) = 135.33 ± 0.17 kcal mol⁻¹ (ref 25); EA(HF) = 3.40 ± 0.00004 kcal mol⁻¹ (Blandel, C.; Cacciani, P.; Delacrétaz, C.; Trainham, R. Phys. Rev. A 1989, 40, 3698); \( \Delta G_{a,cid}^{0}(HF) = 19.30 \pm 0.01 \text{ kcal mol}^{-1} \) (ref 14, and \( \Delta H_{a,cid}^{0}(HF) - \Delta H_{a,cid}^{0}(H_2O) = 0.9 \pm 0.1 \text{ kcal mol}^{-1} \) (ref 14).


(27) \( \Delta G_{a,cid}^{0}(H_2O) = 383.9 \pm 0.3 \text{ kcal mol}^{-1} \) is calculated (eq 10) from Dₚ(HO-H) = 117.9 ± 0.3 kcal mol⁻¹ (ref 14), EA(OH) = 42.14 ± 0.04 kcal mol⁻¹ (Schulz, P. A.; Mende, R. D.; Jones, P. L.; Lineberger, W. C.; J. Chem. Phys. 1982, 77, 1153); \( \Delta G_{a,cid}^{0}(H_2O) = 22.1 \pm 0.2 \text{ kcal mol}^{-1} \) (ref 14), and \( \Delta H_{a,cid}^{0}(H_2O) - \Delta H_{a,cid}^{0}(H_2O) = 1.2 \pm 0.1 \text{ kcal mol}^{-1} \) (ref 14).
HF, $\Delta G_{\text{acid}}(\text{HCCH}) = 369.9 \pm 0.3 \text{ kcal mol}^{-1}$. Using the correlation in Figure 2, which yields a weighted average of the two values, we obtain a final value of $\Delta G_{\text{acid}}(\text{HCCH}) = 369.8 \pm 0.6 \text{ kcal mol}^{-1}$, 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$_2$O. Previously discussed is the discrepancy of 2 kcal mol$^{-1}$ between the gas-phase acidity values for methanol and ethanol and the same acidities derived from experimental values of $D(R&H)$ and $E_A(RO)$, $R = \text{CH}_3$ and C$_2$H$_5$, 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 (99.999%) were employed. C$_2$H$_4$ was produced by first making C$_2$H$_2$CO 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$_3^-$ with C$_2$H$_4$ 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 the reaction 14 has been reduced by 16% from the total reaction ion depletion rate to correct for contributions from clustering and from a trace reactive acetylene impurity to yield the proton transfer rate constant, $k_{11} = (2.7 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$.

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 $\text{NH}_3^-$ 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$_3^-$ with acetylene, we obtained a product spectrum in which the C$_2$H$^+$ intensity was 10% of the CH$_3$CH$^+$ signal. The known rate constant$^{12}$ for the reaction of NH$_3^-$ with acetylene is 1.84 $\times 10^{-10}$ cm$^3$ s$^{-1}$. These values yield a rate constant for $\text{NH}_3^-$ + C$_2$H$_4$ of $k_{11} = 2.6 \times 10^{-13}$ cm$^3$ s$^{-1}$, compared to the directly measured rate constant of $k_{11} = 2.7 \times 10^{-13}$ cm$^3$ s$^{-1}$. This excellent agreement lends credibility to this exceedingly small rate constant.

The reaction rates given in Table II yield $\Delta G_{\text{trans}}(14) = 4.54 \pm 0.24 \text{ kcal mol}^{-1}$. From the gas-phase acidity of ammonia,$^3$ $\Delta G_{\text{acid}}(\text{NH}_3) = 396.5 \pm 0.4 \text{ kcal mol}^{-1}$, we obtain $\Delta G_{\text{acid}}(\text{C}_2\text{H}_4) = 401.0 \pm 0.5 \text{ kcal mol}^{-1}$. This yields $\Delta H_{\text{acid}}(\text{C}_2\text{H}_4) = 399.4 \pm 0.4 \text{ kcal mol}^{-1}$ in good agreement with the temperature-independent experimental value$^2$ of $\Delta H_{\text{acid}}(\text{C}_2\text{H}_4) = 407 \pm 3 \text{ kcal mol}^{-1}$ obtained from threshold energies of endothermic atom abstraction reactions. An estimate$^2$ based on the product branching ratio in the reaction of OH$^-$ with CH$_3$CHSi(CH$_3$)$_3$ gave $\Delta H_{\text{acid}}(\text{C}_2\text{H}_4) = 407.5 \pm 0.1 \text{ kcal mol}^{-1}$.

Vinyl.

Because vinyl radical was not an available neutral reagent, the gas-phase acidity of C$_2$H$_3$ could not be determined by equilibrium measurements. Instead, we established $\Delta G_{\text{acid}}(\text{C}_2\text{H}_3\text{CH}_3)$ by bracketing the proton affinity of C$_2$H$_3^-$ 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$_3^-$ with ethylene is sufficiently slow that it did not interfere with this measurement. CH$_3^-$ did not react with water ($\Delta G_{\text{acid}}(\text{H}_2\text{O}) = 383.9 \pm 0.3 \text{ kcal mol}^{-1}$), giving an upper limit of $k_{11} = 4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Assuming the exoergic reverse reaction occurs upon every collision ($k_{11} \gg k_{12}$) and using the reactivity of near thermoneutral, $\Delta G_{\text{trans}} \leq 0$. Guo and Grabowski$^2$ have used flowing afterglow techniques to measure a rate constant of $k_{11} = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, which corresponds to 60% of the collision rate. These observations bracket the gas-phase acidity of vinyl: 375.1 $\pm 0.6 \text{ kcal mol}^{-1} \leq \Delta G_{\text{acid}}(\text{C}_2\text{H}_3\text{CH}_3) \leq 380.4 \pm 0.3 \text{ kcal mol}^{-1}$.

For convenience, we present this result as $\Delta G_{\text{acid}}(\text{C}_2\text{H}_3\text{CH}_3) = 377.6 \pm 3 \text{ kcal mol}^{-1}$.

Ethynyl.

C$_3^-$ has a large hydrogen affinity and rapidly reacted with neutral reagents to form C$_2^+$ which then reacted further. Interference of this process prevented us from obtaining a firm bracket on the gas-phase acidity of C$_3^-$. Product branching ratio measurements showed that C$_2^-$ reacts completely with the more exothermic atom abstraction channel. Consequently, we observe only a lower bound, $\Delta G_{\text{acid}}(\text{C}_3^-) = 341.5 \pm 1.9 \text{ kcal mol}^{-1}$.

**Discussion**

Experimental electron affinities and gas-phase acidities are presented in Table IV. With these experimental results and auxiliary heats of formation$^{14,15}$ listed in Table V, we can complete several thermochromic analyses as shown in Table VI. We first employ eq 8 to determine experimental R–H bond dissociation energies for ethylene, vinyl, and vinyl (RH). Using these values and established heats of formation of C$_2$H$_4$, HCCN, and H$_2$, 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$_2$, C$_3$, CH$_2$, and CH$_3$. Of these, only $\Delta H^\circ(\text{C}_3)$ appears to be subject to unresolved experimental discrepancies.$^9$


The heat of formation of C$_3$ as adopted by JANAF (ref 14) is derived from a spectroscopic extrapolation for the bond dissociation energy, $D(C) = 143.2 \pm 0.3 \text{ kcal mol}^{-1}$ (Messinger, G.; Krauss, L. Z. Naturforsch. 1967, 22, 144, 1973, 12, 347), $f 137$ (Huber and Herzberg$^{2}$ 1979, 11, 313), $f 145 \pm 0.5 \text{ kcal mol}^{-1}$ (Brewer, L.; Hicks, T. W.; Klorigian, O. H. J. Chem. Phys. 1963, 36, 182), $f 143 \pm 0.1 \text{ kcal mol}^{-1}$ (Kordis, L.; Gingher, K. A. J. Chem. Phys. 1973, 58, 5058), $f 139.3 \pm 0.6 \text{ kcal mol}^{-1}$ (Zavitsanos, P. D.; Carlson, G. A. J. Chem. Phys. 1973, 59, 2666), $f 179.7 \pm 0.6 \text{ kcal mol}^{-1}$ (Uov, B. V.; Novotny, I.; Pelieva, L. A. J. Phys. Chem. (Engl. Transl.) 1980, 32, 553; Zh. Prikl. Spektrosk. 1980, 32, 965). See also: Brewer, L.; Hagan, L. H. Int. J. Mass Spectrom. Ion Proc. 1979, 11, 233. Lacking a definitive determination, we consider these values to be only approximate, with possible systematic error, but with error bars to include other values, $D(C) = 141.0 \pm 2.5 \text{ kcal mol}^{-1}$. However, we do not vary the values obtained for D(3-HCC, D(3-HC(C)), and $\Delta G_{\text{trans}}$ in Table VI and ref 149.

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

### Electronic Affinities

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<tr>
<th>species</th>
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<th>this work</th>
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<th>E(_A)</th>
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<td>C(_2)H</td>
<td>C(_2)H X (2^2\Delta) (</td>
<td>\rightarrow ) C(_2)H (X ; 1^2\Sigma^+)</td>
<td>68.5 (\pm) 0.2</td>
<td>68.6 (\pm) 0.3</td>
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<tr>
<td>CH(_2)C</td>
<td>CH(_2)C X (1^2\Sigma^+) (</td>
<td>\rightarrow ) CH(_2)C (X ; 1^2\Sigma^+)</td>
<td>11.3 (\pm) 0.2</td>
<td>11.5 (\pm) 0.2</td>
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<tr>
<td>CH(_2)CH</td>
<td>CH(_2)CH (X ; 1^2\Sigma^+) (</td>
<td>\rightarrow ) CH(_2)CH (X ; 1^2\Sigma^+)</td>
<td>15.4 (\pm) 0.6</td>
<td>15.4 (\pm) 0.6</td>
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<tr>
<td>C(_3)</td>
<td>C(_3) (X ; 1^2\Sigma^+) (</td>
<td>\rightarrow ) C(_3) X (1^2\Sigma^+)</td>
<td>75.3 (\pm) 0.5</td>
<td>75.8 (\pm) 0.5</td>
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### Gas-Phase Acidities

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<th>(\Delta S^\bullet)(_{\text{acid},298})</th>
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<td>HCCH</td>
<td>369.8 (\pm) 0.6</td>
<td>26.8 (\pm) 0.5</td>
<td>377.8 (\pm) 0.6</td>
<td>376.4 (\pm) 0.6</td>
<td>368.5 (\pm) 2.0</td>
<td></td>
</tr>
<tr>
<td>CH(_2)CH</td>
<td>377.6 (\pm) 3.1 (f)</td>
<td>23.9 (\pm) 1.0 (f)</td>
<td>384.7 (\pm) 3.4</td>
<td>383.3 (\pm) 3.4</td>
<td>378 (\pm) 3.4 (f)</td>
<td></td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>401.0 (\pm) 0.5</td>
<td>28.1 (\pm) 0.5</td>
<td>409.4 (\pm) 0.6</td>
<td>408.0 (\pm) 0.6</td>
<td>399 (\pm) 3.4 (f)</td>
<td></td>
</tr>
<tr>
<td>CH(_2)</td>
<td>(\geq 345.1 \pm 1.9) (f)</td>
<td>22.1 (\pm) 1.0 (f)</td>
<td>(\geq 348.1 \pm 2.0)</td>
<td>(\geq 347.0 \pm 2.0)</td>
<td>351 (\pm) 1.7</td>
<td></td>
</tr>
<tr>
<td>CH(_2)OH</td>
<td>375.1 (\pm) 0.6</td>
<td>22 (\pm) 2</td>
<td>381.7 (\pm) 0.8</td>
<td>374 (\pm) 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_2)OH</td>
<td>372.0 (\pm) 0.6</td>
<td>22 (\pm) 2</td>
<td>378.6 (\pm) 0.8</td>
<td>370.7 (\pm) 2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-Pr(_2)OH</td>
<td>370.1 (\pm) 0.6</td>
<td>22 (\pm) 2</td>
<td>376 (\pm) 0.8</td>
<td>368.8 (\pm) 2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tert-BuOH</td>
<td>369.3 (\pm) 0.6</td>
<td>22 (\pm) 2</td>
<td>375.9 (\pm) 0.8</td>
<td>368.1 (\pm) 2.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Previously recommended values from the compilation of Lias et al. (ref. 13), except as noted. \(f\) Calculated from 0 K or 298 K value using heat capacity data described in the text. \(f\) Derived from \(\Delta H^\bullet\)\(_{\text{gas},298}\) (see ref. 19) and E\(_A\)(C). \(f\) Derived from \(E_A(CH)\) = 79.9 \(\pm\) 0.4 kcal mol\(^{-1}\) (ref. 40), \(\Delta H^\bullet(C)\), and \(\Delta H^\bullet(H)\).

Derived anion heats of formation, anion C-H bond dissociation energies, and gas-phase acidities are also presented in Table V. The derived value of \(\Delta H^\bullet_{\text{acid},298}(C_2H) = 355.6 \pm 2.6\) kcal mol\(^{-1}\) agrees with our experimental bound \(\Delta H^\bullet_{\text{acid},298}(C_2H) = 348.1 \pm 2.0\) kcal mol\(^{-1}\), and is consistent with the observed absence of proton transfer between C\(_2\)H and chloroform (\(\Delta H^\bullet_{\text{acid},298}(CHCl_3) = 357.1 \pm 6.2\) kcal mol\(^{-1}\)).

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 \(E_A(CHC-H) = 131.3 \pm 0.7\) kcal mol\(^{-1}\) agrees with the previous value based on eq 5, 130.4 \(\pm\) 5.5 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 \(E_A(CHC-H)\) involve determination of the translational energy release in the photolysis of acetylene in a molecular beam. Wodtke and Lee measured the velocity of the C\(_2\)H photofragment by time-of-flight with mass spectrometric detection, and obtained \(E_A(CHC-H) = 132.2 \pm 2\) kcal mol\(^{-1}\), in good agreement with the present value. In a conceptually similar experiment, Wittig and co-workers measured the velocity of the hydrogen atom fragment by Doppler multi-photon ionization spectroscopy, and found \(E_A(CHC-H) = 127 \pm 1.5\) 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 showed a sharp cutoff above 132.9 \(\pm\) 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 observed unimolecular lifetime decreases induced by a magnetic field, yielding an upper bound of \(\leq 132.3\) kcal mol\(^{-1}\). In more recent work, Field and co-workers observed decreases in fluorescence lifetimes induced by a Stark field, and assigned this to predissociation, giving a significantly lower upper limit, \(E_A(CHC-H) = 126.647 \pm 0.002\) kcal mol\(^{-1}\).

A bond energy based on the threshold for the photoionization process HCC\(_H^+ + h\nu \rightarrow C_2H^+ + H^+ + e^-\) using synchrotron radiation gave a value of \(E_A(CHC-H) = 132.6 \pm 1.2\) kcal mol\(^{-1}\), strictly an upper limit.

Values based on the appearance potential of C\(_2\)H\(_2\) and the ionization potential of C\(_2\)H fall over a range of 124-135 kcal mol\(^{-1}\), depending on the determination of IP(C\(_2\)H). Bond energies based on pyrolysis kinetics are significantly lower than any of the more recent experiments. A model used to explain C\(_2\)H 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 and Field 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, but for C\(_2\)H 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 of this electronic transition agree well with the experimental values for X \(2^2\Sigma^+\) C\(_2\)H, indicating that the

\(f\) Derived from \(E_A(CH)\) (see ref. 39) and \(\Delta H^\bullet(C)\). \(f\) Derived from \(E_A(CH)\) = 79.9 \(\pm\) 0.4 kcal mol\(^{-1}\) (ref. 40), \(\Delta H^\bullet(C)\), and \(\Delta H^\bullet(H)\).

\(f\) Thermal corrections between 0 K and 298 K calculated as required using heat capacity data described in text and Table I. \(f\) Derived from \(E_A(CH)\) (see ref. 39) and \(\Delta H^\bullet(C)\). \(f\) Derived from \(E_A(CH)\) = 79.9 \(\pm\) 0.4 kcal mol\(^{-1}\) (ref. 40), \(\Delta H^\bullet(C)\), and \(\Delta H^\bullet(H)\).
Table VI. Hydrocarbon Thermochemistry (kcal mol⁻¹)

<table>
<thead>
<tr>
<th>Quantity</th>
<th>0 K</th>
<th>298 K</th>
<th>Derivation</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(HCC-H)</td>
<td>13.1 ± 0.7</td>
<td>13.2 ± 0.7</td>
<td>ΔΗ_fus(HCC + EA(C₂H) - IP(H))</td>
</tr>
<tr>
<td>D(CH₃CH-H)</td>
<td>109.7 ± 0.8</td>
<td>111.2 ± 0.8</td>
<td>ΔΗ_fus(C₂H₅) + EA(CH₃CH) - IP(H)</td>
</tr>
<tr>
<td>D(CH₄C-H)</td>
<td>81.0 ± 3.5</td>
<td>82.7 ± 3.5</td>
<td>ΔΗ_fus(CH₃CH) + EA(CH₂CH) - IP(H)</td>
</tr>
</tbody>
</table>

ΔΗ_fus(HCC) = 134.3 ± 0.7
ΔΗ_fus(CH₃CH) = 72.7 ± 0.8
ΔΗ_fus(CH₄C) = 102.1 ± 4.0

Derived C-H Bond Dissociation Energies
D(H-HCCH) = 33.6 ± 0.8
D(H-HCC) = 83.9 ± 4.2
D(H-HC) = 116.3 ± 2.6

Derived C-C Bond Dissociation Energies
D(CH₃=CH₂) = 171.0 ± 1.2
D(CH₃CH) = 163.0 ± 1.1
D(CH₄C) = 162.0 ± 4.2
D(CH≡C) = 177.4 ± 0.8
D(CH≡CCH) = 228.8 ± 0.7

Anion Heats of Formation
ΔΗ(CH₂C≡H) = 57.3 ± 0.6
ΔΗ(CH₂C≡CH) = 90.8 ± 4.0
ΔΗ(CH₂C≡C) = 66.7 ± 0.7
ΔΗ(CH≡C) = 123.7 ± 2.5

Anion C-H Bond Dissociation Energies
D(H-HCC) = 85.1 ± 3.7
D(H-HCC) = 26.7 ± 4.2
D(H-C≡C) = 109.5 ± 2.6

Gas-Phase Acidity
ΔΗ_fus(CH₂C≡H) = 329.0 ± 4.2
ΔΗ_fus(CH≡C) = 354.6 ± 2.6

| Table VII. CH Bond Dissociation Energy of Acetylene (kcal mol⁻¹) * |
|-----------------------|---------------------|-------------------------------------------------------------------|
| D(CH₂C≡CH)            | D(CH₂C≡CH)          | D(CH₂C≡CH) + EA(C₂H) + IP(H)                                       |
| 171.0 ± 1.2            | 171.0 ± 1.2         |                                                                  |
| 163.0 ± 1.1            | 163.0 ± 1.1         |                                                                  |
| 162.0 ± 4.2            | 162.0 ± 4.2         |                                                                  |
| 177.4 ± 0.8            | 177.4 ± 0.8         |                                                                  |
| 228.8 ± 0.7            | 228.8 ± 0.7         |                                                                  |
| 57.3 ± 0.6             | 57.3 ± 0.6          |                                                                  |
| 90.8 ± 4.0             | 90.8 ± 4.0          |                                                                  |
| 66.7 ± 0.7             | 66.7 ± 0.7          |                                                                  |
| 123.7 ± 2.5            | 123.7 ± 2.5         |                                                                  |
| 85.1 ± 3.7             | 85.1 ± 3.7          |                                                                  |
| 26.7 ± 4.2             | 26.7 ± 4.2          |                                                                  |
| 109.5 ± 2.6            | 109.5 ± 2.6         |                                                                  |
| 329.0 ± 4.2            | 329.0 ± 4.2         |                                                                  |
| 354.6 ± 2.6            | 354.6 ± 2.6         |                                                                  |

* Literature values for ΔΗ_fus(C₂H) converted to ΔD(CH₂C≡CH) using auxiliary heats of formation given in Table V. Corrections from 298 K to 0 K calculated using heat capacity data described in the text, D(CH₂C≡CH) = D(CH₂C≡CH) - D(CH₂C≡CH) + 1.6 kcal mol⁻¹.

A II C₂H excited state cannot be implicated. Hot band frequencies agree with precision to add value to the C II CH system. No electronically excited states of C₂H⁺ are expected or observed. If the sake of argument we accept field's upper limit for the acetylene bond energy, D(CH₂C≡CH) ≤ 166.65 kcal mol⁻¹, we can use eq 10 with the present value for EA(C₂H) to derive an alternate value for the gas-phase acidity of acetylene. Field's bond energy yields ΔG°₂₉₈(HCC) = 365.15 kcal mol⁻¹ versus our value of 369.8 ± 0.6 kcal mol⁻¹. The acetylene bond energy of hydrogen fluoride is ΔG°₂₉₈(HF) = 365.6 ± 0.2 kcal mol⁻¹, a consequence of the lower bond energy would be that the F⁻ + HCC 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 in 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. 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 fastest reaction in the ground-state reaction indeed had a large barrier, an extraordinarily high population of > 60% vibrationally excited C₂H⁺ 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 HCC⁺ 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 acities from equilibrium measurements and absolute acities for HF and H₂O obtained from precisely known bond energies and electrone 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 HCC⁺ 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.

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(CH₂-
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 bond dissociation energy of 105 kcal mol\(^{-1}\), the electron affinity of vinyl radical must be smaller by 5 kcal mol\(^{-1}\); i.e., \(\text{EA}(\text{C}_2\text{H}_4) = 0.46\) 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 deuteronated vinyl anions.\(^{17}\)

The structural identity of the ion as \(\text{CH}_2=\text{CH}^+\) 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, \(\text{CH}_2\text{C}_3^+\), 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 \(\text{EA}(\text{C}_2\text{H}_4)\) were about 0.46 eV rather than the measured value of 0.67 eV, then some electron transfer from \(\text{C}_2\text{H}_4^+\) to oxygen, \(\text{EA}(\text{O}_2) = 0.451 \pm 0.007\) eV, should be observable under our experimental conditions. We therefore injected \(\text{C}_2\text{H}_4^+\) into our flow tube and added an excess of \(\text{O}_2\). No \(\text{O}_2^-\) ions were produced, but \(\text{HO}_2^- (70\%)\) and \(\text{HCC}^- (40\%)\) 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 \(\text{O}_2^-\) signal appeared and increased until it equaled the intensity of \(\text{HO}_2^-\) at approximately 0.18 eV (4 kcal mol\(^{-1}\) center-of-mass kinetic energy. These observations are fully compatible with \(\text{EA}(\text{C}_2\text{H}_4) = 0.67\) 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\(^{13}\) would then be nearly the same; i.e., the reaction \(\text{NH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{NH}_4^+ + \text{C}_2\text{H}_3\) (eq 14, Table II) would be nearly thermoneutral rather than 5 kcal mol\(^{-1}\) endothermic. Quantum chemical experiments show this cannot be true. Addition of a large excess of ethylene into a stream of \(\text{NH}_3\) in the SIFT produces only a trace of the vinyl anion. Addition of ethylene to \(\text{ND}_2\) produces \(\text{NHD}^-\) and \(\text{ND}_2\text{NH}^-\) by hydrogen/deuterium exchange faster than \(\text{C}_2\text{H}_3^+\) is formed,\(^{29}\) 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, \(\text{NH}_3\) is immediately produced and the vinyl anion signal 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 \times 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 \(\text{O}_2\) or in the photoelectron spectrum. Reactions of \(\text{NH}_3^+\) with impurities in the flow tube is ruled out by the 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.


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 NH₃, 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 Vinylidene-Acetylene Isomerization.

Our value of $\Delta H_f$ (CH₂=CH), combined with $\Delta H_f$(HCCH), yields the enthalpy of the isomerization of acetylene to vinylidene:

$$\Delta H_f = 47.4 \pm 4.0 \text{ kcal mol}^{-1}$$

Within the uncertainty, which represents the bracketed experimental range (not a standard deviation), this value is in agreement with an upper limit, $\Delta H_f$ (HCCH) ≤ 44.4 ± 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 of shock tube data yields $\Delta H_f$ ≤ 44 ± 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, 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, $D_0$(CH₂=CH–H) = 110.2 kcal mol⁻¹, and $D_0$(HCCH–H) = 132.8 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 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 CH₂=CH₂ and HCECH 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

These two primary results are based on completely independent errors in the experiments reported here have produced no "smoking gun", and we have confidence in our values. Do(HCC-H) = 131.3 ± 0.7 kcal mol⁻¹ and Do(C₂H₃-H) = 109.7 ± 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 sp³, sp², 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: Do(CH₄-H) = 103.24 ± 0.12 kcal mol⁻¹ (ref 14), Do-(CH₂CH₂-H) = 109.7 ± 0.8 kcal mol⁻¹, and Do-(HCC-H) = 131.3 ± 0.7 kcal mol⁻¹.

In the closed-shell molecules CH₃=CH₂ and HC≡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 CH₂=CH₂ radical from ethylene, but subsequent cleavage of the vinyl α-CH bond, eq 18, requires only 81 kcal mol⁻¹. The reduced CH bond

\[ \text{CH}_2=\text{CH}^* \rightarrow \text{H} + \text{CH}_2=\text{C} \]  

energy may be attributed to the singlet-coupling of the remaining electron pair, which stabilizes the singlet diradical vinylidene product, CH₂=CH (X⁺ ¹A₁). Removal of a CH bond from vinylidene, eq 19, uncouples the electron pair but the CC bond order

\[ \text{CH}_2=\text{C} \rightarrow \text{H} + \text{HC} \equiv \text{C} \]  

increases upon formation of ethynyl radical. We find Do-(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 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 H₂O.

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 CH₃CH 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 (PCy₃)₂M(H)O₂CH 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 ¹³CO₂ exchange reactions of the trans-(Cy₃P)₂M(H)O₂CH (M = Ni, Pd) derivatives to afford the corresponding trans-(Cy₃P)₂M(¹³CO₂)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 ΔH° = 22.1 (9) kcal mol⁻¹ and ΔS° = -5 (3) cal mol⁻¹deg⁻¹, whereas the analogous parameters for the palladium complex were found to be ΔH° = 21 (2) kcal mol⁻¹ and ΔS° = 4 (8) cal mol⁻¹deg⁻¹. The reaction pathways are proposed to proceed via rate-determining CO₂ extrusion to provide the dihydride complexes, followed by rapid ¹³CO₂ 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 (Cy₃P)₂Pd(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-(Cy₃P)₂Ni(O₂CH)D are indicative of a reaction pathway coincident with that defined for intermolecular CO₂ exchange.

Introduction

It is of importance to mechanistically understand the C—H bond forming reaction accompanying the insertion of CO₂ 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,