Rate Coefficients of $\text{C}_2\text{H}$ with $\text{C}_2\text{H}_4$, $\text{C}_2\text{H}_6$, and $\text{H}_2$ from 150 to 359 K

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Rate Coefficients of C₂H with C₂H₄, C₂H₆, and H₂ from 150 to 359 K

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Rate coefficients for the reactions C₂H with C₂H₄, C₂H₆, and H₂ are measured over the temperature range 150−359 K using transient infrared laser absorption spectroscopy. The ethynyl radical is formed by photolysis of C₂H₂ with a pulsed excimer laser at 193 nm, and its transient absorption is monitored with a color center laser on the Q₁(9) line of the A²Π−X²Σ transition at 3593.68 cm⁻¹. Over the experimental temperature range 150−359 K the rate constants of C₂H with C₂H₄, C₂H₆, and H₂ can be fit to the Arrhenius expressions

\[ k_{C_2H_4} = (7.8 ± 0.6) \times 10^{-11} \exp(134 ± 44)/T \],

\[ k_{C_2H_6} = (3.5 ± 0.3) \times 10^{-11} \exp(2.9 ± 16)/T \],

and

\[ k_{H_2} = (1.2 ± 0.3) \times 10^{-11} \exp([-998 ± 57])/T \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \],

respectively. The data for C₂H with C₂H₄ and C₂H₆ indicate a negligible activation energy to product formation shown by the mild negative temperature dependence of both reactions. When the H₂ data are plotted together with the most recent high-temperature results from 295 to 854 K, a slight curvature is observed. The H₂ data can be fit to the non-Arrhenius form

\[ k_{H_2} = 9.2 \times 10^{-18} T^{1.72+0.09} \exp([-478 ± 165])/T \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \].

The curvature in the Arrhenius plot is discussed in terms of both quantum mechanical tunneling of the H atom from H₂ to the C₂H radical and bending mode contributions to the partition function.

Introduction

The ethynyl radical, C₂H, is of fundamental importance in combustion chemistry and in planetary atmospheres. The ethynyl radical is a reactive intermediate in the pyrolysis of acetylene at temperatures in excess of 1800 K. It is also a reactive species on Titan, a moon of Saturn, where the atmospheric temperature is altitude-dependent (94 K at the surface and 160 K at 300 km above the surface). To understand the importance of various ethynyl reactions in the two drastically different environments, it is desirable to know the rate coefficients for C₂H with such species as C₂H₄, C₂H₆, and H₂ over an extremely broad temperature range. In this work we are able to provide the first experimental data on low-temperature rate coefficients of the reactions

\[ C_2H + C_2H_4 \rightarrow \text{products} \] (1)

\[ C_2H + C_2H_6 \rightarrow C_2H_5 + C_2H \] (2)

\[ C_2H + H \rightarrow C_2H_2 + H \] (3)

using transient infrared laser absorption spectroscopy.

The exothermicity of reaction 1 is such that there are two different thermodynamically accessible product channels available:

\[ C_2H + C_2H_4 \rightarrow C_4H_4 + H \]

\[ \Delta H = -95.4 \text{ kJ mol}^{-1} \]

(1a)

\[ \rightarrow C_2H_3 + C_2H_2 \]

\[ \Delta H = -90.4 \text{ kJ mol}^{-1} \]

(1b)

The C₄H₄ species in reaction 1a is the vinyl acetylene isomer. Reaction 1b is a possible source of vinyl radicals, C₂H₃, in Titan’s atmosphere. It has been proposed by Yung et al. that vinyl radicals can undergo a disproportionation reaction to form acetylene and ethylene, scavenge a hydrogen atom, or act as a source of C₃ compounds:

\[ 2C_2H_3 \rightarrow C_2H_2 + C_2H_4 \]

(4)

\[ C_2H_3 + H \rightarrow C_2H_2 + H_2 \]

(5)

\[ C_2H_3 + CH_3 + M \rightarrow C_3H_5 + M \]

(6)

The vinyl radical, like the ethynyl radical, is one of many species responsible for the synthesis of higher hydrocarbons in Titan’s atmosphere through reactions with other molecules (C₂H₂, CH₄, C₂H₆, and C₂H₄ just to name a few). Reactions 4 and 6 are just a few examples of the hundreds of possible combinations of radical−radical reactions for which low-temperature rate coefficients are not known.

The reaction of C₂H + C₂H₆ leads to the production of ethyl radicals, C₂H₅, which opens pathways for the production of propane, C₃H₈, in Titan’s atmosphere via the following scheme:

\[ 2(C_2H + hv) \rightarrow C_2H + H \]

(7)

\[ C_2H + CH_4 \rightarrow C_2H_2 + CH_3 \]

(8)

\[ C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5 \]

(2)

\[ CH_3 + C_2H_5 + M \rightarrow C_3H_8 + M \]

(9)

net: \[ CH_4 + C_2H_6 \rightarrow C_3H_8 + 2H \]

(10)

In addition, a pressure-dependent study by Lander et al. indicated a slight increase in \( k_{C_2H_6} \) (C₂H + C₂H₆) with increasing helium number density. If this finding is valid, it raises new questions as to the mechanism involved, which may include the formation of an addition complex.

Since the room temperature rate constant for C₂H + H₂ is very slow and difficult to measure accurately, scientists interested in modeling planetary atmospheres have had to rely...
on theoretical calculations or extrapolations from high-temperature data. For example, the reaction of
\[ \text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H} \] (3)
is listed in the proposed scheme of Yung et al. as contributing to the production of C_2H_6 in the atmospheres of both Jupiter and Saturn.\textsuperscript{3,4,6}  

The reaction of C\textsubscript{2}H + H\textsubscript{2} has been studied theoretically by both Harding et al.\textsuperscript{11} and Herbst.\textsuperscript{9} Harding and co-workers calculated \(k_{\text{th}}\), with Wigner tunneling corrections, from 300 to 2000 K for reaction 3 as \(6.8 \times 10^{-17}\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}\). The calculated fit shows significant curvature in the Arrhenius plot. Herbst calculated low-temperature rate coefficients for reaction 3 from 10 to 300 K using statistical phase space theory. The rate coefficients, \(k_{\text{th}}\), are calculated with and without tunneling contributions. There is a steady decrease in \(k_{\text{th}}\) from 300 to 40 K, but the calculation with tunneling contributions shows that \(k_{\text{th}}\) begins to increase from \(~1.2 \times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}\) at 40 K to \(2.2 \times 10^{-15}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}\) at 10 K. For the non-tunneling contribution calculation, \(k_{\text{th}}\) decreases rapidly from \(1 \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}\) at 300 K to \(~6 \times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}\) at 150 K. Clearly, more theoretical and experimental work is needed to determine whether or not tunneling plays a large enough role to "see" its effect on \(k_{\text{th}}\) with temperature. The goal in studying C\textsubscript{2}H + H\textsubscript{2} reaches beyond measuring accurate rate coefficients for photochemical models. The objective is to distinguish any experimental evidence for tunneling at low temperatures and provide a basis for more theoretical work on this fundamental reaction.

Extrapolations of rate coefficients from high-temperature data can lead to significant errors at low temperatures due to a negative temperature dependence in certain reactions, as was shown for C\textsubscript{2}H + C\textsubscript{2}H\textsubscript{2}.\textsuperscript{10} Several groups have measured rate coefficients for C\textsubscript{2}H with C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and H\textsubscript{2} at 300 K or at higher temperatures.\textsuperscript{5,6,11-19} Up to this point, there have been no temperature-dependent rate coefficient measurements of C\textsubscript{2}H with C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{6}, and despite the importance of C\textsubscript{2}H + H\textsubscript{2}, there remains no experimental rate coefficient data for this reaction at low temperature.

The Arrhenius plot for reaction 1 shows a mild negative temperature dependence from 150 to 359 K. In addition, reaction 2 shows little or no temperature dependence of its rate coefficients over 153–357 K. Both sets of data are fit to Arrhenius expressions in which \(k_{\text{C_2H}}\) and \(k_{\text{C_2H_4}}\) are given by \((7.8 \pm 0.6) \times 10^{-11}\text{exp}[(134 \pm 44)/T] \text{ and } (3.5 \pm 0.3) \times 10^{-11}\text{ exp}[(2.9 \pm 16)/T] \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}\), respectively. The data for C\textsubscript{2}H + H\textsubscript{2} show a positive temperature dependence from 150 to 359 K which can be fit to the Arrhenius expression \(k_{\text{th}} = (1.2 \pm 0.3) \times 10^{-11}\text{exp}[(-998 \pm 57)/T] \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}\), when combined with previous high-temperature measurements, there is evidence for curvature in the Arrhenius plot.

**Experimental Section**

The rate coefficients for C\textsubscript{2}H with C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and H\textsubscript{2} are measured using transient infrared laser absorption spectroscopy. A schematic of the experimental setup is shown in Figure 1. The details of this setup have been described in numerous papers by this group so only a brief outline will be given here.\textsuperscript{10,20,21}

Ethynyl radicals are produced in the meter long, temperature variable flow cell at 193 nm by a pulsed excimer laser which was run at 55 mJ/pulse at 10 Hz. The absorption cell is constructed from quartz with Brewster windows for a multipass setup. The cell consists of an inner zone and an outer volume. In the inner jacket, the gases flow across the photolysis region through a series of transverse inlets and outlets. The transverse flow arrangement allows high laser repetition rates with minimal photolysis of the same gas volume. With a typical flow rate of \(2.7 \times 10^{20}\text{ molecules s}^{-1}\), the photolysis volume is replenished every 12 laser pulses. After accounting for UV laser loss on the Brewster windows of the cell, the C\textsubscript{2}H concentration was estimated to be no greater than \(7.5 \times 10^{10}\text{ cm}^{-3}\) for the highest acetylene pressures. (The acetylene number density ranges from \(1.3 \times 10^{14}\text{ to } 4.8 \times 10^{14}\text{ cm}^{-3}\).) This estimation is based on using \(1.35 \times 10^{-19}\text{ cm}^{-2}\) for the absorption cross section at 193 nm and 0.26 for the quantum yield for C\textsubscript{2}H production.\textsuperscript{23} A 1500–6000-fold excess of C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, or H\textsubscript{2} with respect to C\textsubscript{2}H is always present in these experiments. Contributions from radical–radical or secondary reactions can be neglected since the time between collisions for C\textsubscript{2}H and C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, or H\textsubscript{2} is 1000 times shorter than the time between collisions of two C\textsubscript{2}H radicals. Rate coefficients are measured at various ethene/ethane densities of \((0.2–5.2) \times 10^{15}\text{ cm}^{-3}\) and hydrogen densities of \((0.6–9.0) \times 10^{17}\text{ cm}^{-3}\). The helium density is varied over the range \((0.5–2.7) \times 10^{18}\text{ cm}^{-3}\) to test for a pressure dependence in the rate coefficients of C\textsubscript{2}H with C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, or H\textsubscript{2}.

In the outer jacket either cooled pentane or isopentane is circulated by a micropump to achieve temperatures as low as 150 K. (It should be noted that not every rate coefficient can be measured down to 150 K because of the low C\textsubscript{2}H\textsubscript{2} concentrations required to keep \(k_{\text{C_2H}_2}\) below 40%.) In experiments performed above room temperature, heated water was circulated around the inner cell.

The C\textsubscript{2}H radical is probed in absorption by a high-resolution color center laser tuned to the Q\textsubscript{H}(9) line at 3593.68 cm\textsuperscript{-1} of the \(A^1\Pi-X^3\Sigma^+\) transition.\textsuperscript{11} A scanning Fabry-Perot spectrum analyzer is used to ensure the color center is running on one longitudinal mode, and a home-built scanning Michelson interferometer wavemeter is used to monitor the color center's wavelength.

The probe beam, after three to five multipasses, is directed onto a 50 MHz Ge:Au detector which has a 20 mm\textsuperscript{2} sensitive area. Transient decay traces typically have a signal-to-noise ratio of 10–15 and are amplified and then coadded by a 100 MHz digital oscilloscope. Typical data collection consists of averaging the transient signal for 1500–2000 excimer pulses. All gases used in this experiment flow through a mixing cell before entering the low-temperature cell. Helium is used to thermally equilibrate the gas mixture with the cell walls. All gases are obtained commercially with the following purities: He, 99.99%; C\textsubscript{2}H\textsubscript{4}, 99.6%; H\textsubscript{2}, 99.9999%. The acetone is
removed from the acetylene by an activated charcoal filter. The
temperature of the gas mixture is measured by a series of three
type K thermocouples along the length of the cell. One thermo-
couple is inserted at each end of the cell, and the other is placed
in the middle of the cell. This configuration is chosen to ensure
that there are no thermal gradients along the length of the cell.
Partial pressures of each gas are determined by calibrated mass
flow meters and the measured total pressure inside the cell.

Analysis of Kinetic Data

The ethynyl radical is monitored directly from its ground state
C₂H(X2Σ⁺(0,0,0)). In addition, it is necessary that the upper
states of C₂H are fully quenched before the reaction of C₂H-
(X2Σ⁺(0,0,0)) with C₂H₄, C₂H₆, and H₂ occurs. Previous
experiments by Lander et al.⁷ and Farhat et al.¹¹ performed
under similar conditions, have shown that relaxation of the C₂H-
(X(0,0,1)) state occurs in approximately 1 µs. In this study, as
well as in theirs, the reaction of C₂H(X2Σ⁺(0,0,0)) with C₂H₄,
C₂H₆, and H₂ takes place over tens of microseconds. Therefore,
complete vibrational relaxation should have occurred before any
ground state measurements were made. To further ensure
complete vibrational relaxation of C₂H, the fits only include
data for t > 3τᵣₑₑ.

The rate coefficients measured in this study are done under
pseudo-first-order conditions in which [X] (where X = C₂H₄,
C₂H₆, or H₂) and [C₂H₂] >> [C₂H]. The rate of change of [C₂H]
can be expressed as

\[
d([C₂H])/dt = -(kₓ[X] + k_{C₂H₂}[C₂H₂])\]  

After integration, this yields

\[
[C₂H] = [C₂H]₀ \exp(-k_{oₜₜ})\]  

where

\[
k_{oₜₜ} = kₓ[X] + k_{C₂H₂}[C₂H₂]\]  

\[
k_{oₜₜ} - k_{C₂H₂}[C₂H₂] = kₓ[X] = k'ₓ\]  

The observed decay rates, kₒₜₜ, are obtained by fitting the averaged
transient signal to a single-exponential decay plus a constant, eq 15, to fit the arbitrary offset of the base line; see Figure 2.

\[
y = A \exp(-k_{oₜₜ}) + \text{constant}\]  

The values of kₒₜₜ are corrected for the C₂H + C₂H₂ contribution
taken from our own work¹⁰ by subtraction in eq 14. The resulting
k'ₓ values are plotted against their respective X concentrations,
and a linear least-squares fit is used to determine kₓ; see Figures 3 and 4. Errors in kₓ are calculated by
combining the accumulated uncertainties in the corrected decay
fits, which includes errors in kₒₜₜ, with the uncertainties in
temperature and in measuring the X concentration. The error
in kₓ is typically 15–25%.

Table 1 summarizes the measured rate coefficients for C₂H
with C₂H₄, C₂H₆, and H₂ from 150 to 359 K. The data for
C₂H with C₂H₄ and C₂H₆ are plotted in Figure 5 and indicate a
slight negative temperature dependence for kC₂H₄ and almost no
temperature dependence for kC₂H₆ over the temperature range
150–357 K. Both sets of data are fit to Arrhenius expressions
in which kC₂H₄ and kC₂H₆ are given by (7.8 ± 0.6) × 10⁻¹¹ exp[
(134 ± 44)/T] and (3.5 ± 0.3) × 10⁻¹¹ exp[(2.9 ± 16)/T] cm³
molecule⁻¹ s⁻¹, respectively. The rate coefficients for C₂H +
H₂ show a positive temperature dependence from 178 to 359 K

\[
m = \text{1000 cm}⁻¹ \text{ molecule}⁻¹ \text{s}⁻¹ \]

\[
T = \text{150 to 359 K} \]

\[
kC₂H₄ \text{ versus } [C₂H₄] \text{ at } 198 \text{ K. The rate coefficient}
kC₂H₄ \text{ is equal to (3.9 ± 0.6) × 10⁻¹¹ cm}³ \text{ molecule}⁻¹ \text{s}⁻¹,}
\]

which can be fit to the Arrhenius expression

\[
kC₂H₄ = (1.2 ± 0.3) \times 10⁻¹¹ \exp((-998 ± 57)/T) \text{ cm}³ \text{ molecule}⁻¹ \text{s}⁻¹; \]

\[
in Figure 6. In addition, no pressure dependence is found for the reactions
of C₂H with C₂H₄, C₂H₆, or H₂ over the experimental conditions
at 300 K.

Discussion

C₂H + C₂H₄ and C₂H₆. In the case of C₂H + C₂H₄, the
negative temperature dependence and lack of a pressure
dependence is attributed to a short-lived addition complex which
undergoes unimolecular dissociation to products before it can
be stabilized. The rate coefficient measured at 150 K is lower
than the one measured at 173 K, but the difficulty in measuring
kC₂H₄ at 150 K, due to the low C₂H₂ concentrations required,
degrades the transient absorption signal. One cannot say with
confidence that the measured rate coefficient at 150 K for C₂H+
C₂H₄ is significant, for example, representing a small barrier
to a C₂H₃ complex.

The rate coefficient kC₂H₆ exhibits no temperature dependence
from 153 to 357 K, comparable to that of kC₂H₆+C₂H₁ from 75 to
300 K, and no pressure dependence with varying helium
densities. Since the current experimental setup prevents reach-
Figure 4. Plot of $k_{\text{H}_2}$ versus $[\text{H}_2]$ at 355 K. The slope of this plot is equal to $(6.7 \pm 0.9) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

Figure 5. Arrhenius plot of $\text{C}_2\text{H}$ with $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$; ○, this work for $\text{C}_2\text{H}$ with $\text{C}_2\text{H}_4$; ●, this work for $\text{C}_2\text{H}$ with $\text{C}_2\text{H}_6$; ▲, Lander et al. for $\text{C}_2\text{H}$ with $\text{C}_2\text{H}_4$; □, Lander et al. for $\text{C}_2\text{H}$ with $\text{C}_2\text{H}_6$; ■, Laufer. The Arrhenius fit to $\text{C}_2\text{H}$ with $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$ is $(7.8 \pm 0.6) \times 10^{-11} \exp[(-134 \pm 44)/T]$ and $(3.5 \pm 0.3) \times 10^{-11} \exp[(2.9 \pm 16)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively.

Figure 6. Arrhenius plot of $\text{C}_2\text{H} + \text{H}_2$: ●, this work; ○, Farhat et al.; □, Koshi et al.; ■, Lange et al.; ▲, Laufer et al.; ∇, Renlund et al.; Δ, Okabe; ◊, Peeters et al.; ▽, Stephens et al.; ○, Herbst calculation. The solid line is the Arrhenius fit to this work and is equal to $(1.2 \pm 0.3) \times 10^{-11} \exp((-998 \pm 57)/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The dotted line is the non-Arrhenius fit to all the data points and is equal to $(9.2 \pm 10^{10})\exp(-478 \pm 165)/T$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The dash-dotted line is the ab initio calculation by Harding et al.

Table 1: Summary of Rate Coefficients of $\text{C}_2\text{H}$ with $\text{H}_2$, $\text{C}_2\text{H}_4$, and $\text{C}_2\text{H}_6$ from 150 to 359 K

<table>
<thead>
<tr>
<th>temp (K)</th>
<th>$k_{\text{C}_2\text{H}_4}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>temp (K)</th>
<th>$k_{\text{C}_2\text{H}_6}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>temp (K)</th>
<th>$k_{\text{H}_2}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>357</td>
<td>$(0.9 \pm 0.2) \times 10^{-10}$</td>
<td>357</td>
<td>$(3.2 \pm 0.5) \times 10^{-11}$</td>
<td>359</td>
<td>$(7.5 \pm 0.8) \times 10^{-13}$</td>
</tr>
<tr>
<td>357</td>
<td>$(1.2 \pm 0.2) \times 10^{-10}$</td>
<td>355</td>
<td>$(3.6 \pm 0.5) \times 10^{-11}$</td>
<td>355</td>
<td>$(6.7 \pm 0.9) \times 10^{-13}$</td>
</tr>
<tr>
<td>356</td>
<td>$(1.1 \pm 0.2) \times 10^{-10}$</td>
<td>355</td>
<td>$(3.5 \pm 0.5) \times 10^{-11}$</td>
<td>300</td>
<td>$(4.6 \pm 0.7) \times 10^{-13}$</td>
</tr>
<tr>
<td>298</td>
<td>$(1.4 \pm 0.2) \times 10^{-10}$</td>
<td>298</td>
<td>$(3.4 \pm 0.5) \times 10^{-11}$</td>
<td>228</td>
<td>$(2.1 \pm 0.4) \times 10^{-13}$</td>
</tr>
<tr>
<td>298</td>
<td>$(1.3 \pm 0.2) \times 10^{-10}$</td>
<td>298</td>
<td>$(3.9 \pm 0.6) \times 10^{-11}$</td>
<td>215</td>
<td>$(0.9 \pm 0.3) \times 10^{-13}$</td>
</tr>
<tr>
<td>298</td>
<td>$(1.1 \pm 0.2) \times 10^{-10}$</td>
<td>298</td>
<td>$(3.4 \pm 0.5) \times 10^{-11}$</td>
<td>213</td>
<td>$(1.1 \pm 0.2) \times 10^{-13}$</td>
</tr>
<tr>
<td>216</td>
<td>$(1.6 \pm 0.1) \times 10^{-10}$</td>
<td>198</td>
<td>$(3.5 \pm 0.6) \times 10^{-11}$</td>
<td>191</td>
<td>$(5.3 \pm 0.9) \times 10^{-14}$</td>
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<tr>
<td>197</td>
<td>$(1.5 \pm 0.2) \times 10^{-10}$</td>
<td>198</td>
<td>$(3.9 \pm 0.6) \times 10^{-11}$</td>
<td>178</td>
<td>$(5.0 \pm 1.1) \times 10^{-14}$</td>
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<tr>
<td>173</td>
<td>$(2.1 \pm 0.3) \times 10^{-10}$</td>
<td>180</td>
<td>$(3.3 \pm 0.4) \times 10^{-11}$</td>
<td>173</td>
<td>$(4.0 \pm 0.6) \times 10^{-11}$</td>
</tr>
<tr>
<td>150</td>
<td>$(1.4 \pm 1.0) \times 10^{-10}$</td>
<td>173</td>
<td>$(3.4 \pm 0.8) \times 10^{-11}$</td>
<td>163</td>
<td>$(3.4 \pm 0.8) \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>153</td>
<td>$(3.3 \pm 0.6) \times 10^{-11}$</td>
<td></td>
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</tr>
</tbody>
</table>

The addition complex. It is worth noting that Lander et al.\(^7\) did see a slight pressure dependence for reaction 2 at room temperature over the same helium number densities. There is no obvious explanation for why their pressure dependence result for reaction 2 contradicts our findings for the same reaction.

The reactions of the $\text{C}_2\text{H}$ radical with $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$ exhibit similar temperature and pressure dependencies as the CN radical does with $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$.\(^{24,25}\) Reactions of the CN radical have been studied down to temperatures reaching 25 K using a pulsed laser photolysis, time-resolved laser-induced fluorescence technique by Sims and co-workers.\(^{24}\) The reaction of CN + $\text{C}_2\text{H}_4$ is found to show a mild negative temperature dependence (see Figure 7). However, the rate coefficient shows a sharp decrease from 44 to 25 K. The Arrhenius plot for the reaction of CN + $\text{C}_2\text{H}_4$ in Figure 7 shows that the measured value of $k_{\text{CN} + \text{C}_2\text{H}_4}$ at 25 K is less than $k_{\text{CN} + \text{C}_2\text{H}_6}$ at 44 K. Sims et al. indicated that this could signal a small potential barrier along the path leading to $\text{CH}_2\text{CH}_2\text{CN}$ formation. This reaction also exhibits no dependence on total pressure. Sims et al. rationalized their observations by stating that the reaction proceeds through an addition—elimination mechanism, resulting in an exothermic displacement of an H atom by the CN radical.

The rate coefficient $k_{\text{CN} + \text{C}_2\text{H}_6}$ for CN + $\text{C}_2\text{H}_6$ displays a pronounced curvature in its Arrhenius plot; see Figure 7. From...
Compared to ethene, ethane does not possess the \( \pi \) electrons the radical's attraction to the electron-rich double bond in \( \text{C}_2\text{H}_4 \). Temperature decreases. The factor of 3-4 difference between inherent that the measured rate coefficients at room temperature gesting that the rate-determining abstraction by the ethynyl radical. Since the mechanism involves reactions, and \( \text{C}_2\text{H}_4^- \) in these reactions, there is little or no barrier to form the addition favorability orientation for a reaction to occur.

In addition to comparing reactions 1 and 2 to their CN counterparts, it is beneficial to relate them to other \( \text{C}_2\text{H} \) reactions. Table 2 lists several rate coefficients at room temperature of the \( \text{C}_2\text{H} \) reactions with hydrocarbons and \( \text{H}_2 \) and various thermodynamic properties. All of these reactions are very exothermic, but their rate coefficients vary by 3 orders of magnitude from \( \text{C}_2\text{H} + \text{C}_2\text{H}_2 \) to \( \text{C}_2\text{H} + \text{H}_2 \). Interestingly, of the five reactions listed in Table 2, the fastest are those with the largest \( \text{C} - \text{H} \) bond dissociation energies: \( \text{C}_2\text{H} \) with \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_4 \). Since the measured energy of activation is negative in these reactions, there is little or no barrier to form the addition complex. Therefore, the rate-determining step in each of these reactions, and \( \text{C}_2\text{H} + \text{C}_2\text{H}_6 \), is most likely the formation of the addition complex. The last two reactions listed in Table 2, \( \text{C}_2\text{H} \) with \( \text{CH}_2 \) and \( \text{H}_2 \), have a positive energy of activation, suggesting that the rate-determining step is the direct \( \text{H} \) atom abstraction by the ethynyl radical. Since the mechanism involves a direct abstraction rather than one of complex formation, it is inherent that the measured rate coefficients at room temperature are the slowest of the five and decrease sharply as the temperature decreases. The factor of 3-4 difference between \( k_{\text{C}_2\text{H}_4} \) and \( k_{\text{C}_2\text{H}_6} \) at room temperature can possibly be traced to the radical's attraction to the electron-rich double bond in \( \text{C}_2\text{H}_4 \). Compared to ethene, ethane does not possess the \( \pi \) electrons for \( \text{C}_2\text{H} \) to attack. In order to form a complex with \( \text{C}_2\text{H}_4 \), the \( \text{C}_2\text{H} \) must attack either the \( \text{C} - \text{H} \) or \( \text{C} - \text{C} \sigma \) electrons. If the \( \text{C}_2\text{H} \) radical were to attack the \( \text{C} - \text{C} \) bond in \( \text{C}_2\text{H}_6 \), the two methyl groups would provide some steric hindrance which could accounting for \( k_{\text{C}_2\text{H}_4} > k_{\text{C}_2\text{H}_6} \) at room temperature. The same argument can be stated for \( k_{\text{C}_2\text{H}_4} \) in the reaction of \( \text{C}_2\text{H} + \text{C}_2\text{H}_2 \). The \( \pi \) electrons in acetylene are exposed for the \( \text{C}_2\text{H} \) radical to capture, and the room temperature rate coefficient \( k_{\text{C}_2\text{H}_4} \) is an order of magnitude faster than \( k_{\text{C}_2\text{H}_6} \).

\( \text{C}_2\text{H} + \text{H}_2 \). A summary of all the current rate coefficients measured for \( \text{C}_2\text{H} + \text{H}_2 \) is given in Table 3. The data for \( \text{C}_2\text{H} + \text{H}_2 \) from 178 to 359 K can be fit to an Arrhenius plot of \( k_{\text{H}_2} = (1.2 \pm 0.3) \times 10^{-11} \exp(-998 \pm 57/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \) represented by the solid line in Figure 6. Upon closer examination of the combined data from Farhat et al., Koshi et al., and this work, a slight curvature is observed from 178 to 854 K. The combined data are best fit to a non-Arrhenius form of \( k_{\text{H}_2} = 9.2 \times 10^{-18} \exp(-478 \pm 165/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \), represented by the dashed line in Figure 6. The question as to whether or not the curvature in Figure 6 is real or simply due to experimental error must be addressed.

Farhat et al. did a similar set of experiments as described in this work over a temperature range 295-854 K. The ethynyl radical was produced by acetylene photolysis at 193 nm and detected in absorption with a color center laser. Their data can be fit to an Arrhenius expression of the form \( k_{\text{H}_2} = 6.9 \times 10^{-11} \exp[-1480/T] \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \), but they chose to fit their data to a non-Arrhenius expression of the form \( k_{\text{H}_2} = (9.44 \pm 0.24) \times 10^{-14} \exp(-1003 \pm 20/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \). The room temperature values of \( k_{\text{H}_2} \) for this work and Farhat et al. calculated from the fits shown in Table 3 agree within experimental error.

Koshi et al., using laser photolysis time-resolved mass spectrometry, measured \( k_{\text{H}_2} \) over the temperature range 298-438 K and found an Arrhenius dependence of \( k_{\text{H}_2} = (1.8 \pm 1.0) \times 10^{-11} \exp(-1090 \pm 299/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \). In their experiment, the concentration of \( \text{C}_2\text{H}_2 \) is monitored and first used to measure the rate coefficients of \( \text{C}_2\text{H} + \text{C}_2\text{H}_2 \). When \( \text{H}_2 \) is added to the gas flow, the concentration of \( \text{C}_2\text{H}_2 \) decreases due to reaction 1. The ratio of \( k_{\text{C}_2\text{H}_2}/k_{\text{H}_2} \), is measured based on the \( \text{C}_2\text{H}_2 \) concentration and reported in their work. The room temperature value of \( k_{\text{H}_2} \) in the work by Koshi et al., \((5.1 \pm 2.0) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \), agrees within error with the averaged measured value from this work and Farhat et al., which are \((4.6 \pm 0.8) \times 10^{-13} \) and \((4.7 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \), respectively. Due to the differences in the methods, the curvature in Figure 6 should be regarded with some caution; nevertheless, in the discussion that follows we consider some possible sources of the curvature.

The latest high temperature work was done by Peeters et al. using laser photodissociation/chemiluminescence. Ethynyl radicals were generated from \( \text{C}_2\text{H}_2 \) or \( \text{C}_2\text{H}_2\text{F}_2 \) photodissociation by 193 nm light from an excimer. The pseudo-first-order decay of \( \text{C}_2\text{H} \) was monitored by depletion of the chemiluminescence of \( \text{CH}(A^2\Delta) \) produced by the radical reaction with \( \text{O}_2 \). They measured \( k_{\text{H}_2} \) from 295 to 440 K and fit their data to the expression \( k_{\text{H}_2} = 1.31 \times 10^{-17} \exp(-174/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \). In conjunction with measurements taken by Koshi et al. and Farhat et al., the measurements made by Peeters et al. for reaction 3 follow the trend of \( k_{\text{H}_2} \) increasing with temperature; see Figure 6.

When analyzing reaction 3, it is again useful to consult a similar reaction such as

\[
\text{CN} + \text{H}_2 \rightarrow \text{H} + \text{HCN}
\] (16)

Although CN is a diatomic radical, it is isoelectronic with \( \text{C}_2\text{H} \), and the measured rate coefficients with \( \text{C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{O}_2, \)
The difference in internal energy between products and reactants for the vinyl acetylene isomer.

**TABLE 3: Summary of Rate Coefficients for C2H + H2**

<table>
<thead>
<tr>
<th>Reference</th>
<th>kH2 (cm³ molecule⁻¹ s⁻¹)</th>
<th>Temp (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>(1.2 ± 0.3) x 10⁻¹⁰</td>
<td>178-359</td>
</tr>
<tr>
<td>Farhat et al.¹¹</td>
<td>(9.4 ± 0.24) x 10⁻¹⁰ exp[(-998 ± 57)/T]</td>
<td>295-854</td>
</tr>
<tr>
<td>Koshi et al.¹²</td>
<td>(1.8 ± 1.0) x 10⁻¹¹ exp[(-1003 ± 20)/T]</td>
<td>298-438</td>
</tr>
<tr>
<td>Lange and Wagner¹³</td>
<td>(1.7 ± 1.0) x 10⁻⁵</td>
<td>320</td>
</tr>
<tr>
<td>Laufer and Bass¹⁴</td>
<td>(1.5 ± 1.0) x 10⁻⁵</td>
<td>298</td>
</tr>
<tr>
<td>Renlund et al.¹⁵</td>
<td>(1.2 ± 0.3) x 10⁻⁵</td>
<td>298</td>
</tr>
<tr>
<td>Okabe¹⁶</td>
<td>(9.7 ± 1.0) x 10⁻⁶</td>
<td>298</td>
</tr>
<tr>
<td>Stephens et al.¹⁷</td>
<td>(4.8 ± 0.3) x 10⁻⁵</td>
<td>293-450</td>
</tr>
<tr>
<td>Peeters et al.¹⁹</td>
<td>1.31 x 10⁻⁷ exp(-174/T)</td>
<td>295-440</td>
</tr>
</tbody>
</table>

- Recalculated using the measured ratio and the present-day C2H + C2H rate constant of (1.3 ± 0.2) x 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹.

**TABLE 4: Reactions Involving H Atom Abstractions**

<table>
<thead>
<tr>
<th>reaction</th>
<th>V (kJ mol⁻¹)</th>
<th>ΔE (kJ mol⁻¹)</th>
<th>v² (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O[π]H + H₂</td>
<td>52.3</td>
<td>12.1</td>
<td>736, 736</td>
</tr>
<tr>
<td>CH₃ + H</td>
<td>56.4</td>
<td>10.8</td>
<td>592, 592</td>
</tr>
<tr>
<td>CH₃ + H</td>
<td>44.7</td>
<td>-10.8</td>
<td>592, 592</td>
</tr>
<tr>
<td>H + H₂CO</td>
<td>20.5</td>
<td>39.4</td>
<td>325, 590</td>
</tr>
<tr>
<td>OH + H₂</td>
<td>25.9</td>
<td>-67.3</td>
<td>440, 686</td>
</tr>
<tr>
<td>CN + H₆</td>
<td>17.1</td>
<td>-105.8</td>
<td>165, 165</td>
</tr>
<tr>
<td>C₂H₆ + H</td>
<td>9.6</td>
<td>-129.7</td>
<td>139, 139</td>
</tr>
</tbody>
</table>

- Table 4 is taken from ref 27. ³V Classical barrier at the saddle point. ³ΔE The difference in internal energy between products and reactants. ³v² The two lowest bending frequencies at the saddle point. ³V² and ΔE, taken from Wagner and Bair, do not include zero-point corrections.

and CH₂ show similar temperature dependencies as their C₂H counterparts. Reaction 16 has been studied by several groups over the combined temperature range 209-1000 K.²⁶-²⁹ The measured rate coefficients of reaction 16 exhibit a positive temperature dependence in addition to a mild curvature in the Arrhenius plot. One study, by Sims and Smith, gives the modified Arrhenius fit to reaction 16 CN(ν=0) as (2.4 ± 0.7) x 10⁻¹² (77298) exp[(-1340 ± 90)/T] cm³ molecule⁻¹ s⁻¹ from 295 to 768 K.²⁶ A theoretical study by Wagner and Bair²⁷ has shown that the H₂CN³⁻ transition state closely resembles the separated reactants, which is consistent with Hammond's postulate for exothermic reactions.²⁹ The H–H bond distance is increased only by 0.07 Å at the saddle point, and the C–N bond distance remains constant. Both Sims and Smith and Wagner and Bair have concluded that the curvature in the Arrhenius plot for reaction 16 is due to the temperature dependence of the partition function associated with the doubly degenerate low-frequency bending mode in the H₂CN³⁻ transition state.

Wagner and Bair also compare their results for CN + H₂ to those of other H atom abstraction reactions; see Table 4. The first three reactions in Table 4 are close to thermoneutral and have barriers exceeding 40 kJ mol⁻¹ and possess bending degrees of freedom with vibrations greater than 500 cm⁻¹. The rate coefficients for these reactions exhibit a steep positive temperature dependence, but vary little from Arrhenius form.

The middle two reactions display noticeable curvature in their Arrhenius plots and have at least one bending frequency below 500 cm⁻¹. The final two reactions, C₂H + H₂ and CN + H₂, have the lowest barriers, V², and the lowest bending frequencies in the group. Their rate coefficients show substantial curvature in their respective Arrhenius plots.

Both Harding et al.²⁷ and Herbst²⁴ have performed theoretical calculations on the reaction C₂H + H₂. Harding from 300 to >2000 K and Herbst from 10 to 300 K; see Figures 6 and 8. Harding and co-workers calculate that reaction 3 has an early saddle point with the H₂–H₂ bond distance in the H₂–H₂– C–C–H⁻¹ transition state only 6% larger than in the H₂ reactant and the H₂–C–H⁻¹ bond 52% greater than in the C₂H₂ product. This calculation also confirms Hammond's postulate that more exothermic reactions have reactant-like transition states. The fit by Harding et al., including Wigner tunneling corrections, is for a barrier height of 9.6 kJ mol⁻¹ and shows significant curvature. Harding and co-workers performed this calculation at different barrier heights, V². When the barrier is decreased, their calculated rate coefficients increase with respect to the Arrhenius plot in Figure 6, and the fit shows more curvature. Conversely, when the barrier is increased, the rate coefficients decrease with respect to their Arrhenius plot in Figure 6, and the fit shows less curvature. Although the calculated rate coefficients are lower than the values measured here and those by Farhat et al.²⁷ and Koshi et al.,²⁷ the general trend of kH₂ and curvature is followed.

Herbst, using statistical phase space theory and the vibrational frequencies and rotational constants from Harding et al.,²⁷ calculated rate coefficients from 300 to 10 K for reaction 3. At room temperature, Herbst reports that the tunneling contribution to kH₂ is ~40%, and then kH₂ starts to decrease as the temperature is lowered. The rate coefficients for kH₂ decrease to a minimum value at ~40 K of approximately 1.2 x 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹. Afterward, kH₂ increases to a value of 2.2 x 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ at 10 K; see Figure 8. For clarity, only four of his calculated points are shown in Figure 6 due to the range of "1/T space" the calculation spans. Herbst claims that the increase in kH₂ is due to a decrease in the density of reactant states which control the dissociation rate instead of an increase in the tunneling rate. However, Herbst is quick to note that his model is highly sensitive to several undefined parameters such as the transition state barrier, V², and the imaginary frequency of vibration, v⁴. A "slight" decrease in the transition state barrier increases kH₂ by an order of magnitude at 10 K. A change in the transition state frequency by ±200 cm⁻¹ results in kH₂, fluctuating in both directions by an order of magnitude.

In light of the stated results in the previous paragraphs, one can make some clarifications on the curvature in the combined experimental data of Farhat et al., Koshi et al., and this work. Despite the larger scatter of points in this data below room temperature, the curvature of the modified Arrhenius fit to kH₂ from 178 to 854 K appears to be real. Arguments as to what is causing it can be traced partly to the CN + H₂ studies by Sims et al. and Wagner et al. Both groups made it clear that
the curvature in the Arrhenius plot of CN + H₂ is due to the temperature dependence of the partition function associated with the doubly degenerate low-frequency bending mode in the H₂C₃N⁺ transition state. Pronounced curvature in Arrhenius plots is displayed by H atom abstraction reactions in Table 4 that are highly exothermic, have low barriers, and have low bending frequencies in the transition state. The reaction of C₂H + H₂ must likely follows this trend. Therefore, at least part of the curvature in the experimental data from 178 to 854 K can be attributed to the temperature dependence of the partition function linked to the low-frequency bending mode in the H₂C₃H⁺ transition state.

However, one cannot conclusively state whether the curvature in the Arrhenius plot of C₂H + H₂ is due solely to either tunneling or to the partition function associated the low-frequency bending mode in the H₂C₂H⁺ transition state. Advanced theories will also contribute to the curvature in the Arrhenius plot of C₂H + H₂.

One cannot conclusively state whether the curvature in the Arrhenius plot of C₂H + H₂ is due solely to either tunneling or to the partition function associated the low-frequency bending mode in the H₂C₂H⁺ transition state. Advanced theories will need to take into account both explanations.

Conclusion

The rate coefficients of C₂H with C₂H₄, C₂H₆, and H₂ have been measured from 150 to 359 K. The reaction of C₂H + C₂H₄ displays a mild negative temperature dependence similar to that of CN + C₂H₄ which is characteristic of an addition–elimination mechanism. The C₂H data are fit to an Arrhenius expression equal to (7.8 ± 0.6) × 10⁻¹¹ exp[(134 ± 44)/T] cm³ molecule⁻¹ s⁻¹. Likewise, the reaction mechanism of C₂H + C₂H₂ also consists of an addition–elimination step. Within the calculated error bars, the rate coefficients of reaction 3 display no temperature dependence from 153 to 357 K. The Arrhenius fit for this reaction is equal to (3.5 ± 0.3) × 10⁻¹¹ exp[(2.9 ± 16)/T] cm³ molecule⁻¹ s⁻¹.

The Arrhenius fit to the data for C₂H and H₂ can be expressed as \( k_{11} = (1.2 ± 0.3) \times 10^{-11} \exp\left(-998 ± 57/T\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). The positive temperature dependence is consistent with reactions involving a hydrogen abstraction as the rate-determining step and a positive energy of activation \( E_a = 8.3 ± 0.5 \text{ kJ mol}^{-1} \) for C₂H + H₂. The curvature in the Arrhenius plot of C₂H + H₂ can be attributed to a combination of H atom tunneling and a temperature dependence in the partition function associated with the low-frequency bending mode in the H₂C₂H⁺ transition state.

Acknowledgment. We gratefully acknowledge the National Aeronautics and Space Administration for support of this research and the Department of Energy for additional support.

References and Notes


Figure 8. Arrhenius plot of C₂H + H₂ using calculated rate coefficients by Herbst: •, calculation with tunneling corrections; □, calculation without tunneling corrections.