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 C$_2$H with C$_2$H$_4$, C$_2$H$_6$, and H$_2$ from 150 to 359 K

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Rate coefficients for the reactions C$_2$H with C$_2$H$_4$, C$_2$H$_6$, and H$_2$ are measured over the temperature range 150–359 K using transient infrared laser absorption spectroscopy. The ethynyl radical is formed by photolysis of C$_2$H$_2$ with a pulsed excimer laser at 193 nm, and its transient absorption is monitored with a color center laser on the Q$_{11}(9)$ line of the A$^2\Pi-X^2\Sigma$ transition at 3593.68 cm$^{-1}$. Over the experimental temperature range 150–359 K the rate constants of C$_2$H with C$_2$H$_4$, C$_2$H$_6$, and H$_2$ can be fit to the Arrhenius expressions $k_{C_2H_4} = (7.8 \pm 0.6) \times 10^{-11} \exp[(134 \pm 44)/T]$, $k_{C_2H_6} = (3.5 \pm 0.3) \times 10^{-11} \exp[(2.9 \pm 16)/T]$, and $k_{H_2} = (1.2 \pm 0.3) \times 10^{-11} \exp[(-998 \pm 57)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. The data for C$_2$H with C$_2$H$_4$ and C$_2$H$_6$ indicate a negligible activation energy to product formation shown by the mild negative temperature dependence of both reactions. When the H$_2$ data are plotted together with the most recent high-temperature results from 295 to 854 K, a slight curvature is observed. The H$_2$ data can be fit to the non-Arrhenius form $k_{H_2} = 9.2 \times 10^{-12} T^{1.72 \pm 0.59} \exp[(-478 \pm 165)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The curvature in the Arrhenius plot is discussed in terms of both quantum mechanical tunneling of the H atom from H$_2$ to the C$_2$H radical and bending mode contributions to the partition function.

Introduction

The ethynyl radical, C$_2$H, is of fundamental importance in combustion chemistry and in planetary atmospheres.$^{1-3}$ 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).$^2$ To understand the importance of various ethynyl reactions in the two drastically different environments, it is desirable to know the rate coefficients for C$_2$H with such species as C$_2$H$_4$, C$_2$H$_6$, and H$_2$ 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

$\text{C}_2\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{products}$  \hspace{1cm} (1)

$\text{C}_2\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{C}_2\text{H}_2$  \hspace{1cm} (2)

$\text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}$  \hspace{1cm} (3)

using transient infrared laser absorption spectroscopy.

The exothermicity of reaction 1 is such that there are two different thermodynamically accessible product channels available.$^3-^5$

$\text{C}_2\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_4 + \text{H}$  \hspace{1cm} $\Delta H = -95.4 \text{ kJ mol}^{-1}$  \hspace{1cm} (1a)

$\rightarrow \text{C}_2\text{H}_3 + \text{C}_2\text{H}_2$  \hspace{1cm} $\Delta H = -90.4 \text{ kJ mol}^{-1}$  \hspace{1cm} (1b)

The C$_4$H$_4$ species in reaction 1a is the vinyl acetylene isomer. Reaction 1b is a possible source of vinyl radicals, C$_2$H$_3$, in Titan’s atmosphere. It has been proposed by Yung et al.$^2$ that vinyl radicals can undergo a disproportionation reaction to form acetylene and ethylene, scavenge a hydrogen atom, or act as a source of C$_3$ compounds:

$2\text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4$  \hspace{1cm} (4)

$\text{C}_2\text{H}_3 + \text{H} \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$  \hspace{1cm} (5)

$\text{C}_2\text{H}_3 + \text{CH}_3 + \text{M} \rightarrow \text{C}_2\text{H}_5 + \text{M}$  \hspace{1cm} (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 (C$_2$H$_2$, CH$_4$, C$_2$H$_6$, and C$_2$H$_4$ 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 C$_2$H + C$_2$H$_6$ leads to the production of ethyl radicals, C$_2$H$_5$, which opens pathways for the production of propane, C$_3$H$_8$, in Titan’s atmosphere via the following scheme.$^7$:

$2(\text{C}_2\text{H}_2 + \text{hv} \rightarrow \text{C}_2\text{H} + \text{H})$  \hspace{1cm} (7)

$\text{C}_2\text{H} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3$  \hspace{1cm} (8)

$\text{C}_2\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_5$  \hspace{1cm} (2)

$\text{CH}_3 + \text{C}_2\text{H}_5 + \text{M} \rightarrow \text{C}_3\text{H}_8 + \text{M}$  \hspace{1cm} (9)

net: CH$_3$ + C$_2$H$_6$ → C$_3$H$_8$ + 2H  \hspace{1cm} (10)

In addition, a pressure-dependent study by Lander et al.$^7$ indicated a slight increase in $k_{\text{C}_2\text{H}_4}$ (C$_2$H + C$_2$H$_6$) 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 C$_2$H + H$_2$ is very slow and difficult to measure accurately, scientists interested in modeling planetary atmospheres have had to rely...
in the inner jacket, the gases flow across the photolysis region setup. The cell consists of an inner zone and an outer volume. was run at 55 mJ/pulse at 10 Hz. The absorption cell is variable flow cell at 193 nm by a pulsed excimer laser which by this group so only a brief outline will be given here. 1°,2° The details of this setup have been described in numerous papers. A schematic of the experimental setup is shown in Figure 1.

Experimental

rate coefficients of C₂H with C₂H₄, C₂H₆, and H₂ 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 x 10^{20} 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 C₂H concentration was estimated to be no greater than 7.5 x 10^{10} cm⁻³ for the highest acetylene pressures. (The acetylene number density ranges from 1.3 x 10^{14} to 4.8 x 10^{14} cm⁻³.) This estimation is based on using 1.35 x 10^{19} cm⁻³ for the absorption cross section at 193 nm and 0.26 for the quantum yield for C₂H production. 2° A 1500–6000-fold excess of C₂H₄, C₂H₆, or H₂ with respect to C₂H is always present in these experiments. Contributions from radical–radical or secondary reactions can be neglected since the time between collisions for C₂H and C₂H₄, C₂H₆, or H₂ is 1000 times shorter than the time between collisions of two C₂H radicals. Rate coefficients are measured at various ethene/ethane densities of (0.2–5.2) x 10^{15} cm⁻³ and hydrogen densities of (0.6–9.0) x 10^{17} cm⁻³. The helium density is varied over the range (0.5–2.7) x 10^{18} cm⁻³ to test for a pressure dependence in the rate coefficients of C₂H with C₂H₄, C₂H₆, or H₂.

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 C₂H₂ concentrations required to keep k_{CH}[C₂H₂] contributions below 40%). In experiments performed above room temperature, heated water was circulated around the inner cell.

The C₂H radical is probed in absorption by a high-resolution color center laser tuned to the Q₁₁(9) line at 3593.68 cm⁻¹ of the A²Π–XΣ transition. 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 wavenumber 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 mm² 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%; C₂H₄, 99.6%; H₂, 99.9999%. The acetone is

Experimental Section

The rate coefficients for C₂H with C₂H₄, C₂H₆, and H₂ 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. 10,2° 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
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 thermocouple 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 \( \text{C}_2\text{H}(X^2\Sigma^+(0,0,0)) \). In addition, it is necessary that the upper states of \( \text{C}_2\text{H} \) are fully quenched before the reaction of \( \text{C}_2\text{H}(X^2\Sigma^+(0,0,0)) \) with \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \) and \( \text{H}_2 \) occurs. Previous experiments by Lander et al.\(^7\) and Farhat et al.\(^11\) performed under similar conditions, have shown that relaxation of the \( \text{C}_2\text{H}(X(0,0,1)) \) state occurs in approximately 1 \( \mu \)s. In this study, as well as in theirs, the reaction of \( \text{C}_2\text{H}(X^2\Sigma^+(0,0,0)) \) with \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \) and \( \text{H}_2 \) 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 \( \text{C}_2\text{H} \), the fits only include data for \( t > 3 \tau_{\text{rise}} \).

The rate coefficients measured in this study are done under pseudo-first-order conditions in which [X] (where \( X = \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \) or \( \text{H}_2 \)) and \([\text{C}_2\text{H}_2] \gg [\text{C}_2\text{H}] \). The rate of change of \([\text{C}_2\text{H}] \) can be expressed as

\[
d([\text{C}_2\text{H}])/dt = -[\text{C}_2\text{H}](k_X[X] + k_{\text{C}_2\text{H}_2}[\text{C}_2\text{H}_2])
\]

After integration, this yields

\[
[C_2H] = [C_2H]_0 \exp(-k_{\text{obs}}t)
\]

where

\[
k_{\text{obs}} = k_X[X] + k_{\text{C}_2\text{H}_2}[\text{C}_2\text{H}_2]
\]

and

\[
k_X[X] = k_{\text{C}_2\text{H}_2}[\text{C}_2\text{H}_2] = k_X[X] = k'_X
\]

The observed decay rates, \( k_{\text{obs}} \), 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.

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

The values of \( k_{\text{obs}} \) are corrected for the \( \text{C}_2\text{H} + \text{C}_2\text{H}_2 \) contribution taken from our own work\(^10\) 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 \( k'_X \); see Figures 3 and 4. Errors in \( k'_X \) are calculated by combining the accumulated uncertainties in the corrected decay fits, which includes errors in \( k_{\text{C}_2\text{H}_2} \), with the uncertainties in temperature and in measuring the X concentration. The error in \( k'_X \) is typically 15–25%.

Table 1 summarizes the measured rate coefficients for \( \text{C}_2\text{H} \) with \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \) and \( \text{H}_2 \) from 150 to 359 K. The data for \( \text{C}_2\text{H} \) with \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \) are plotted in Figure 5 and indicate a slight negative temperature dependence for \( k_{\text{C}_2\text{H}_4} \) and almost no temperature dependence for \( k_{\text{C}_2\text{H}_6} \) over the temperature range 150–357 K. Both sets of data are fit to Arrhenius expressions in which \( k_{\text{C}_2\text{H}_4} \) and \( k_{\text{C}_2\text{H}_6} \) are given by \((7.8 \pm 0.6) \times 10^{-11} \exp\left[(134 \pm 44)/T\right] \) and \((3.5 \pm 0.3) \times 10^{-11} \exp\left[(2.9 \pm 16)/T\right] \) \( \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \), respectively. The rate coefficients for \( \text{C}_2\text{H} + \text{H}_2 \) show a positive temperature dependence from 178 to 359 K.

![Figure 2](image-url) C\(_2\)H decay and fit due to reaction with C\(_2\)H\(_4\) (upper curve). The lower plot is the residuals to the single-exponential decay.

![Figure 3](image-url) Plot of \( k'_{\text{C}_2\text{H}_4} \) versus [\( \text{C}_2\text{H}_4 \)] at 198 K. The rate coefficient \( k_{\text{C}_2\text{H}_4} \) is equal to \((3.9 \pm 0.6) \times 10^{-11} \) \( \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \), which can be fit to the Arrhenius expression \( k_{\text{C}_2\text{H}_4} = (1.2 \pm 0.3) \times 10^{-11} \exp\left[-(998 \pm 57)/T\right] \) \( \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \); see Figure 6. In addition, no pressure dependence is found for the reactions of \( \text{C}_2\text{H} \) with \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \) or \( \text{H}_2 \) over the experimental conditions at 300 K.

Discussion

\( \text{C}_2\text{H} + \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \). In the case of \( \text{C}_2\text{H} + \text{C}_2\text{H}_4 \), 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 \( k_{\text{C}_2\text{H}_4} \) at 150 K, due to the low \( \text{C}_2\text{H}_2 \) concentrations required, degrades the transient absorption signal. One cannot say with confidence that the measured rate coefficient at 150 K for \( \text{C}_2\text{H} + \text{C}_2\text{H}_4 \) is significant, for example, representing a small barrier to a \( \text{C}_2\text{H}_4 \) complex.

The rate coefficient \( k_{\text{C}_2\text{H}_4} \) exhibits no temperature dependence from 153 to 357 K, comparable to that of \( k_{\text{CN} + \text{C}_2\text{H}_4} \) from 75 to 300 K,\(^24\) and no pressure dependence with varying helium densities. Since the current experimental setup prevents reach-
temperatures lower than \(213 \text{ K} \) is less than \(215 \text{ K} \). For reaction \(2 \) at room temperature does not have a slight pressure dependence at \(25 \text{ K} \) is less than \(355 \text{ K} \) and \(357 \text{ K} \) is found to show a mild negative temperature dependence (see Figure 7). The reaction of \( \text{CN} + \text{C}_2\text{H}_4 \) is found to show a milw negative temperature dependence (see Figure 7). However, the rate coefficient shows a sharp decrease 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 \( \text{C}_2\text{H}_3 \) radical with \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \) exhibit similar temperature and pressure dependencies as the \( \text{CN} \) radical does with \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \) 24,25. Reactions of the \( \text{CN} \) radical have been studied down to temperatures reaching \(25 \text{ K} \) using a pulsed laser photolysis, time-resolved laser-induced fluorescence technique by Sims and co-workers. 26 The reaction of \( \text{CN} + \text{C}_2\text{H}_4 \) was shown to have 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 \( \text{CN} + \text{C}_2\text{H}_4 \) in Figure 7 shows that the measured value of \( k_{\text{CN} + \text{C}_2\text{H}_4} \) at \(25 \text{ K} \) is less than \( k_{\text{CN} + \text{C}_2\text{H}_4} \) at \(44 \text{ K} \). Sims et al. indicated that this could result in a small potential barrier along the path leading to \( \text{C}_2\text{H}_2\text{CN} \) 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 \( \text{CN} \) radical.

The rate coefficient \( k_{\text{CN} + \text{C}_2\text{H}_6} \) for \( \text{CN} + \text{C}_2\text{H}_6 \) displays a pronounced curvature in its Arrhenius plot; see Figure 7.

**Figure 4.** Plot of \( k'_{\text{H}_2} \) versus [\( \text{H}_2 \)] at \(355 \text{ K} \). The slope of this plot is equal to \( (6.7 \pm 0.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

**Figure 5.** Arrhenius plot of \( \text{C}_2\text{H} \) with \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \): \( \bullet \), this work for \( \text{C}_2\text{H} + \text{C}_2\text{H}_4 \); \( \bigcirc \), Lander et al. for \( \text{C}_2\text{H} + \text{C}_2\text{H}_4 \); \( \bigtriangleup \), Lander et al. for \( \text{C}_2\text{H} + \text{C}_2\text{H}_6 \); \( \blacktriangle \), 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 \( (7.8 \pm 0.6) \times 10^{-11} \exp\left[(134 \pm 44)/T\right] \) and \( (3.5 \pm 0.3) \times 10^{-11} \exp\left[(2.9 \pm 16)/T\right] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), respectively.

**Figure 6.** Arrhenius plot of \( \text{C}_2\text{H} + \text{H}_2 \): \( \bullet \), this work; \( \bigcirc \), Farhat et al.; \( \bigtriangleup \), Koshi et al.; \( \blacktriangle \), Lange et al.; \( \blacklozenge \), Laufer et al.; \( \bigtriangledown \), Renlund et al.; \( \bigtriangledown \), Okabe; \( \blacklozenge \), Peeters et al.; \( \bigtriangledown \), Stephens et al.; \( \bigcirc \), Herbst calculation. The solid line is the Arrhenius fit to this work and is equal to \( (1.2 \pm 0.3) \times 10^{-11} \exp\left[(-998 \pm 57)/T\right] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). The dotted line is the non-Arrhenius fit to all the data points and is equal to \( 9.2 \times 10^{-11} \exp\left[(-998 \pm 57)/T\right] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

**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>
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<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>
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<td>( (3.6 \pm 0.5) \times 10^{-11} )</td>
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<td>355</td>
<td>( (3.5 \pm 0.5) \times 10^{-11} )</td>
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<td>( (3.3 \pm 0.6) \times 10^{-11} )</td>
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C₂H must attack either the C-H or C-C bond. Compared to ethene, ethane does not possess the π electrons in its radical’s attraction to the electron-rich double bond in C₂H₄.

Various thermodynamic properties. All of these reactions are measured for C2H + H₂. The energy of activation is negative for reaction 1. The ratio of k₁/C₂H₂ is measured based on the C₂H₂ concentration and reported in their work. The room temperature value of k₁, 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 k₁ = 6.9 × 10⁻¹¹ exp[-1480/T] cm³ molecule⁻¹ s⁻¹, but they chose to fit their data to a non-Arrhenius expression of the form k₁ = (9.44 ± 0.24) × 10⁻¹⁴ exp[-1003/20T] cm³ molecule⁻¹ s⁻¹.

The room temperature values of k₁ 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 k₁ over the temperature range 298–438 K and found an Arrhenius dependence of k₁ = (1.8 ± 1.0) × 10⁻¹¹ exp[-1090 ± 299/T] cm³ molecule⁻¹ s⁻¹. In their experiment, the concentration of C₂H₂ is monitored and first used to measure the rate coefficients of C₂H + C₂H₂. When H₂ is added to the gas flow, the concentration of C₂H₂ decreases due to reaction 1. The ratio of k₁/C₂H₂ is measured based on the C₂H₂ concentration and reported in their work. The room temperature value of k₁, represented by the solid line in Figure 6, is (5.1 ± 2.0) × 10⁻¹³ cm³ molecule⁻¹ s⁻¹. Agrees within error with the averaged measured value from this work and Farhat et al., which are (4.6 ± 0.8) × 10⁻¹³ and (4.7 ± 0.5) × 10⁻¹³ cm³ molecule⁻¹ 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 C₂H₃ or C₂HCF₃ photodissociation by 193 nm light from an excimer. The pseudo-first-order decay of C₂H was monitored by depletion of the chemiluminescence of CH₆(A²Σ) produced by the radical reaction with O₂. They measured k₁ from 295 to 440 K and fit their data to the expression k₁ = 1.31 × 10⁻¹⁴ exp[-174/T] cm³ molecule⁻¹ 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 k₁ increasing with temperature; see Figure 6.

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

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

Although CN is a diatomic radical, it is isoelectronic with C₂H, and the measured rate coefficients with C₂H₂, C₂H₄, C₂H₆, O₂, C₂Hple,
TABLE 2: Comparison of Various C₂H Reactions

<table>
<thead>
<tr>
<th>reaction</th>
<th>ΔH</th>
<th>E_a</th>
<th>D∞</th>
<th>k^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H + C₂H₂ → C₂H₂ + H</td>
<td>-102</td>
<td>-0.7 ± 0.1</td>
<td>H₂C⁻⁻H 549.3</td>
<td>(1.3 ± 0.2) x 10⁻¹⁰</td>
</tr>
<tr>
<td>C₂H + C₂H₆ → products</td>
<td>f</td>
<td>-1.1 ± 0.4</td>
<td>H₂C⁻⁻H 465.2</td>
<td>(1.3 ± 0.2) x 10⁻¹⁰</td>
</tr>
<tr>
<td>C₂H + CH₃ → C₂H₂ + C₂H₃</td>
<td>-133</td>
<td>-0.02 ± 0.10</td>
<td>H₂C⁻⁻H 410</td>
<td>(3.6 ± 0.3) x 10⁻¹²</td>
</tr>
<tr>
<td>C₂H + OH → C₂H₂ + H</td>
<td>-117</td>
<td>4.3 ± 0.1</td>
<td>H₂C⁻⁻H 438</td>
<td>(2.3 ± 0.1) x 10⁻¹²</td>
</tr>
<tr>
<td>C₂H + H₂ → C₂H₂ + H</td>
<td>-116</td>
<td>8.3 ± 0.5</td>
<td>H⁻⁻H 436</td>
<td>(4.6 ± 0.7) x 10⁻¹³</td>
</tr>
</tbody>
</table>

* Units of kJ mol⁻¹; ref 31. * Units of kJ mol⁻¹. * Units of kJ mol⁻¹, ref 32. * Rate coefficients measured at 300 K and in units of cm³ molecule⁻¹ s⁻¹. * Reference 33. * Rate coefficients of reaction 30 and in units of cm³ molecule⁻¹ s⁻¹. * Reference 26. * Rate coefficients of reaction 31 and in units of cm³ molecule⁻¹ s⁻¹. * Reference 27. * Rate coefficients of reaction 32 and in units of cm³ molecule⁻¹ s⁻¹. * Reference 28. * Rate coefficients of reaction 33 and in units of cm³ molecule⁻¹ s⁻¹. * Reference 29. * Rate coefficients of reaction 34 and in units of cm³ molecule⁻¹ s⁻¹. * Reference 30.

TABLE 3: Summary of Rate Coefficients for C₂H + H₂

<table>
<thead>
<tr>
<th>Reference</th>
<th>k(H₂) (cm³ molecule⁻¹ s⁻¹)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>this work</td>
<td>(1.2 ± 0.3) x 10⁻¹¹</td>
<td>178 - 359</td>
</tr>
<tr>
<td>Farhat et al.</td>
<td>(9.4 ± 0.24) x 10⁻¹¹</td>
<td>295 - 854</td>
</tr>
<tr>
<td>Koshi et al.</td>
<td>(1.8 ± 1.0) x 10⁻¹¹</td>
<td>298 - 438</td>
</tr>
<tr>
<td>Lange and Wagner</td>
<td>(1.7 ± 1.0) x 10⁻¹¹</td>
<td>320</td>
</tr>
<tr>
<td>Laufer and Bass</td>
<td>(1.5 ± 1.0) x 10⁻¹¹</td>
<td>298</td>
</tr>
<tr>
<td>Renlund et al.</td>
<td>(1.2 ± 0.3) x 10⁻¹¹</td>
<td>298</td>
</tr>
<tr>
<td>Okabe</td>
<td>(9.7 ± 10⁻¹¹)</td>
<td>298</td>
</tr>
<tr>
<td>Stephens et al.</td>
<td>(4.8 ± 0.3) x 10⁻¹¹</td>
<td>298 - 439</td>
</tr>
<tr>
<td>Peeters et al.</td>
<td>(1.31 x 10⁻¹⁸)²</td>
<td>295 - 440</td>
</tr>
</tbody>
</table>

* Recalculated using the measured ratio and the present-day C₂H + H₂ rate constant of (1.3 ± 0.2) x 10⁻¹² cm³ molecule⁻¹ s⁻¹.

TABLE 4: Reactions Involving H Atom Abstraction

<table>
<thead>
<tr>
<th>reaction</th>
<th>V (kJ mol⁻¹)</th>
<th>ΔE (kJ mol⁻¹)</th>
<th>k (cm³ molecule⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O²⁺ → 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>59.4</td>
<td>325, 590</td>
</tr>
<tr>
<td>OH + H₂</td>
<td>25.9</td>
<td>-17.3</td>
<td>440, 686</td>
</tr>
<tr>
<td>CN + H₂</td>
<td>17.1</td>
<td>-105.8</td>
<td>165, 165</td>
</tr>
<tr>
<td>C₂H + H₂</td>
<td>9.6</td>
<td>-129.7</td>
<td>139, 139</td>
</tr>
</tbody>
</table>

* Table 4 is taken from ref 27. * V is Classical barrier at the saddle point. * ΔE The difference in internal energy between products and reactants. * k is The two lowest bending frequencies at the saddle point. * v is 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 this trend is highly sensitive to several undefined parameters such as the transition state barrier, V², and the imaginary frequency of vibration, V¹. 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 H₂CN⁻ 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 most 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 H₂C₂H⁺ transition state.

However, one must consider how much tunneling plays a role in this reaction, especially since the fit by Harding and co-workers, although low compared to the data, displays the same curvature that the experimental data exhibits. The ab initio calculation by Harding et al. includes Wigner tunneling corrections and is conceivably offset from the experimental data because the barrier height used in the calculation is too high. If the barrier height was lowered below 9.6 kJ mol⁻¹, then the fit by Harding et al. would overlap the combined experimental results from 178 to 854 K by Farhat et al., Koshi et al., and this work. Taking this into account, H atom tunneling could 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 modes in the H₂C₂H⁺ transition state. Advanced theories will need to take into account both explanations.

**Conclusion**

The rate coefficients of C₂H with C₃H₄, C₂H₆, and H₂ have been measured from 150 to 359 K. The reaction of C₂H + C₃H₄ 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 + C₂H₆ 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 \( k_{H2} = (1.2 ± 0.3) × 10^{-11} \exp(-998 ± 57)/T \) cm³ molecule⁻¹ 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 (\( E_a = 8.3 ± 0.5 \) 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.

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**References and Notes**


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