Rate Coefficients of C\textsubscript{2}H with C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and H\textsubscript{2} from 150 to 359 K

Brian J. Opansky and Stephen R. Leone

JILA, National Institute of Standards and Technology and University of Colorado, Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440
Rate Coefficients of C₂H with C₂H₄, C₂H₆, and H₂ from 150 to 359 K

Brian J. Opansky and Stephen R. Leone*

JILA, National Institute of Standards and Technology and University of Colorado,
Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440

Received: July 2, 1996; In Final Form: October 3, 1996

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

\[ k_{C2H_2} = (7.8 \pm 0.6) \times 10^{-11} \exp[(134 \pm 44)/T], \]

\[ k_{C2H_6} = (3.5 \pm 0.3) \times 10^{-11} \exp[(2.9 \pm 16)/T], \]

and \( k_{H_2} = (1.2 \pm 0.3) \times 10^{-11} \exp[(-998 \pm 57)/T] \) cm³ molecule⁻¹ 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

\[ kc_{C2H_2} = (9.2 \pm 0.3) \times 10^{0.6} \exp[(2.9 \pm 16)/T], \]

\[ kc_{C2H_4} = (1.2 \pm 0.3) \times 10^{0.6} \exp[(2.9 \pm 16)/T]. \]

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.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 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

\[
\text{C}_2\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{products}
\]

\[
\text{C}_2\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{C}_2\text{H}_2
\]

\[
\text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}
\]

using transient infrared laser absorption spectroscopy.

The exothermicity of reaction 1 is such that there are two different thermodynamically accessible product channels available³⁻⁵

\[
\text{C}_2\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_4 + \text{H}
\]

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

\[
\rightarrow \text{C}_2\text{H}_3 + \text{C}_2\text{H}_2
\]

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

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.² 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:

\[
2\text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4
\]

\[
\text{C}_2\text{H}_3 + \text{H} \rightarrow \text{C}_2\text{H}_2 + \text{H}_2
\]

\[
\text{C}_2\text{H}_3 + \text{CH}_3 + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M}
\]

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.⁶

\[
2(\text{C}_2\text{H}_2 + \text{hv} \rightarrow \text{C}_2\text{H} + \text{H})
\]

\[
\text{C}_2\text{H} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3
\]

\[
\text{C}_2\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_3
\]

\[
\text{CH}_3 + \text{C}_2\text{H}_5 + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M}
\]

\[
\text{net: C}_2\text{H} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_3
\]

In addition, a pressure-dependent study by Lander et al.⁷ indicated a slight increase in \( k_{C2H_2} (\text{C}_2\text{H} + \text{C}_2\text{H}_6) \) 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 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

$$\text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H} \quad (3)$$

is listed in the proposed scheme of Yung et al. as contributing to the production of \(\text{C}_2\text{H}_6\) in the atmospheres of both Jupiter and Saturn.\(^{5,6}\)

The reaction of \(\text{C}_2\text{H} + \text{H}_2\) has been studied theoretically by both Harding et al.\(^{7}\) and Herbst.\(^{8}\) Harding and co-workers calculated \(k_{ih}\), with Wigner tunneling corrections, from 300 to 2000 K for reaction 3 as \(6.8 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). 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, \(k_{ih}\), are calculated with and without tunneling contributions. There is a steady decrease in \(k_{ih}\) from 300 to 40 K, but the calculation with tunneling contributions shows that \(k_{ih}\) begins to increase from \(\sim 1.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) 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, \(k_{ih}\) decreases rapidly from \(1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at 300 K to \(\sim 6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) 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 \(k_{ih}\) with temperature. The goal in studying \(\text{C}_2\text{H} + \text{H}_2\) 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 \(\text{C}_2\text{H} + \text{C}_2\text{H}_2\).\(^{10}\) Several groups have measured rate coefficients for \(\text{C}_2\text{H}_4\) with \(\text{H}_2\), \(\text{C}_2\text{H}_5\), and \(\text{H}_2\) at 300 K or at higher temperatures.\(^{11-19}\) Up to this point, there have been no temperature-dependent reaction rate coefficients for \(\text{C}_2\text{H} + \text{H}_2\), despite the importance of \(\text{C}_2\text{H} + \text{H}_2\). 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 \(k_{ih}\) and \(k_{ih}\) are given by \((7.8 \pm 0.6) \times 10^{-11} \exp[(134 \pm 44)/T]\) and \((3.5 \pm 0.3) \times 10^{-11} \exp[(2.9 \pm 16)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), respectively. The data for \(\text{C}_2\text{H}_5 + \text{H}_2\) show a positive temperature dependence from 150 to 359 K because of the low \(\text{C}_2\text{H}_5\) concentrations required to keep \(k_{ih}[\text{C}_2\text{H}_5]\) contributions below 40%. In experiments performed above room temperature, heated water was circulated around the inner cell.

The \(\text{C}_2\text{H}\) radical is probed in absorption by a high-resolution color center laser tuned to the \(\text{C}_2\text{H}(9)\) line at 3593.68 cm\(^{-1}\) of the \(A\Sigma^+ \leftarrow X\Pi\) 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 multipass, is directed onto a 50 MHz Ge:Au detector which has a 20 nm² 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: \(\text{He}, 99.999\%\); \(\text{C}_2\text{H}_4, 99.6\%\); \(\text{H}_2, 99.9999\%\). 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 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 C\(_2\)H(X\(^2\Sigma^+(0,0,0))\). In addition, it is necessary that the upper states of C\(_2\)H are fully quenched before the reaction of C\(_2\)H- (X\(^2\Sigma^+(0,0,0))\) with C\(_2\)H\(_4\), C\(_2\)H\(_6\), and 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 C\(_2\)H-(X(0,0,1)) state occurs in approximately 1 \(\mu\)s. In this study, as well as in theirs, the reaction of C\(_2\)H(X\(^2\Sigma^+(0,0,0))\) with C\(_2\)H\(_4\), C\(_2\)H\(_6\), and 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 C\(_2\)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 = C\(_2\)H\(_4\), C\(_2\)H\(_6\), or H\(_2\)) and \([\text{C}_2\text{H}_2]\) \(\gg [\text{C}_2\text{H}]\). The rate of change of [C\(_2\)H] can be expressed as

\[
d(C_2H)/dt = -[C_2H](k_X[X] + k_{C_2H_2}[C_2H_2]) \tag{11}
\]

After integration, this yields

\[
[C_2H]_t = [C_2H]_0 \exp(-k_{\text{obs}}t) \tag{12}
\]

where

\[
k_{\text{obs}} = k_X[X] + k_{C_2H_2}[C_2H_2] \tag{13}
\]

\[
k_{\text{obs}} - k_{C_2H_2}[C_2H_2] = k_X[X] = k_X' \tag{14}
\]

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.

\[
y = A \exp(-k_{\text{obs}}t) + \text{constant} \tag{15}
\]

The values of \(k_{\text{obs}}\) are corrected for the C\(_2\)H + C\(_2\)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 \(k_{C_2H_2}\), 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 C\(_2\)H with C\(_2\)H\(_4\), C\(_2\)H\(_6\), and H\(_2\) from 150 to 359 K. The data for C\(_2\)H with C\(_2\)H\(_4\) and C\(_2\)H\(_6\) are plotted in Figure 5 and indicate a slight negative temperature dependence for \(k_{C_2H_4}\), and almost no temperature dependence for \(k_{C_2H_6}\) over the temperature range 150–357 K. Both sets of data are fit to Arrhenius expressions in which \(k_{C_2H_4}\) and \(k_{C_2H_6}\) are given by (7.8 ± 0.6) \(\times 10^{-11}\) exp\([(-134 ± 44)/T]\) and (3.5 ± 0.3) \(\times 10^{-11}\) exp\([(-29.6 ± 16)/T]\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), respectively. The rate coefficients for C\(_2\)H + H\(_2\) show a positive temperature dependence from 178 to 359 K.

Discussion

C\(_2\)H + C\(_2\)H\(_4\) and C\(_2\)H\(_6\). In the case of C\(_2\)H + C\(_2\)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 \(k_{C_2H_4}\) at 150 K, due to the low C\(_2\)H\(_2\) concentrations required, degrades the transient absorption signal. One cannot say with confidence that the measured rate coefficient at 150 K for C\(_2\)H + C\(_2\)H\(_4\) is significant, for example, representing a small barrier to a C\(_2\)H\(_4\) complex.

The rate coefficient \(k_{C_2H_6}\) exhibits no temperature dependence from 153 to 357 K, comparable to that of \(k_{C_2N+C_2H_4}\) from 75 to 300 K,\(^24\) and no pressure dependence with varying helium densities. Since the current experimental setup prevents reach-
Rate Coefficients of C$_{2}$H with C$_{2}$H$_{4}$, C$_{2}$H$_{6}$, and H$_{2}$

**Figure 4.** Plot of $k'_{C_{2}H}$ versus [H$_{2}$] at 355 K. The slope of this plot is equal to $(6.7 \pm 0.9) \times 10^{-15}$ cm$^{3}$ molecule$^{-1}$ s$^{-1}$.

**Figure 5.** Arrhenius plot of C$_{2}$H with C$_{2}$H$_{4}$ and C$_{2}$H$_{6}$: O, this work for C$_{2}$H + C$_{2}$H$_{4}$; \(\blacktriangle\), this work for C$_{2}$H + C$_{2}$H$_{6}$; \(\blacktriangleleft\), Lander et al. for C$_{2}$H + C$_{2}$H$_{4}$; \(\square\), Lander et al. for C$_{2}$H + C$_{2}$H$_{6}$; \(\blacktriangledown\), Laufer. The Arrhenius fit to C$_{2}$H with C$_{2}$H$_{4}$ and C$_{2}$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 C$_{2}$H + H$_{2}$: \(\bullet\), this work; \(\blacktriangle\), Farhat et al.; \(\blacktriangleleft\), Koshi et al.; \(\blacksquare\), Lange et al.; \(\blacktriangleleft\), Laufer et al.; \(\triangledown\), Renlund et al.; \(\blacktriangleleft\), Okabe; \(\blacktriangle\), Peeters et al.; \(\blacktriangleleft\), Stephens et al.; \(\blacktriangle\), 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 $9.2 \times 10^{-10} \exp[-478 \pm 170]/T$ cm$^{3}$ molecule$^{-1}$ s$^{-1}$. The dash-dotted line is the ab initio calculation by Harding et al.

The reaction of CN + C$_{2}$H radical with C$_{2}$H$_{4}$ and C$_{2}$H$_{6}$ exhibit similar temperature and pressure dependencies as the CN radical does with C$_{2}$H$_{4}$ and C$_{2}$H$_{6}$.

**TABLE 1: Summary of Rate Coefficients of C$_{2}$H with H$_{2}$, C$_{2}$H$_{4}$ and C$_{2}$H$_{6}$ from 150 to 359 K**

<table>
<thead>
<tr>
<th>temp (K)</th>
<th>$k_{C_{2}H_{4}}$ (cm$^{3}$ molecule$^{-1}$ s$^{-1}$)</th>
<th>temp (K)</th>
<th>$k_{C_{2}H_{6}}$ (cm$^{3}$ molecule$^{-1}$ s$^{-1}$)</th>
<th>temp (K)</th>
<th>$k_{H_{2}}$ (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>298</td>
<td>$(3.6 \pm 0.6) \times 10^{-11}$</td>
<td>191</td>
<td>$(5.3 \pm 0.9) \times 10^{-14}$</td>
</tr>
<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>
</tr>
<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>$(4.0 \pm 0.6) \times 10^{-11}$</td>
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<td>$(3.4 \pm 0.8) \times 10^{-11}$</td>
</tr>
<tr>
<td>153</td>
<td>$(3.3 \pm 0.6) \times 10^{-11}$</td>
<td>153</td>
<td>$(3.3 \pm 0.6) \times 10^{-11}$</td>
<td>153</td>
<td>$(3.3 \pm 0.6) \times 10^{-11}$</td>
</tr>
</tbody>
</table>
C₂H must attack either the C–H or C–C for the radical's attraction to the electron-rich double bond in C₂H₄.

Temperature decreases. The factor of 3-4 difference between inherent that the measured rate coefficients at room temperature a direct abstraction rather than one of complex formation, it is suggesting that the rate-determining abstraction by the ethynyl radical. Since the mechanism involves addition complex. The last two reactions listed in Table 2, C₂H and C₂H₄- complexes. Therefore, the rate-determining step in each of these reactions, there is little or no barrier to form the addition complex. The five reactions listed in Table 2, the fastest are those with the largest C–H bond dissociation energies: C₂H + C₂H₂ to C₂H + C₂H₄. Since the measured energy of activation is negative magnitude from very exothermic, but their rate coefficients vary by 3 orders of magnitude from 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 kH₂ = (9.2 ± 0.24) x 10⁻¹⁴ cm⁻³ molecule⁻¹ s⁻¹, but they chose to fit their data to a non-Arrhenius form of kH₂ = (9.44 ± 0.02) x 10⁻¹⁴ cm⁻³ molecule⁻¹ 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 298–438 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 kH₂ = (9.2 ± 0.24) x 10⁻¹⁴ exp[-1470/7] cm⁻³ molecule⁻¹ s⁻¹, but they chose to fit their data to a non-Arrhenius expression of the form kH₂ = (9.44 ± 0.02) x 10⁻¹⁴ exp[-1470/7] cm⁻³ molecule⁻¹ s⁻¹. The room temperature values of kH₂ 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 kH₂ over the temperature range 298–438 K and found an Arrhenius dependence of kH₂ = (1.8 ± 1.0) x 10⁻¹¹ cm⁻³ 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 kC₂H₂/kH₂ is measured based on the C₂H₂ concentration and reported in their work. The room temperature value of kH₂ in the work by Koshi et al., (5.1 ± 2.0) x 10⁻¹⁴ cm⁻³ 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) x 10⁻¹⁴ and (4.7 ± 0.5) x 10⁻¹⁴ cm⁻³ 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 C₂H₂ or C₃H₄CF₃ photodissociation by 193 nm light from an excimer. The pseudo-first-order decay of C₂H was monitored by depletion of the chemiluminescence of CH₃(A²Δ) produced by the radical reaction with O₂. They measured kH₂ from 295 to 440 K and fit their data to the expression kH₂ = 1.31 x 10⁻¹⁷ exp(-174/T) cm⁻³ 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 kH₂ increasing with temperature; see Figure 6.

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

\[ \text{CN} + \text{H₂} \rightarrow \text{H} + \text{HCN} \]  

Although CN is a diatomic radical, it is iso electronic with C₂H, and the measured rate coefficients with C₂H₂, C₂H₄, C₂H₆, O₂, ...
and CI- show similar temperature dependencies as their C2H counterparts.

TABLE 2: Comparison of Various C2H Reactions

<table>
<thead>
<tr>
<th>reaction</th>
<th>ΔH</th>
<th>E_a</th>
<th>D_0</th>
<th>k~</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2H + H2 → C2H2 + H</td>
<td>-102</td>
<td>-0.7 ± 0.1</td>
<td>H2C=H-549.3</td>
<td>(1.3 ± 0.2) × 10^{-10}</td>
</tr>
<tr>
<td>C2H + C2H4 → products</td>
<td>f</td>
<td>-1.1 ± 0.4</td>
<td>H2C=H-465.2</td>
<td>(1.3 ± 0.2) × 10^{-10}</td>
</tr>
<tr>
<td>C2H + CH3 + CH4 →</td>
<td>-133</td>
<td>-0.02 ± 0.10</td>
<td>H2C=H-410</td>
<td>(3.9 ± 0.6) × 10^{-11}</td>
</tr>
<tr>
<td>CH3 + CH3 + CH4 + CH2</td>
<td>-117</td>
<td>4.3 ± 0.1</td>
<td>H2C=H-438</td>
<td>(2.3 ± 0.1) × 10^{-12}</td>
</tr>
<tr>
<td>CH + H2 → CH3 + C2H2</td>
<td>-116</td>
<td>8.3 ± 0.5</td>
<td>H=H-436</td>
<td>(4.6 ± 0.7) × 10^{-13}</td>
</tr>
</tbody>
</table>

* Units of kJ mol^{-1}, ref 31. b Units of kJ mol^{-1}. c Units of kJ mol^{-1}, ref 32. d Reference 33. e Rate coefficients measured at 300 K and in units of cm^3 molecule^{-1} s^{-1}. f Rate coefficients measured at 300 K and in units of cm^3 molecule^{-1} s^{-1}.

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, E_a, and the lowest bending frequencies in the group. Their rate coefficients show substantial curvature in their respective Arrhenius plots.

Both Harding et al. and Herbst 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-H bond distance in the H2-C bond transition state only 6% larger than in the H2 reactant and the H2-C bond 52% greater than in the C2H 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, E_a. 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 decreases 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. and Koshi et al., the general trend of k_H is followed.

Herbst, using statistical phase space theory and the vibrational frequencies and rotational constants from Harding et al., calculated rate coefficients from 300 to 10 K for reaction 3. At room temperature, Herbst reports that the tunneling contribution to k_H is ~40%, and then k_H starts to decrease as the temperature is lowered. The rate coefficients for k_H decrease to a minimum value at ~40 K of approximately 1.2 × 10^{-15} cm^3 molecule^{-1} s^{-1}. Afterward, k_H increases to a value of 2.2 × 10^{-15} cm^3 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 "1/1 space" the calculation spans. Herbst claims that the increase in k_H is due to a decrease in the density of reactant states which control the redissociation 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, E_a, and the imaginary frequency of vibration, v_i. A "slight" decrease in the transition state barrier decreases k_H by an order of magnitude at 10 K. A change in the transition state frequency by ±200 cm^{-1} results in k_H, 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 k_H 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 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 \((7.8 \pm 0.6) \times 10^{-11} \exp[(134 \pm 44)/T] \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1}\). 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 \((3.5 \pm 0.3) \times 10^{-11} \exp[(29.0 \pm 16)/T] \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1}\).

The Arrhenius fit to the data for C₂H and H₂ can be expressed as \(k_{12} = (1.2 \pm 0.3) \times 10^{-11} \exp[(-998 \pm 57)/T] \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1}\). The positive temperature dependence is consistent with reactions involving a hydrogen abstraction as the rate-determining step and a positive energy of activation \(E_a = 8.3 \pm 0.5 \ \text{kJ mol}^{-1}\) 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