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
Rate Coefficients of $C_2H$ with $C_2H_4$, $C_2H_6$, and $H_2$ 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

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

Rate coefficients for the reactions $C_2H$ with $C_2H_4$, $C_2H_6$, 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 $C_2H_2$ 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 A$^2Π$–X$^2Σ$ transition at 3593.68 cm$^{-1}$. Over the experimental temperature range 150–359 K the rate constants of $C_2H$ with $C_2H_4$, $C_2H_6$, 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 $C_2H$ with $C_2H_4$ and $C_2H_6$ 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 $k_{H_2} = 9.2 \times 10^{-10}T^{2.173 \pm 0.50} \exp[(-478 \pm 165)/T]$ 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 $C_2H$ radical and bending mode contributions to the partition function.

Introduction

The ethynyl radical, $C_2H$, is of fundamental importance in combustion chemistry and in planetary atmospheres.1–5 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 $C_2H$ with such species as $C_2H_4$, $C_2H_6$, 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

$$C_2H + C_2H_4 \rightarrow \text{products} \quad (1)$$

$$C_2H + C_2H_6 \rightarrow C_2H_5 + C_2H_2 \quad (2)$$

$$C_2H + H_2 \rightarrow C_2H_2 + H \quad (3)$$

using transient infrared laser absorption spectroscopy.

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

$$C_2H + C_2H_4 \rightarrow C_4H_4 + H \quad \Delta H = -95.4 \text{ kJ mol}^{-1} \quad (1a)$$

$$\rightarrow C_2H_3 + C_2H_2 \quad \Delta H = -90.4 \text{ kJ mol}^{-1} \quad (1b)$$

The $C_4H_4$ species in reaction 1a is the vinyl acetylene isomer. Reaction 1b is a possible source of vinyl radicals, $C_2H_3$, 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:

$$2C_2H_3 \rightarrow C_2H_2 + C_2H_4 \quad (4)$$

$$C_2H_4 + H \rightarrow C_2H_2 + H_2 \quad (5)$$

$$C_2H_5 + CH_3 + M \rightarrow C_2H_4 + CH_5 + M \quad (6)$$

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 ($C_2H_2$, $CH_4$, $C_2H_6$, and $C_2H_4$ 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 $C_2H + C_2H_6$ leads to the production of ethyl radicals, $C_2H_5$, which opens pathways for the production of propane, $C_3H_8$, in Titan’s atmosphere via the following scheme:2,6

$$2(C_2H_2 + hv) \rightarrow C_2H + H_2 \quad (7)$$

$$CH_2 + CH_4 \rightarrow C_2H_2 + CH_3 \quad (8)$$

$$C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5 \quad (2)$$

$$CH_3 + C_2H_5 + M \rightarrow C_2H_6 + C_2H_4 \quad (9)$$

$$\text{net: } CH_4 + C_2H_6 \rightarrow C_2H_4 + 2H \quad (10)$$

In addition, a pressure-dependent study by Lander et al.7 indicated a slight increase in $k_{C_4H_4}$ ($C_2H + C_2H_6$) 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 $C_2H + H_2$ 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
\[ C_2H + H_2 \rightarrow C_2H_2 + H \] is listed in the proposed scheme of Yung et al. as contributing to the production of C2H6 in the atmospheres of both Jupiter and Saturn.

The reaction of C2H + H2 has been studied theoretically by both Harding et al.10 and Herbst. Harding and co-workers calculated \( k_{th} \), 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, \( k_{th} \), are calculated with and without tunneling contributions. There is a steady decrease in \( k_{th} \) from 300 to 40 K, but the calculation with tunneling contributions shows that \( k_{th} \) 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, \( k_{th} \) 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 \( k_{th} \) with temperature. The goal in studying C2H + H2 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 C2H + C2H2.10 Several groups have measured rate coefficients for C2H with C2H4, C2H6, and H2 at 300 K or at higher temperatures. Up to this point, there have been no temperature-dependent rate coefficient measurements of C2H with C2H4 and C2H6, and despite the importance of C2H + H2, 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 \( k_{CH} \) and \( k_{C3H} \) 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 C2H + H2 show a positive temperature dependence from 178 to 359 K which can be fit to the Arrhenius expression \( k_{th} = (1.2 \pm 0.3) \times 10^{-11} \exp((-998 \pm 57)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), but when combined with previous high-temperature measurements, there is evidence for curvature in the Arrhenius plot.

**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.

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 photolytic decomposition 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 C2H 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} 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 nm22 and 0.26 for the quantum yield for \( \text{C}_2\text{H}_3 \) production.23 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 C2H2, 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) \times 10^{15} \text{ cm}^{-3} and hydrogen densities of (0.6–9.0) \times 10^{17} \text{ cm}^{-3}.

The 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 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 \( k_{CH}[\text{C}_2\text{H}_4] \) 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 Q(1)(9) line at 3593.68 cm\(^{-1}\) of the \( \Delta \Pi - \Delta \Sigma \) transition. A scanning Fabry-Perot interferometer wavenumber is used to ensure the color center is running on one longitudinal mode, and a home-built scanning Michelson interferometer 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\(^2\) 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%; C2H4, 99.6%; H2, 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 $C_2H(\Sigma^+(0,0,0))$. In addition, it is necessary that the upper states of $C_2H$ are fully quenched before the reaction of $C_2H$ with $C_2H_4$, $C_2H_6$, and $H_2$ occurs. Previous experiments by Lander et al. and Farhat et al. performed under similar conditions, have shown that relaxation of the $C_2H(X(0,0,1))$ state occurs in approximately 1 ms. In this study, as well as in theirs, the reaction of $C_2H(X^2\Sigma^+(0,0,0))$ with $C_2H_4$, $C_2H_6$, 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 $C_2H$, 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 $X = C_2H_4$, $C_2H_6$, or $H_2$) and $[C_2H_2] >> [C_2H]$. The rate of change of $[C_2H]$ can be expressed as

$$\frac{d[C_2H]}{dt} = -[C_2H](k_X[X] + k_{C_2H_2}[C_2H_2])$$

After integration, this yields

$$[C_2H]_t = [C_2H]_0 \exp[-k_{\text{obs}}t]$$

where

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

$$k_{\text{obs}} - k_{C_2H_2} = k_X[X] = k'_X$$

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 $C_2H + C_2H_2$ contribution taken from our own work 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 $k_{\text{obs}}$, 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 $C_2H$ with $C_2H_4$, $C_2H_6$, and $H_2$ from 150 to 359 K. The data for $C_2H$ with $C_2H_4$ and $C_2H_6$ 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 $(7.8 \pm 0.6) \times 10^{-11}$ 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. The rate coefficients for $C_2H + H_2$ show a positive temperature dependence from 178 to 359 K.

**Discussion**

$C_2H + C_2H_4$ and $C_2H_6$. In the case of $C_2H + C_2H_4$, 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 $C_2H_2$ concentrations required, degrades the transient absorption signal. One cannot say with confidence that the measured rate coefficient at 150 K for $C_2H + C_2H_4$ is significant, for example, representing a small barrier to a $C_2H_3$ complex.

The rate coefficient $k_{C_2H_6}$ exhibits no temperature dependence from 153 to 357 K, comparable to that of $k_{C_2H_4}$, from 75 to 300 K, and no pressure dependence with varying helium densities. Since the current experimental setup prevents reach-
The rate coefficient \( k_{C_2H} \) for the reaction of \( C_2H \) with \( H_2 \) displays a slight pressure dependence at room temperature over the same helium number densities. The rate coefficient shows a sharp decrease from 44 to 25 K. The Arrhenius plot for the reaction of \( CN + C_2H_4 \) at 25 K is less than \( k_{CN+C_2H_4} \) at 44 K. Lander \textit{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 \textit{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 \( k_{CN+C_2H_4} \) for \( CN + C_2H_4 \) displays a pronounced curvature in its Arrhenius plot; see Figure 7. From

**Table 1: Summary of Rate Coefficients of \( C_2H \) with \( H_2, C_2H_4 \), and \( C_2H_6 \) from 150 to 359 K**

<table>
<thead>
<tr>
<th>temp (K)</th>
<th>( k_{C_2H_4} ) (cm(^3) molecule(^{-1}) s(^{-1}))</th>
<th>temp (K)</th>
<th>( k_{C_2H_6} ) (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>
</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>
</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>
</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>
</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>
</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>
</tr>
<tr>
<td>216</td>
<td>( (1.6 \pm 0.1) \times 10^{-10} )</td>
<td>298</td>
<td>( (3.5 \pm 0.6) \times 10^{-11} )</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>
</tr>
<tr>
<td>173</td>
<td>( (2.1 \pm 0.3) \times 10^{-10} )</td>
<td>198</td>
<td>( (3.9 \pm 0.6) \times 10^{-11} )</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>
</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>
</tr>
</tbody>
</table>

**Figure 4.** Plot of \( k_{H_2} \) versus \( [H_2] \) 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 \( C_2H \) with \( C_2H_4 \) and \( C_2H_6 \). The reactions of the \( CN \) radical with \( C_2H_4 \) and \( C_2H_6 \) exhibit similar temperature and pressure dependencies as the \( CN \) radical does with \( C_2H_4 \) and \( C_2H_6 \). 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. The reaction of \( CN + C_2H_4 \) 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.
Compared to ethene, ethane does not possess the π electrons and the C--H bonds are the slowest of the five and decrease sharply as the temperature decreases. The factor of 3-4 difference between their measured rate coefficients at room temperature indicates that the rate-determining step is the direct H atom abstraction by the ethynyl radical. Since the mechanism involves the formation of the adduct complex, the last two reactions listed in Table 2, C2H+ C2I-I6; see Figure 7. Sims and co-workers have no suitable explanation for the sharp increase in rate coefficients at 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. 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 kH2 = (1.8 ± 1.0) x 10^{-11} exp[-1090±299/T] cm^3 molecule^{-1} s^{-1} for CN + C2H4.

To illustrate the problem, consider the reaction of C2H + C2H2. When H2 is added to the gas flow, the concentration of C2H2 decreases due to reaction 1. The ratio of kC2H2/kC2H 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^{-13} 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^{-13} and (4.7 ± 0.5) x 10^{-13} 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 and C2HC12F12 photodissociation by 193 nm light from an excimer. The pseudo-first-order decay of C2H was monitored by depletion of the chemiluminescence of CH(A^2) 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

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

Although CN is a diatomic radical, it is isoelectronic with C2H2 and the measured rate coefficients with C2H4, C2H6, O2, O, C2H2, C2I-I6, and C2H6, C2H4, O2, C2H2, C2I-I6. For the reaction of C2H + C2H2, the factor of 3-4 difference between their measured rate coefficients at room temperature indicates that the rate-determining step is the direct H atom abstraction by the ethynyl radical.
TABLE 2: Comparison of Various C2H Reactions

<table>
<thead>
<tr>
<th>reaction</th>
<th>$\Delta H$</th>
<th>$E_a$</th>
<th>$D_0$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2H + C2H2 $\rightarrow$ C2H2 + H</td>
<td>-102</td>
<td>-0.7 ± 0.1</td>
<td>HCN$^{-}$H 549.3</td>
<td>(1.3 ± 0.2) x 10^{-10}</td>
</tr>
<tr>
<td>C2H + C2H4 $\rightarrow$ products</td>
<td>f</td>
<td>-1.1 ± 0.4</td>
<td>H2C-CH 465.2</td>
<td>(1.3 ± 0.2) x 10^{-10}</td>
</tr>
<tr>
<td>C2H + C2H6 $\rightarrow$ C2H2 + C2H3</td>
<td>-133</td>
<td>-0.02 ± 0.10</td>
<td>H2C$^{-}$H 410</td>
<td>(3.6 ± 0.6) x 10^{-11}</td>
</tr>
<tr>
<td>C2H + CH2 $\rightarrow$ CH2 + C2H2</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 + H $\rightarrow$ 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 reference 33. * Rate coefficients measured at 300 K and in units of cm$^3$ molecule$^{-1}$ s$^{-1}$. * Reference 35.

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-H2 bond distance in the H2-H2$\rightarrow$C2-H2$\rightarrow$H transition state only 6% larger than in the reactant and the H2-C2 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, $E_a$. 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 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. and Koshi et al., the general trend of $k_H$ and curvature is followed.


d Recalculated using the measured ratio and the present-day C2H + C2H2 rate constant of (1.3 ± 0.2) x 10^{-12} cm$^3$ molecule$^{-1}$ s$^{-1}$.

and CH4 show similar temperature dependencies as their C2H counterparts. Reaction 16 has been studied by several groups over the combined temperature range 209–1000 K. 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(v=0) as (2.4 ± 0.7) x 10^{-12} $(77298) \times 10^{-6} \exp[-(1340 ± 90)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$ from 295 to 768 K. A theoretical study by Wagner and Bair has shown that the H2CN$^{-}$ transition state closely resembles the separated reactants, which is consistent with Hammond's postulate for exothermic reactions. 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 H2CN$^{-}$ 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 curvature in the Arrhenius plot of \(\text{CN} + \text{H}_2\) is due to the temperature dependence of the partition function associated with the doubly degenerate low-frequency bending mode in the \(\text{H}_2\text{CN}\) transition state. Pronounced curvature in the 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 \(\text{C}_2\text{H} + \text{H}_2\) 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 \(\text{H}_2\text{C}_2\text{H}^+\) 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 \(\text{C}_2\text{H} + \text{H}_2\).

One cannot conclusively state whether the curvature in the Arrhenius plot of \(\text{C}_2\text{H} + \text{H}_2\) is due solely to either tunneling or to the partition function associated the low-frequency bending modes in the \(\text{H}_2\text{C}_2\text{H}^+\) transition state. Advanced theories will need to take into account both explanations.

Conclusion

The rate coefficients of \(\text{C}_2\text{H}\) with \(\text{C}_2\text{H}_4, \text{C}_2\text{H}_6,\) and \(\text{H}_2\) have been measured from 150 to 359 K. The reaction of \(\text{C}_2\text{H} + \text{C}_2\text{H}_4\) displays a mild negative temperature dependence similar to that of \(\text{CN} + \text{C}_2\text{H}_4\) which is characteristic of an addition-elimination mechanism. The \(\text{C}_2\text{H}\) 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 \(\text{C}_2\text{H} + \text{C}_2\text{H}_6\) 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 \((3.5 \pm 0.3) \times 10^{-11} \exp[(29.3 \pm 16)/T] \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\).

The Arrhenius fit to the data for \(\text{C}_2\text{H}\) and \(\text{H}_2\) can be expressed as \(k = (1.2 \pm 0.3) \times 10^{-11} \exp[-998 \pm 57)/T] \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\). The positive temperature dependence is consistent with reactions involving a hydrogen abstraction as the rate-determining step and a positive energy of activation (\(E_a = 8.3 \pm 0.5\) kJ mol\(^{-1}\) for \(\text{C}_2\text{H} + \text{H}_2\)). The curvature in the Arrhenius plot of \(\text{C}_2\text{H}\) + \(\text{H}_2\) 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 \(\text{H}_2\text{C}_2\text{H}^+\) 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


JP9619604