Rate Coefficients of \( C_2H \) with \( C_2H_4, C_2H_6, \) and \( H_2 \) from 150 to 359 K

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

\[ k_{C2H4} = (7.8 \pm 0.6) \times 10^{-11} \exp[(134 \pm 44)/T], \]

\[ k_{C2H6} = (3.5 \pm 0.3) \times 10^{-11} \exp[(2.9 \pm 1.6)/T], \]

and 

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

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

\[ k_H = 9.2 \times 10^{-18} T^{-1/2} \exp[(-478 \pm 165)/T] \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}. \]

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

**Introduction**

The ethynyl radical, C2H, is of fundamental importance in combustion chemistry and in planetary atmospheres.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

\[ C_2H + C_2H_4 \rightarrow \text{products} \]  
\[ C_2H + C_2H_6 \rightarrow C_2H_3 + C_2H_2 \]  
\[ C_2H + H_2 \rightarrow C_2H_2 + H \]

using transient infrared laser absorption spectroscopy.

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

\[ C_2H + C_2H_4 \rightarrow C_4H_4 + H \]
\[ \Delta H = -95.4 \text{kJ mol}^{-1} \]  
\[ \rightarrow C_2H_3 + C_2H_2 \]
\[ \Delta H = -90.4 \text{kJ mol}^{-1} \]

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:

\[ 2C_2H_3 \rightarrow C_2H_2 + C_2H_4 \]  
\[ C_2H_3 + H \rightarrow C_2H_2 + H_2 \]  
\[ C_2H_3 + CH_3 + M \rightarrow C_2H_4 + M \]

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:3–6

\[ 2(C_2H_3 + h\nu) \rightarrow C_2H_2 + C_2H_4 \]  
\[ C_2H + CH_4 \rightarrow C_2H_2 + CH_3 \]  
\[ C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5 \]  
\[ CH_3 + C_2H_5 + M \rightarrow C_3H_8 + M \]  
\[ \text{net: } CH_4 + C_2H_6 \rightarrow C_3H_8 + 2H \]

In addition, a pressure-dependent study by Lander et al.7 indicated a slight increase in \( k_{C2H4} \) (C2H + C2H6) with increasing helium number density. If this finding is valid, it raises new questions as to the mechanism involved, which may include the formation of an addition complex.

Since the room temperature rate constant for C2H + H2 is very slow and difficult to measure accurately, scientists interested in modeling planetary atmospheres have had to rely...
on theoretical calculations or extrapolations from high-temperature data. For example, the reaction of
\[ \text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_3 + \text{H} \] (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.2,3,6

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 \( k_{\text{th}} \), with Wigner tunneling corrections, from 300 to 2000 K for reaction 3 as \( 6.8 \times 10^{-17} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). The calculated fit shows significant curvature in the Arrhenius plot. Herbst calculated low-temperature rate coefficients for reaction 3 from 10 to 300 K using statistical phase space theory. The rate coefficients, \( k_{\text{th}} \), are calculated with and without tunneling contributions. There is a steady decrease in \( k_{\text{th}} \) from 300 to 40 K, but the calculation with tunneling contributions shows that \( k_{\text{th}} \) begins to increase from \( \sim 1.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) 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, \( k_{\text{th}} \) 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 \( k_{\text{th}} \) 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 \( \text{C}_2\text{H} + \text{C}_2\text{H}_2 \).9 Several groups have measured rate coefficients for \( \text{C}_2\text{H} \) with \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_6 \), and \( \text{H}_2 \) at 300 K or at higher temperatures.8,10-19 Up to this point, there have been no temperature-dependent rate coefficient measurements of \( \text{C}_2\text{H} \) with \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \), and 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 \( k_{\text{C}_2\text{H}} \) and \( k_{\text{C}_2\text{H}_6} \) 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 data for \( \text{C}_2\text{H} + \text{H}_2 \) show a positive temperature dependence, but when combined with previous high-temperature measurements, there is evidence for curvature in the Arrhenius plot.

**Experimental Section**

The rate coefficients for \( \text{C}_2\text{H} \) with \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \) and \( \text{H}_2 \) 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.10,20,21

Ethynyl radicals are produced in the meter long, temperature variable flow cell at 193 nm by a pulsed excimer laser which was run at 55 mJ/pulse at 10 Hz. The absorption cell is constructed from quartz with Brewster windows for a multipass setup. The cell consists of an inner zone and an outer volume. In the inner jacket, the gases flow across the photolysis region through a series of transverse inlets and outlets. The transverse flow arrangement allows high laser repetition rates with minimal photolysis of the same gas volume. With a typical flow rate of \( 2.7 \times 10^{20} \) 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 \( \text{C}_2\text{H} \) concentration was estimated to be no greater than \( 7.5 \times 10^{10} \) cm\(^{-3}\) for the highest acetylene pressures. (The acetylene number density ranges from \( 1.3 \times 10^{14} \) to \( 4.8 \times 10^{14} \) cm\(^{-3}\).) This estimation is based on using \( 1.35 \times 10^{-19} \) cm\(^{-2}\) for the absorption cross section at 193 nm.22 and 0.26 for the quantum yield for \( \text{C}_2\text{H} \) production.23 A 1500–6000-fold excess of \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \) or \( \text{H}_2 \) with respect to \( \text{C}_2\text{H} \) is always present in these experiments. Contributions from radical-radical or secondary reactions can be neglected since the time between collisions for \( \text{C}_2\text{H} \) and \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \) or \( \text{H}_2 \) is 1000 times shorter than the time between collisions of two \( \text{C}_2\text{H} \) radicals. Rate coefficients are measured at various ethene/ethane densities of \( (0.2-5.2) \times 10^{15} \) cm\(^{-3}\) and hydrogen densities of \( (0.6-9.0) \times 10^{17} \) cm\(^{-3}\). The helium density is varied over the range \( (0.5-2.7) \times 10^{18} \) cm\(^{-3}\) to test for a pressure dependence in the rate coefficients of \( \text{C}_2\text{H} \) with \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \) or \( \text{H}_2 \).

In the outer jacket either cooled pentane or isopentane is circulated by a micropump to achieve temperatures as low as 150 K. (It should be noted that not every rate coefficient can be measured down to 150 K because of the low \( \text{C}_2\text{H}_2 \) concentrations required to keep \( k_{\text{C}_2\text{H}_4/\text{C}_2\text{H}_6} \) 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 Q(1)(9) line at 3593.68 cm\(^{-1}\) of the \( \Delta \Pi-\Delta \Sigma \) 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 wavemeter is used to monitor the color center’s wavelength.

The probe beam, after three to five multipasses, is directed onto a 50 MHz Ge:Au detector which has a 20 nm\(^2\) 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%; \( \text{C}_2\text{H}_2 \), 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 \( \text{C}_2\text{H}(X^2\Sigma^+(0,0,0)) \). 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

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

where

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

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

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 \( (7.8 \pm 0.6) \times 10^{-11} \exp[(134 \pm 44)/T] \) 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 \( \text{C}_2\text{H} + \text{H}_2 \) show a positive temperature dependence from 178 to 359 K.

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

![Figure 3. 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 \((3.9 \pm 0.6) \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\).](image)
The lack of temperature dependences is attributed to an addition-elimination mechanism, resulting in an exothermic displacement of an H atom by the CN radical.

The reactions of the C₂H radical with C₂H₄ and C₂H₆ exhibit similar temperature and pressure dependencies as the CN radical does with C₂H₄ and C₂H₆.²⁴,²⁵ Reactions of the CN radical have been studied down to temperatures reaching 25 K using a pulsed laser photolysis, time-resolved laser-induced fluorescence technique by Sims and co-workers.²⁴ The reaction of CN + C₂H₄ is found to show a mild negative temperature dependence (see Figure 7). However, the rate coefficient shows a sharp decrease from 44 to 25 K. The Arrhenius plot for the reaction of CN + C₂H₄ in Figure 7 shows that the measured value of \( k_{\text{CN+C₂H₄}} \) at 25 K is less than \( k_{\text{CN+C₂H₄}} \) at 44 K. Sims et al. indicated that this could signal a small potential barrier along the path leading to CH₂CH₂CN formation. This reaction also exhibits no dependence on total pressure. Sims et al. rationalized their observations by stating that the reaction proceeds through an addition-elimination mechanism, resulting in an exothermic displacement of an H atom by the CN radical.

The rate coefficient \( k_{\text{CN+C₂H₄}} \) for CN + C₂H₄ displays a pronounced curvature in its Arrhenius plot; see Figure 7. From
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 the slowest of the five and decrease sharply as the

Abstraction by the ethynyl radical. Since the mechanism involves addition complex. The last two reactions listed in Table 2, C2H and C2H4, are the least C-H bond dissociation energies: the largest C-H bond dissociation energies:

Very exothermic, but their rate coefficients vary by 3 orders of magnitude from

C2H + H2. A summary of all the current rate coefficients measured for C2H + H2 is given in Table 3. The data for C2H + H2 from 178 to 359 K can be fit to an Arrhenius plot of kH2 = (1.2 ± 0.3) x 10^{-11} exp{(−998 ± 57)/T} cm3 molecule−1 s−1 represented by the solid line in Figure 6. Upon closer examination of the combined data from Farhat et al., Koshi et al., and this work, a slight curvature is observed from 178 to 854 K. The combined data are best fit to a non-Arrhenius form of kH2 = 9.2 x 10^{-18} exp{(−748 ± 165)/T} cm3 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 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 = 6.9 x 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 kH2 = (9.44 ± 0.24) x 10^{-14} exp{(−1003 ± 20)/T} cm3 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} 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 C2H decreases due to reaction 1. The ratio of kC2H/C2H2 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} 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) x 10^{-13} and (4.7 ± 0.5) x 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 C3H3 or C3HCF3 photodissociation by 193 nm light from an excimer. The pseudo-first-order decay of C2H was monitored and depletion of the chemiluminescence of CH(A^2Δ) produced by the radical reaction with O3. They measured kH2 from 295 to 440 K and fit their data to the expression kH2 = 1.31 x 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 kH2 increasing with temperature; see Figure 6.

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

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

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

<table>
<thead>
<tr>
<th>reaction</th>
<th>ΔH</th>
<th>Eₐ</th>
<th>Dₐ</th>
<th>k²</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H + C₂H₂ → C₂H₂ + H</td>
<td>-102</td>
<td>-0.7 ± 0.1</td>
<td>H₂C=2H 549.3</td>
<td>(1.3 ± 0.2) × 10⁻¹⁰</td>
</tr>
<tr>
<td>C₂H + H₂ → products</td>
<td>f</td>
<td>-1.1 ± 0.4</td>
<td>H₂C=2H 465.2</td>
<td>(1.3 ± 0.2) × 10⁻¹⁰</td>
</tr>
<tr>
<td>C₂H + C₂H₂ → C₂H₂ + C₂H₂</td>
<td>-133</td>
<td>-0.02 ± 0.10</td>
<td>H₂C=2H 410</td>
<td>(3.6 ± 0.6) × 10⁻¹⁰</td>
</tr>
<tr>
<td>C₂H + CH₂ → CH₂ + C₂H₂</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>C₂H + H₂ → C₂H₂ + H</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.  † Units of kJ mol⁻¹.  ‡ Units of kJ mol⁻¹, ref 32.  § Reference 33.  † Rate coefficients measured at 300 K and in units of cm³ molecule⁻¹ s⁻¹.  ‡ Rate coefficients measured at 300 K and in units of cm³ 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, Eₐ, and the lowest bending frequencies in the group. Their rate coefficients show substantial curvature in their respective Arrhenius plots.

Both Harding et al.⁶ and Herbst⁷ 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 conclude that reaction 3 has an early saddle point with the H₂=H₂ bond distance in the H₂=H₂ → C₂=C₁=H₁ transition state only 6% larger than in the reactant and the H₂=C bond 52% greater than in the C₂H₂ product. This calculation also confirms Hammond’s postulate that more exotic 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, k². 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.⁶ and Koshi et al.,⁷ the general trend of kₐ and curvature is followed.

Herbst, using statistical phase space theory and the vibrational frequencies and rotational constants from Harding et al.,⁶ calculated rate coefficients from 300 to 10 K for reaction 3. At room temperature, Herbst reports that the tunneling contribution to kₐ is ~40%, and then kₐ starts to decrease as the temperature is lowered. The rate coefficients for kₐ decrease to a minimum value at ~40 K of approximately 1.2 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹. Afterward, kₐ increases to a value of 2.2 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ at 10 K; see Figure 8. For clarity, only four of his calculated rate coefficients are shown in Figure 6 due to the range of "1/T space" the calculation spans. Herbst claims that the increase in kₐ 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, k², and the imaginary frequency of vibration, v¹. A "slight" decrease in the transition state barrier increases kₐ by an order of magnitude at 10 K. A change in the transition state frequency by ±200 cm⁻¹ results in kₐ, 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 kₐ 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

and CH₄ show similar temperature dependencies as their C₂H counterparts.⁴ Reaction 16 has been studied by several groups over the combined temperature range 209–1000 K.²⁶–²⁹ The measured rate coefficients of reaction 16 exhibit a positive temperature dependence in addition to a mild curvature in the Arrhenius plot. One study, by Sims and Smith, gives the modified Arrhenius fit to reaction 16 CN(v=0) as (2.4 ± 0.7) × 10⁻¹² (77K)(8356.4 ± 12exp[(-0.3490 ± 977)/T]) cm³ molecule⁻¹ s⁻¹ from 295 to 768 K.²⁶ A theoretical study by Wagner and Bair²⁷ has shown that the H₂CN² transition state closely resembles the separated reactants, which is consistent with Hammond’s postulate for exothermic reactions.²⁹ The H–H bond distance is increased only by 0.07 Å at the saddle point, and the C–N bond distance remains constant. Both Sims and Smith and Wagner and Bair have concluded that the curvature in the Arrhenius plot for reaction 16 is due to the temperature dependence of the partition function associated with the doubly degenerate low-frequency bending mode in the H₂CN² 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 thermonuclear 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 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 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 Arrhenius fit to the data for C2H and H2 can be expressed as 

\[ \ln(k/\text{molecule}^{-1}\text{s}^{-1}) = 0.3 \times 10^{-11} \exp[-(2.9 \pm 16)/T] \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \]

The Arrhenius fit to the data for C2H and H2 can be expressed as 

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

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.

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References and Notes