Rate coefficients for reactions of ethynyl radical (C$_2$H) with HCN and CH$_3$CN: Implications for the formation of complex nitriles on Titan

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Abstract. Rate coefficients for the reactions of C$_2$H + HCN → products and C$_2$H + CH$_3$CN → products have been measured over the temperature range 262–360 K. These experiments represent an ongoing effort to accurately measure reaction rate coefficients of the ethynyl radical, C$_2$H, relevant to planetary atmospheres such as those of Jupiter and Saturn and its satellite Titan. Laser photolysis of C$_2$H$_2$ is used to produce C$_2$H, and transient infrared laser absorption is employed to measure the decay of C$_2$H to obtain the subsequent reaction rates in a transverse flow cell. Rate constants for the reaction C$_2$H + HCN → products are found to increase significantly with increasing temperature and are measured to be (3.9–6.2) × 10$^{-13}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ over the temperature range of 297–360 K. The rate constants for the reaction C$_2$H + CH$_3$CN → products are also found to increase substantially with increasing temperature and are measured to be (1.0–2.1) × 10$^{-12}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ over the temperature range of 262–360 K. For the reaction C$_2$H + HCN → products, ab initio calculations of transition state structures are used to infer that the major products form via an addition/elimination pathway. The measured rate constants for the reaction C$_2$H + HCN → products are significantly smaller than values currently employed in photochemical models of Titan, which will affect the HC$_3$N distribution.

I. Introduction

Over the last 2 years there have been two new photochemical models of Titan's atmosphere [Lara et al., 1996; Toublanc et al., 1995]. These models differ from the first post-Voyager model [Yung et al., 1984; Yung, 1987] primarily in the updated methane photodissociation scheme [Mordaunt et al., 1993], better characterizations of the eddy diffusion coefficient, and updated reaction rates. Gladstone et al. [1996] also presented a photochemical model for the upper atmosphere of Jupiter based on similar reaction sequences.

With the upcoming Cassini/Huygens mission to Saturn and its largest satellite Titan, there is renewed interest in understanding the photochemical processes that take place in the atmosphere of Titan. This interest generally arises from the presence of a dense N$_2$-CH$_4$ atmosphere which is thought to possess many similarities with the prebiotic chemistry of the Earth [Raulin et al., 1994]. Efforts to unravel the processes that lead to the formation of life are not new, with attempts to simulate Earth's primitive atmosphere originating over 40 years ago [Miller, 1953]. Numerous experiments have been carried out to simulate the synthesis of organic molecules in Titan's atmosphere, including UV radiation, high-energy particles (H$^+$, e, γ), and electric discharges. These laboratory simulations of Titan's atmosphere produce a remarkable mixture of C$_n$ through C$_9$ compounds as well as various nitriles [Cabane and Chassefière, 1995].

Hydrogen cyanide (HCN), cyanocetylene (HCN$_2$), and cyanoacetylene (C$_2$H$_2$N) have been identified as components of Titan's atmosphere with the Voyager 1 infrared spectrometer (IRIS) [Coustenis, 1990; Coustenis et al., 1991], while ethanenitrile (CH$_3$CN), commonly referred to as acetonitrile, methyl cyanide, or cyanomethane, has been detected via ground-based millimeter spectroscopy [Bézard et al., 1993]. The models of Lara et al. [1996], Toublanc et al. [1995], and Yung et al. [1987] and Yung [1984] postulate that HCN is formed from the reaction of ground state nitrogen atoms when they react with ground state methylene:

(R1) \[ N(\bar{S}) + \text{CH}_2 \rightarrow \text{HCN} + H \]

Yung et al. also included the reaction of ground state nitrogen with methyl radicals.

(R2) \[ N(\bar{S}) + \text{CH}_3 \rightarrow \text{HCN} + \text{H}_2 \]

Toublanc et al. [1995] and Lara et al. [1996] proposed the following mechanism for the formation of CH$_3$CN:

(R3) \[
\text{net: } \text{HCN} + \text{CH}_3 \rightarrow \text{CH}_3\text{CN} + \text{H} 
\]

Lara et al. also included a second photochemical process involving ethane:

(R4) \[
\text{net: } \text{HCN} + \text{C}_2\text{H}_6 \rightarrow \text{CH}_3\text{CN} + \text{CH}_3 
\]
The main loss processes for CH₃CN are considered to be photolysis and vapor condensation. These compounds, as well as acetylene and the corresponding radicals, are the main chemical species thought to be involved in the production of complex nitriles. Each of the above models for Titan include the following two schemes for the production of cyanoacetylene, HC₃N:

\[
\begin{align*}
\text{R5} & \quad \text{net:} \quad \text{C}_2\text{H} + \text{HCN} \rightarrow \text{HC}_3\text{N} + 2\text{H} \\
\text{R6} & \quad \text{net:} \quad \text{C}_2\text{H}_2 + \text{HCN} \rightarrow \text{HC}_3\text{N} + \text{H} + 2\text{H}
\end{align*}
\]

The competing, exothermic H atom abstraction reaction, C₂H + HCN → C₂H₂ + CN, was not considered.

The current research is focused on the reactivity of the ethynyl radical, C₂H, with HCN and CH₃CN:

\[
\begin{align*}
\text{R7a} & \quad \text{C}_2\text{H} + \text{HCN} \rightarrow \text{products} \\
\text{R8a} & \quad \text{C}_2\text{H} + \text{CH}_3\text{CN} \rightarrow \text{products}
\end{align*}
\]

There are no experimental data to define the products of these reactions. Both hydrogen abstraction reactions and addition/elimination processes are thermodynamically possible:

\[
\begin{align*}
\text{R7b} & \quad \text{C}_2\text{H} + \text{HCN} \rightarrow \text{C}_2\text{H}_2 + \text{CN} \\
\Delta H_{\text{r,so}} & = -38 \text{ kJ mol}^{-1}
\end{align*}
\]

\[
\begin{align*}
\text{R7c} & \quad \text{C}_2\text{H} + \text{HCN} \rightarrow \text{HC} = \text{CC} = \text{N} + \text{H} \\
\Delta H_{\text{r,so}} & = -126 \text{ kJ mol}^{-1}
\end{align*}
\]

\[
\begin{align*}
\text{R8b} & \quad \text{C}_2\text{H} + \text{CH}_3\text{CN} \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3\text{CN} \\
\Delta H_{\text{r,so}} & = -180 \text{ kJ mol}^{-1}
\end{align*}
\]

\[
\begin{align*}
\text{R8c} & \quad \text{C}_2\text{H} + \text{CH}_3\text{CN} \rightarrow \text{HC} = \text{CC} = \text{N} + \text{CH}_3 \\
\Delta H_{\text{r,so}} & = -150 \text{ kJ mol}^{-1}
\end{align*}
\]

(Values of ΔHᵣᵣ are calculated on the basis of available ΔHᵣᵣ values from Weast [1990] except for cyanoacetylene, which is from Okabe and Dibeler [1973].)

The measurements presented here for the reaction rates of C₂H with the nitrogen containing species, HCN and CH₃CN, are the first direct measurements of the total rate coefficients for these reactions. Since acetylene and polyynes are some of the primary photochemically active species in the atmosphere of Titan, the coupling of the resulting C₂H radicals with the potentially reactive nitrogen compounds is important. In this paper, rate constants for the reactions of C₂H with HCN and CH₃CN are obtained; possible product pathways and the impact of the results on photochemical models are discussed.

2. Experiment

The experimental technique used in the determination of low-temperature rate coefficients of the ethynyl radical has been described in detail [Pedersen et al., 1993; Opansky and Leone, 1996], and only a brief overview is presented here. A schematic of the experimental arrangement is shown in Figure 1. The ethynyl radicals are produced by photolysis of acetylene in a flow cell using a pulsed excimer laser operating at 193 nm (70 mJ/pulse at 10 Hz). The transient decay of the C₂H concentration is probed by a single-mode infrared F-center laser operating at 3593.68 cm⁻¹, which is used to monitor the absorption of the Q₁(0) line of the A¹Σ⁺ → X²Σ⁺ (000) transition. The longitudinal mode structure of the F-center laser is monitored with a scanning Fabry-Perot spectrum analyzer, and a traveling wave meter is used for measuring the wavelength [Hall and Lee, 1976].

The kinetic experiments are performed in a 1 m long, 2.5 cm diameter, variable temperature flow cell. The photolysis and probe lasers are overlapped over the full length of the cell, and a three-times multipass of the probe beam is employed to increase the absorption path length. Gases are introduced into and removed from the cell via a series of transverse inlets and pump-outs, which allows rapid removal of the photolysis products from the probe volume. The cell was cooled by the circulation of pentane or isobutane through an outer jacket after having passed through a copper coil submerged in an ethanol/liquid nitrogen slush bath. Temperatures of ~155 K are easily obtained with this method. Due to the slowness of the C₂H + HCN reaction and the limited vapor pressure of CH₃CN, measurements were restricted to low temperatures of 297 K for HCN and 262 K for CH₃CN. Measurements above room temperature to ~360 K are made by circulating water through the outer jacket while the copper coils are placed in a water reservoir in which the temperature is controlled by an immersion heater. The temperature in the flow cell is measured by three K-type thermocouples positioned along the length of the cell, and partial pressures of each gas are calculated from the measured flow rates using calibrated mass flow meters and the total pressure. Typical number densities for C₂H₂ are (2–6) × 10¹⁴ cm⁻³; number densities for HCN and CH₃CN are (0.5–3) × 10¹⁶ cm⁻³ and (2–8) × 10¹⁰, respectively, with a buffer gas of helium in large excess. Using an absorption cross section for C₂H₂ at 193 nm of 1.35 × 10⁻¹⁹ cm⁻² and a quantum yield of 0.26 [Satyapal and Bersohn, 1991], the upper limit for [C₂H₂] is estimated to be 6.5 × 10¹⁷ cm⁻³. The total pressure for typical data acquisition on the CH₃CN reaction is between 3.7 and 4.1 kPa (28–31 torr); pressure dependence measurements are conducted over the range of 1.3–12 kPa (10–90 torr). Reaction
The observed decay rates of C₂H, k_{obs}, are obtained by fitting the transient signal to the following equation:

\[ \frac{d[C₂H]}{dt} = -[C₂H](k_{RCN}[RCN] + k_{acyl}[C₂H₂]) \]  

where R represents either H or CH₃. After integration of (1),

\[ [C₂H] = [C₂H]₀ \exp \left[ -k_{obs}(t) \right] \]  

where

\[ k_{obs} = k_{RCN}[RCN] + k_{acyl}[C₂H₂] \]  

\[ k_{obs} - k_{acyl}[C₂H₂] = k_{RCN}[RCN] = k'_{RCN} \]  

The rate of change for [C₂H] can be expressed as

\[ d[CH₃CN]/dt = \frac{-[CH₃CN]}{[C₂H]}(k_{HCN} + k_{C₂H₂}) \]  

where \( k_{HCN} \) is the reaction rate coefficient for the HCN reaction and \( k_{C₂H₂} \) is that for the C₂H₂ reaction, both are independent of pressure over this range. This large pressure range was required because of the use of a 1% HCN mixture in He; therefore the number density of He is directly related to the possible HCN concentrations obtained. All gases flow through a mixing cell before entering the low-temperature cell. He, 99.99%, C₂H₂, 99.6%, and HCN, 1.0% in helium, are received, except acetylene, from which acetone was removed by an activated charcoal filter. Commercially available liquid CH₃CN, 99.9%, was vacuum distilled and degassed.

The probe beam is directed onto a 50 MHz liquid N₂ cooled Ge:Au infrared detector with a sensitive area of 20 mm². The transient signals are amplified and co-added using a digital oscilloscope to improve the signal-to-noise ratio. About 1500-3000 transient absorption signals are averaged before the data are stored and analyzed.

3. Results

Rate coefficients are measured under pseudo-first-order conditions where [HCN], [CH₃CN], and [C₂H₂] are \( \gg [C₂H] \). The rate of change for \([C₂H] \) can be expressed as

\[ \frac{d[C₂H]}{dt} = -[C₂H]k_{HCN}[HCN] \]  

where \( k_{HCN} \) is the reaction rate coefficient for the HCN reaction and \( k_{C₂H₂} \) is that for the C₂H₂ reaction, both are independent of pressure over this range. This large pressure range was required because of the use of a 1% HCN mixture in He; therefore the number density of He is directly related to the possible HCN concentrations obtained. All gases flow through a mixing cell before entering the low-temperature cell. He, 99.99%, C₂H₂, 99.6%, and HCN, 1.0% in helium, are received, except acetylene, from which acetone was removed by an activated charcoal filter. Commercially available liquid CH₃CN, 99.9%, was vacuum distilled and degassed.

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An example of a typical C₂H transient decay and corresponding fit for the reaction with HCN is shown in Figure 2. The values of \( k_{HCN} \) are corrected for the C₂H + C₂H₂ contribution by subtraction in (4) using the most recent measurements for C₂H + C₂H₂ contribution [Opansky and Leone, 1996]. The contribution of C₂H + C₂H₂ to \( k_{HCN} \) is between 35 and 70% for the determination of \( k_{HCN} \) and less than 40% for the determination of \( k_{CH₃CN} \). The resulting \( k_{HCN} \) values are plotted as a function of concentration and fit using a linear least squares routine. The resultant slope is equal to \( k_{HCN} \); this is shown in Figure 3 for HCN and CH₃CN. The uncertainty in \( k_{HCN} \) is determined by computing the standard deviation of the mean for each of the plots of \( k_{HCN} \). The reported errors are \( \pm 2\sigma \). The experimental results for C₂H + HCN and CH₃CN are summarized in Table 1, and the corresponding Arrhenius plots are shown in Figure 4. The data can be expressed using the Arrhenius form

\[ k_{RCN} = A \exp \left[ \frac{-E_a}{(RT)} \right] \]  

where \( E_a = (5.3 \pm 2.2) \times 10^{-12} \text{ exp} \left[ (-6.4 \pm 1.2 \text{ kJ/mol})/(RT) \right] \) and \( A = (3.9 \pm 1.2) \times 10^{12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \). The relatively large uncertainty of the Arrhenius parameters is due to the narrow temperature range of the experiments. The observed transient signals can be fit to first-order exponential decays. The standard deviation of each rate constant at a given temperature is taken as the overall experimental uncertainty of each data point (20–30%). The most likely source of systematic error is a reduction in the actual number density of the reactant species due to condensation. The ex-

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

Figure 2. (upper trace) Typical C₂H transient absorption signal at \( T = 360 \text{ K}, \) total pressure 12.3 kPa, \([C₂H₂] = 2.8 \times 10^{14} \text{ molecules cm}^{-3}, [HCN] = 2.5 \times 10^{16} \text{ molecules cm}^{-3}, \) and \( k_{obs} = 0.059 \pm 0.001 \text{ s}^{-1} \) (uncertainty represents 95% confidence limit). (lower trace) Residuals to fitted experimental decay.

Figure 3. Plot of \( k'_{RCN} \) versus \([RCN] \): diamonds, CH₃CN at \( T = 297 \text{ K} \) and \( k_{CH₃CN} = (1.3 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}; \) circles, HCN at \( T = 297 \text{ K} \) and \( k_{HCN} = (3.9 \pm 1.2) \times 10^{13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}. \)

Table 1. Summary of Rate Constants for C₂H + RCN

<table>
<thead>
<tr>
<th>Temperatures, T (K)</th>
<th>( k_{HCN} )</th>
<th>( k_{CH₃CN} )</th>
</tr>
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<tbody>
<tr>
<td>297</td>
<td>( 3.9 \pm 1.2 ) \times 10^{-11}</td>
<td>( 1.0 \pm 0.2 ) \times 10^{-12}</td>
</tr>
<tr>
<td>330</td>
<td>( 4.9 \pm 1.3 ) \times 10^{-13}</td>
<td>( 1.3 \pm 0.2 ) \times 10^{-12}</td>
</tr>
<tr>
<td>360</td>
<td>( 6.2 \pm 1.8 ) \times 10^{-11}</td>
<td>( 1.2 \pm 0.2 ) \times 10^{-12}</td>
</tr>
<tr>
<td></td>
<td>( 3.9 \pm 1.2 ) \times 10^{-12}</td>
<td>( 1.3 \pm 0.2 ) \times 10^{-12}</td>
</tr>
</tbody>
</table>

Here \( k_{HCN} = (5.3 \pm 2.2) \times 10^{-12} \text{ exp} \left[ (-6.4 \pm 1.2 \text{ kJ/mol})/(RT) \right] \) and \( k_{CH₃CN} = (1.8 \pm 1.2) \times 10^{-11} \text{ exp} \left[ (-6.4 \pm 2.0 \text{ kJ/mol})/(RT) \right] \). Values are in units of cm³ molecules⁻¹ s⁻¹.
experiments involving HCN were all performed at temperatures ≥297 K, where HCN does not condense; however, in the case of CH$_3$CN, attempts to measure rate constants below 262 K resulted in erratic pressure measurements, attributed to condensation of CH$_3$CN in the flow cell.

Under the current experimental conditions, the minimum C$_2$H$_2$ density necessary for detection of the C$_2$H radical is approximately 1 × 10$^{13}$ molecules cm$^{-3}$. The rate constant for the reaction of C$_2$H with the precursor C$_2$H$_2$ is rapid, 1.36 × 10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K [Pederson et al., 1993; Opansky and Leone, 1996]. The combination of this extremely fast reaction and the high density of HCN needed to make rate coefficient measurements presents a serious limitation in the current experiment. Thus we are able to measure the HCN reaction only at temperatures of 297 K and above. An attempt to measure the rate constant at 200 K was made to determine whether the rate might show non-Arrhenius behavior and increase again at even lower temperatures; however, there was no evidence that the rate increases at this temperature, and only the experimental decay from the reaction of C$_2$H with the precursor molecule acetylene was observable. Use of a pure sample of HCN would allow for higher densities of the reactant and thus increase the observed first-order decay rate; however, this would also lead to larger concentrations of CN radicals from the resulting HCN photolysis (under the current experimental conditions, the CN radical concentration is estimated to be of the same order as C$_2$H). Another solution would be to improve the sensitivity of the experimental arrangement, by implementing a two-detector signal subtraction scheme to reduce noise from amplitude fluctuations in the laser. Nevertheless, limitations due to the HCN vapor pressure would also make lower temperature measurements difficult. This vapor pressure limitation is observed for CH$_3$CN. Although the lowest possible experimental temperature is approximately 150 K, rate constants for CH$_3$CN could only be determined above 262 K. Measurements at temperatures below 262 K were not possible because of condensation of the CH$_3$CN vapor.

4. Discussion

The experimental results for the reactions of C$_2$H + HCN and C$_2$H + CH$_3$CN show positive temperature dependencies, indicating barriers to reaction, as well as small rate coefficients.

There has been one previous study that examined only the overall product photochemistry of acetylene and hydrogen cyanide mixtures [Becker and Hong, 1983]. In those experiments, photolysis of C$_2$H$_2$ and HCN mixtures were exposed to 185 nm light from a low-pressure mercury lamp (10$^7$ photons/s) for 2 min. Gaseous products were then analyzed by gas chromatography/mass spectroscopy. Photolysis products for 5:1 mixtures of HCN/C$_2$H$_2$ were similar to those of C$_2$H$_2$ (where C$_2$H$_2$, diacetylene, was the major product) except for the formation of a significant amount of acrylonitrile, C$_2$H$_3$CN. Trace amounts of HC$_3$N were reported. Under these conditions, only 10% of the light is absorbed by HCN. At higher HCN/C$_2$H$_2$ ratios, where 40–60% of the light is absorbed by HCN, HC$_3$N becomes a major product. As discussed above, the formation of HC$_3$N is believed to be generated by the possible reactions

\[(\text{R7c'})\]
\[\text{C}_2\text{H} + \text{HCN} \rightarrow \text{HC}_3\text{N} + \text{H}\]
\[\Delta H_{\text{m}} = -126 \text{ kJ mol}^{-1}\]

\[(\text{R9})\]
\[\text{CN} + \text{C}_2\text{H}_2 \rightarrow \text{HC}_3\text{N} + \text{H}\]
\[\Delta H_{\text{m}} = -88 \text{ kJ mol}^{-1}\]

Becker and Hong concluded that reaction (R9) was the major process for the formation of HC$_3$N in their photochemical studies, even though both reactions are exothermic.

The temperature dependence of the kinetic rate coefficients can provide information on the possible mechanisms of the chemical reactions. Although data have been obtained at only three temperatures, the rate constant for C$_2$H + HCN is decreasing substantially with decreasing temperature. Attempts to measure rate constants at temperatures below 297 K were not possible because of the slow rate of the reaction. A positive temperature dependence and large activation energy are typical of either hydrogen abstraction reactions or addition/elimination reactions that proceed over a barrier in the reaction coordinate. An Arrhenius plot that has little or no temperature dependence or a negative temperature dependence is often associated with an addition/elimination reaction.

In order to better understand the possible pathways for the reaction C$_2$H + HCN → products, ab initio calculations have been carried out on the transition states corresponding to both the addition/elimination process (products = HC$_3$N + H) and the hydrogen abstraction mechanism (products = C$_2$H$_2$ + CN). The calculations are carried out with a commercial software package using the 6-31 g (d,p) basis set [Frisch et al., 1995]. Geometries for both transition states and individual molecules are calculated using full Møller-Plesset second-order perturbation theory (MP2). Transition state structures are confirmed in a corresponding vibrational frequency calculation [Foresman and Frisch, 1996]. Final energies are calculated using the quadratic configuration interaction with single and double excitation substitutions (QCISD). The results of these calculations are shown in Figure 5. Classic barriers are determined without corrections for zero-point or thermal energies. The results show that the transition state corresponding...
to the hydrogen abstraction mechanisms lies approximately 43 kJ mol⁻¹ (10 kcal mol⁻¹) higher in energy than the transition state for the addition/elimination mechanism, which suggests that the addition/elimination mechanism is the dominant reaction pathway. Although the calculated classic barrier of 15.9 kJ mol⁻¹ (3.8 kcal mol⁻¹) overestimates the experimental value of 6.4 kJ mol⁻¹ (1.5 kcal mol⁻¹), the presence of a barrier along the reaction coordinate agrees qualitatively with the observed positive temperature dependence.

The measurements for the reaction of C₂H with CH₃CN give rate constants that are very close to those measured previously for methane, CH₄ (k_methane = 1.2 × 10⁻¹⁰ exp [-4.1 kJ/mol]/(RT): 154 < T < 359). Over the observed temperature range, the reaction has a positive temperature dependence and large activation energy. The slower reaction rate for CH₃CN (compared to CH₄) could represent a steric factor due to the presence of the CN group of the CH₃CN; however, based on the experimental measurements and calculations for the C₂H + HCN reaction, an addition/elimination mechanism is likely to contribute to the observed rate constant for C₂H with CH₃CN.

Since this is the first experimental work to directly measure the rate coefficients for reactions (R7a), it is useful to make the comparison with the analogous reactions involving the CN radical, which is isoelectronic with C₂H:

$$k_{R10} = 2.5 \times 10^{-17} T^{-0.71} \exp \left(-\frac{770}{T}\right) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}.$$  In those experiments, only the disappearance of CN was monitored, and no information was obtained on the product channels. The result corresponds to the present work on C₂H + HCN, in that the rate constant for the addition/elimination reaction is relatively small and the reaction shows a strong positive temperature dependence. Yang et al. [1992] calculated a reaction barrier of 13.8 kJ mol⁻¹ (3.3 kcal mol⁻¹) for the reaction CH₃CN → CN + H₂, which is isoelectronic with C₂H.

5. Implications for Formation of Cyanoacetylene on Titan

We first focus on the implications of this work for the chemical formation of cyanoacetylene, HC₃N. Photochemical models of Titan have used various rate constants for reactions (R7c), C₂H + HCN → HC₃N + H and (R9), CN + C₂H₂ → HC₃N + H, which are summarized in Table 2. The rate coefficients used in the models for (R7c), also shown in Figure 4, can be compared to the experimental results obtained here. The results show that the rate constant used in the most recent photochemical model [Lara et al., 1996] is too fast by almost a factor of 30 when compared to the room temperature values obtained here. The two earlier models [Yung et al., 1984; Yung, 1987; Toublanc et al., 1995] use a value which is only a factor of 5 faster than the measured room temperature results. If we make the assumption that the reaction follows the measured Arrhenius behavior, the expected rate constant would be ~1 × 10⁻¹³ at 200 K and ~5 × 10⁻¹⁴ at 170 K (the latter temperature being close to the value of the lower stratosphere on Titan) and the discrepancy only increases.

The photochemical models of Titan make comparisons of their vertical distributions of cyanoacetylene with available Voyager/IRIS data. Lara et al. [1996] pointed out a discrepancy between the mixing ratio of HC₃N determined by Voyager/IRIS data and the value in their model profiles. The results showed that the concentration and column density depended strongly on the eddy diffusion coefficient. Using the eddy diffusion coefficient proposed in their model resulted in vertical profiles for the HC₃N mixing ratio that were too high by nearly 2 orders of magnitude when compared with the available Voyager/IRIS data. Lara et al. noted that the most important reactions in their modeling of HC₃N production are reactions (R7c) and (R9). As mentioned above, the rate constant for (R7c) used in their photochemical model is nearly a factor of 30 faster than the value measured in the current experiments. That value of the rate constant was recommended by Monks et al. [1993] assuming analogous behavior with the addition/elimination reaction C₂H + C₂H₂ → C₂H₃ (CH₃) + H. The overprediction of HC₃N may be further aggravated by the rate constant used for reaction (R9). Using the non-Arrhenius expression given by Lara et al. [1996], the rate cal-

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**Table 2.** Comparison of Experimental Rate Constants for Reactions Leading to HC₃N With Values Used in Recent Photochemical Models of Titan

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>C₂H + HCN → HC₃N + H</td>
<td>5.3 × 10⁻¹² exp (-770/T)ᵃ</td>
<td>2.2 × 10⁻¹²</td>
<td>⋯</td>
<td>2.2 × 10⁻¹²</td>
<td>1.1 × 10⁻¹³</td>
</tr>
<tr>
<td>CN + C₂H₂ → HC₃N + H</td>
<td>~4 × 10⁻¹⁰ᵇ</td>
<td>5 × 10⁻¹¹</td>
<td>2.3 × 10⁻¹¹</td>
<td>3.49 × 10⁻¹¹ exp⁵³¹⁷</td>
<td>5.67 × 10⁻⁹ ᵇ⁰·⁵⁵ exp⁻⁴/³⁷</td>
</tr>
</tbody>
</table>

*Values are in units of cm³ molecules⁻¹ s⁻¹.

ᵃCurrent results.

ᵇFrom Sims et al. [1993], 25 < T < 80 K.
The variations between the three models demonstrate the need for further refinement in both experimental and theoretical investigations.

### Table 3. Parameters and Production Rates of HCN Via C$_2$H + HCN and CN + C$_2$H$_2$ Reaction Pathways

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Yang et al. [1984]</th>
<th>Toublanc et al. [1995]</th>
<th>Lara et al. [1996]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C$_2$H] at 750 km</td>
<td>$3 \times 10^3$ molecules cm$^{-3}$</td>
<td>$10^{-4}$</td>
<td>$2 \times 10^{-5}$ at 400 km$^2$</td>
</tr>
<tr>
<td>[CN] at 750 km</td>
<td>$4 \times 10^4$ molecules cm$^{-3}$</td>
<td>$1.5 \times 10^{-3}$</td>
<td>$8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Mixing ratio C$_2$H$_2$</td>
<td>$7 \times 10^{-4}$</td>
<td>$2.2 \times 10^{-12}$</td>
<td>$1.1 \times 10^{-11}$</td>
</tr>
<tr>
<td>$k$(C$_2$H + HCN)$^b$</td>
<td>$2.2 \times 10^{-12}$</td>
<td>$1 \times 10^{-11}$ (T = 170 K)</td>
<td>$9 \times 10^{-6}$ (T = 170 K)</td>
</tr>
<tr>
<td>$k$(CN + C$_2$H$_2$)</td>
<td>$5 \times 10^{-11}$</td>
<td>$5 \times 10^{-11}$ molecules cm$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$n$(750 km)</td>
<td>$5 \times 10^{-11}$ molecules cm$^{-3}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Production Rates of HCN, molecules cm$^{-3}$ s$^{-1}$

<table>
<thead>
<tr>
<th>Reaction Pathway</th>
<th>This work</th>
<th>Yang et al. [1984]</th>
<th>Toublanc et al. [1995]</th>
<th>Lara et al. [1996]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H + HCN → HCN + H</td>
<td>0.008$^a$</td>
<td>0.3</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>CN + C$_2$H$_2$ → HCN + H</td>
<td>14$^b$</td>
<td>2</td>
<td>75</td>
<td>3600</td>
</tr>
</tbody>
</table>

$^a$Assumed to have small variance between 400 and 750 km.  
$^b$All rate constants have units cm$^3$ molecules$^{-1}$ s$^{-1}$.  
$^c$Using $k = 5 \times 10^{-14}$ (from Arrhenius expression at 170 K based on this work).  
$^d$Using $k = 4 \times 10^{-15}$ [from Sims et al., 1993].
ical work. The use of updated rate coefficients such as those presented here and by other research groups, as well as a prudent analysis of the reaction pathways should allow future models to better estimate atmospheric abundances of major and minor constituents on Titan. The upcoming Cassini/Huygens mission will greatly enhance our current knowledge of Titan's atmosphere.

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References


Frisch, M. J., et al., Gaussian 94, Revision D.4, Gaussian, Pittsburgh, Pa., 1996.


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