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Kinetics of C_2H Reactions with Hydrocarbons and Nitriles in the 104−296 K Temperature Range

Boris Nizamov and Stephen R. Leone*

Departments of Chemistry and Physics and Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720

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Reactions of C_2H with isobutane (k_1), 1-butene (k_2), isobutylene (k_3), 1,3-butadiene (k_4), methyl cyanide (k_5), ethyl cyanide (k_6), and propyl cyanide (k_7) are studied at low temperature using a pulsed Laval nozzle apparatus. The C_2H radical is prepared by 193-nm photolysis of acetylene, and the C_2H concentration is monitored using CH(A $^2\Delta$) chemiluminescence from the $C_2H + O_2$ reaction. The rate constants at low and high temperatures are $k_1 = (1.3 \pm 0.3) \times 10^{-10}$ and $(1.0 \pm 0.2) \times 10^{-10}$ for isobutane, $k_2 = (2.1 \pm 0.4) \times 10^{-10}$ and $(2.2 \pm 0.4) \times 10^{-10}$ for 1-butene, $k_3 = (1.4 \pm 0.3) \times 10^{-10}$ and $(1.2 \pm 0.2) \times 10^{-10}$ for isobutylene, and $k_4 = (2.9 \pm 0.6) \times 10^{-10}$ and $(3.3 \pm 0.6) \times 10^{-10}$ for 1,3-butadiene at $T = 104$ and 296 K, respectively (in units of cm^3 molecule^{-1} s^{-1}). Comparison with existing data shows a trend of a decrease in activation energy with increasing size of the hydrocarbon chain. For these reactions of hydrocarbons containing four carbon atoms, the activation energy is zero within experimental uncertainty, and the rate constants do not depend on temperature in the 104−296 K temperature range. The rate constants for C_2H reactions with methyl cyanide, ethyl cyanide, and propyl cyanide are measured at three temperatures, 104, 165, and 298 K. Measured rate constants are fit to an Arrhenius expression and are $k_5 = (1.8 \pm 0.35) \times 10^{-11} \exp(-766 \pm 38/T)$, $k_6 = (1.5 \pm 0.3) \times 10^{-11} \exp(-145 \pm 10/T)$, and $k_7 = (2.1 \pm 0.4) \times 10^{-11} \exp(-51 \pm 4/T)$ (in units of cm^3 molecule^{-1} s^{-1}, T is in Kelvin). At $T = 296$ K, k_3, k_5, k_6, and k_7 are measured as a function of total pressure and show no pressure dependence in the 0.6−8 Torr (0.08−1.07 kPa) pressure range. Results from this work are compared with the results of previous investigations of C_2H reactions at low temperature and are discussed in relation to the atmospheres of Saturn and Titan.

1. Introduction

The ethynyl radical (C_2H) is an important intermediate in combustion,[1,2] interstellar chemistry,[3−6] and planetary atmospheres.[7,8] This radical plays an important part in the photochemistry of Titan's atmosphere,[9−11] and there is a significant need to understand the low-temperature reactivity of C_2H to interpret the data generated by the Voyager missions[12−14] and the new information that the Cassini mission[15] will obtain. The accuracy of the photochemical models of Titan's atmosphere significantly depends, among other things, on the availability of accurate rate constants and product branching ratios of C_2H reactions in the 70−170 K temperature range, and this work is a part of the research program aimed at providing such data. More general interest in the C_2H reactions at low temperatures arises from the notion that reactions at low collision energies are sensitive to the properties of the entrance channel, and new information about the long-range part of the potential energy surface (PES) can be obtained from low-temperature kinetics studies. The dynamics of reactions at low temperature offer intriguing differences from room-temperature mechanisms, including long-lived collisions, attractive potential surfaces, and tunneling.

A significant amount of work on C_2H reactions with hydrocarbons at low temperatures has been done.[16−25] Rate constants of C_2H reactions in the temperature range important for Titan's atmosphere have been measured for reactions with a variety of hydrocarbon molecules such as methane, acetylene, methylacetylene, allene, ethene, propene, 1-butene, ethane, propane, and *n*-butane.[17−19,22] There are also several theoretical and experimental investigations of C_2H reactions with hydrocarbons at temperatures higher than room temperature.[26−28] Thus, reactions of C_2H with hydrocarbons have been investigated over a wide temperature range, and mechanisms of these reactions are reasonably well understood. At low temperatures, two main mechanisms of C_2H reactions with hydrocarbons are direct hydrogen atom abstraction and addition/elimination (substitution of one of the hydrogen atoms or alkyl group for C_2H). The addition/elimination channel is especially important for interstellar chemistry because it explains the formation of polyynes (H−(C_n)−H). It has been shown that saturated hydrocarbons react with C_2H mainly via direct hydrogen atom abstraction[26,27] and unsaturated hydrocarbons react with C_2H either via addition/elimination[29,30] or direct hydrogen atom abstraction depending on which site of the molecule is the object of C_2H radical attack. Both channels are exothermic, and there is a small barrier for the hydrogen atom abstraction reaction from alkanes with a chain size smaller than four carbon atoms and no barrier for addition to unsaturated hydrocarbons.

Nitrogen-containing compounds such as hydrogen cyanide (HCN), cyanoacetylene (HC_3N), cyanogen (C_2N_2), methyl cyanide (CH_3CN), and others have been identified as components of Titan's atmosphere.[31−33] Reactions of the C_2H radical with more reactive and more abundant nitrogen-containing species play a role in the synthesis of heavier molecules and

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* To whom correspondence to be addressed. E-mail: srl@cchem.berkeley.edu. Phone: 510-643-5467. Fax: 510-642-6262.

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are important for understanding the formation of photochemical smog that is present in Titan's atmosphere. There have been relatively few studies of C_2H reactions with nitrogen-containing molecules compared to the number of investigations done on C_2H reactions with hydrocarbon molecules. In one study, the rate constants for C_2H reactions with HCN and CH_3CN were measured over the 262−360 K temperature range.[34] The products of these two reactions were not investigated in that work, and important questions about products and mechanisms of C_2H reactions with nitriles remain to be answered. Because of the problem of reagent condensation at low temperature, measurements of the rate constants for the $C_2H + HCN$ and $C_2H + CH_3CN$ reactions could not be made for the temperature range important in Titan's atmosphere. The present work extends the temperature range over which the rate constants for the $C_2H + CH_3CN$ reaction are measured down to 165 K. This will allow more reliable extrapolation to the 70−170 K temperature range important for Titan. Because the rate constant for the $C_2H + HCN$ reaction at room temperature is small and the activation energy for this reaction is large (6.4 kJ/mol), measurement of the rate constants for $C_2H + HCN$ was not attempted with the present method.

Continuing previous work on the kinetics of reactions relevant for Titan's photochemistry, the rate constants of seven reactions of C_2H with four hydrocarbons—isobutane ($(CH_3)_2CHCH_3$), 1-butene ($CH_2CHCH_2CH_3$), isobutylene ($(CH_3)_2CCH_2$), and 1,3-butadiene ($CH_2CHCHCH_2$)—and three nitriles—methyl cyanide (CH_3CN), ethyl cyanide (C_2H_5CN), and propyl cyanide (C_3H_7CN)—are measured over the 104−296 K temperature range. Rate constants for C_2H reactions with isobutane, 1-butene, isobutylene, and 1,3-butadiene are compared to the rate constants of C_2H with other hydrocarbons. The rate constants for C_2H reactions with methyl cyanide, ethyl cyanide, and propyl cyanide (RCN) are compared to the rate constants for C_2H reactions with corresponding alkanes, RH. The results are discussed in terms of the atmospheric kinetics of Saturn and Titan.

2. Experimental Section

The pulsed Laval nozzle apparatus has been described in detail previously.[35] Briefly, a Laval nozzle block is mounted on a translational stage inside a vacuum chamber, which is pumped by a mechanical pump (pumping speed ~60 L/s). Low temperatures (165 and 104 K) are produced by the supersonic expansion of gas through low Mach number (M) $M = 2$ and 3 Laval nozzles, respectively. The gas admitted into the chamber through the Laval nozzle block is mainly nitrogen, with small amounts of acetylene, which is the C_2H precursor, and O_2 for monitoring of the C_2H concentration and the reactant. The supersonic expansion is formed by opening a pair of solenoid valves in a preexpansion chamber for ~5 ms. The expansion through the Laval nozzle results in a collimated supersonic gas flow, which has uniform density and temperature distributions. The background pressure is adjusted using a gate valve to obtain the best collimation of the flow. Three milliseconds after the valves are opened, an initial concentration of the C_2H radical is produced by 193-nm photolysis of acetylene using an excimer laser. Typical photolysis energies inside the vacuum chamber are ~30 mJ/cm^2 in an ~10-ns pulse. The laser beam is coaxial with the supersonic flow. Absorption of the photolysis beam by gases in the supersonic expansion is small, and photolysis produces a uniform distribution of the initial C_2H concentration along the length of the supersonic expansion. The C_2H concentration is monitored using the chemiluminescence tracer method, by adding oxygen to the gas flow. In this method, the concentration of C_2H is followed in time by observing $CH(A\ ^2\Delta) \rightarrow (X\ ^2\Pi)$ chemiluminescence produced by the $C_2H + O_2$ reaction. The chemiluminescence signal is detected using a photomultiplier tube (PMT) with a 430-nm band-pass filter (10-nm band pass) and recorded using a multichannel scaler in a photon counting regime. Typically, a radical decay profile is obtained by accumulating signal from 6000 photolysis laser pulses. Time delays for the opening of the pulsed valves, the pulsing of the excimer laser, and the multichannel scaler trigger are generated using a multiple channel digital delay generator. The experiment is run at a 10-Hz repetition rate.

The photolysis energy is low enough so that the contribution of radical−radical and secondary reactions to the removal kinetics of C_2H radicals is small. Under typical conditions of the experiment, the initial concentration of C_2H radicals is on the order of 10^{11} molecules cm^{-3}. For this initial concentration, it is possible to neglect the self-recombination of C_2H, and pseudo-first-order conditions for the measurement of the rate constants are met. The absorption cross sections of methyl cyanide, ethyl cyanide, and propyl cyanide reactants at 193 nm are very small; therefore, there are no complications arising from the possibility that C_2H might react with radicals produced by the photolysis of these reactants. Among the four hydrocarbons, only 1,3-butadiene has a large absorption at 193 nm, and the photolysis laser may dissociate up to 10% of this reactant. The branching ratios of the products from 193-nm photolysis of 1,3-butadiene are known.[36] It is possible to estimate the systematic error in the determination of the $C_2H + C_4H_6$ rate constant (k_4) due to C_2H reactions with the photofragments of 193-nm photolysis of 1,3-butadiene given the branching ratios of the photofragments and the rate constants. For two C_2H reactions with the photofragments $C_2H + C_4H_5$ and $C_2H + C_3H_3$, the rate constants are not known. If the rate constant for the $C_2H + C_4H_5$ reaction is taken to be equal to the rate constant for the $C_2H + C_4H_6$ reaction and the rate constant for the $C_2H + C_3H_3$ reaction is taken to be equal to the rate constant for $C_2H + C_3H_4$ (methyl acetylene), then the systematic error in the determination of k_4 is less than 3%. To summarize, the determination of the rate constants for all seven reactions studied in this work is not affected by the interference of other reactions under the conditions of this experiment.

The temperature of the supersonic expansion is determined by recording the laser-induced fluorescence (LIF) rotational spectrum of the OH A−X electronic transition. Fluorescence is excited via the $A\ ^2\Sigma^+\ (v' = 1) \leftarrow X\ ^2\Pi\ (v'' = 0)$ transition using the frequency-doubled output of a dye laser pumped by a frequency-doubled Nd:YAG laser and detected via the $A\ ^2\Sigma^+\ (v' = 1) \rightarrow X\ ^2\Pi\ (v'' = 1)$ transition using a band-pass filter. The temperature was determined by plotting the natural logarithm of the intensities of the OH $A\ ^2\Sigma^+\ (v' = 1) \leftarrow X\ ^2\Pi\ (v'' = 0)$ rotational lines divided by the degeneracy of the lower rotational states versus the lower rotational state energies. More details about the determination of the temperature in the Laval nozzle supersonic expansion can be found in an earlier report.[16]

The total gas density is calculated using the measured background pressure in the chamber (which should be equal to the pressure in the supersonic expansion) and the temperature of the expansion. The concentration of the reactant is calculated from the total gas density in the supersonic expansion (the total density is typically $(2.1 \pm 0.2) \times 10^{16}$ cm^{-3} for the $M = 3$ nozzle and $(5.7 \pm 0.7) \times 10^{16}$ cm^{-3} for the $M = 2$ nozzle) and the flow rates of the carrier gas, acetylene, oxygen, and the reactant (isobutane, 1-butene, isobutylene, and 1,3-butadiene), which are monitored using flow meters. Because the room-temperature vapor pressures of methyl cyanide, ethyl cyanide, and propyl cyanide are low relative to the pressure in the line connecting the gas-handling manifold and the nozzle block, nitriles are introduced by bubbling part of the nitrogen flow through liquid nitrile samples. Concentrations of the nitriles are varied by changing the ratio of the pure nitrogen flow and the flow through the bubbler. For these three reactants, the concentrations are measured either by measuring the change in the total flow due to the addition of the reactant or by measuring the infrared absorption using an FTIR spectrometer. The total flow rate is measured by measuring a rate of pressure increase in a known volume. Because the flow of the nitrogen is kept constant, the increase in the flow rate when nitrogen is bubbled though the liquid nitrile sample is equal to the flow rate of nitrile vapor. Both the flow measurement method and the FTIR method give the same result within statistical uncertainty. It is worth mentioning that the value of the rate constant for the C_2H reaction with methyl cyanide at room temperature measured in this work is in excellent agreement with the value from an earlier determination,[34] which gives confidence that there are no systematic errors in measuring the nitrile concentrations. The purities of gases are as follows: N_2 99.999%, C_2H_2 99.6%, O_2 99.998%, isobutane 99.9%, 1-butene 99.9%, isobutylene 99.9%, and 1,3-butadiene 99.9%. The purities of methyl cyanide, ethyl cyanide, acrylonitrile, and propyl cyanide are 99%. Because acetylene is stabilized by acetone, it is purified further by passing it through an activated carbon filter. All other chemicals are used without further purification, except for the degassing of the nitrile samples by several freeze−pump−thaw cycles.

For room-temperature measurements, the gas mixture is continuously flowed into the chamber through a port in one of the flanges, bypassing the Laval nozzle block. The pressure (p) range for the room-temperature measurements is $0.6 < p < 8.0$ Torr (0.08−1.07 kPa).

3. Results

Rate constants are measured under pseudo-first-order conditions where the concentration of the reagent is much larger than the C_2H concentration. The kinetics of the C_2H removal under these conditions can be expressed as

$$-\frac{d[C_2H]}{dt} = [C_2H](k[R] + k_{oxygen}[O_2] + k_{acetylene}[C_2H_2]) = k_{obs}[C_2H] \quad (1)$$

where R is the reagent and k is the rate constant for the C_2H + R reaction. The bimolecular rate constants, k, are determined by plotting the observed first-order decay rate constants, k_{obs}, versus the reagent concentration, [R].

Chemiluminescence from the electronically excited CH(A $^2\Delta$) radical produced in the C_2H reaction with O_2 is used to follow the C_2H concentration in time. Details of the 193-nm photolysis of C_2H_2 to create an initial concentration of C_2H radicals and the chemiluminescence tracer method were discussed previously.[37] Under the conditions of our experiment, the chemiluminescence signal is proportional to the C_2H concentration. A typical decay of the chemiluminescence signal is shown in Figure 1a. As can be seen, the plot of the natural logarithm of the signal versus time is linear, confirming that the experiment is done under pseudo-first-order conditions and that the initial concentration of C_2H is uniform along the flow axis. First-order decay rate constants, k_{obs}, are determined from plots such as the one shown in Figure 1a by linear least-squares fitting. Fitting is done starting at a 25 μs delay after the photolysis laser pulse to avoid interference from the scattered laser light and emission produced by the photolysis laser pulse. Figure 1b shows a plot of the first-order decay constants against the reactant concentration for the C_2H reaction with isobutane and butadiene at T = 104 K. The slopes of the lines give the corresponding bimolecular rate constants, k, for isobutane and 1,3-butadiene. The rate constants for the other reactions are obtained from similar plots. The intercept of the first-order rate constant versus the reactant concentration plot is mainly due to C_2H reactions with acetylene and oxygen and to a lesser extent is due to the diffusion of C_2H radicals out of the irradiated zone.

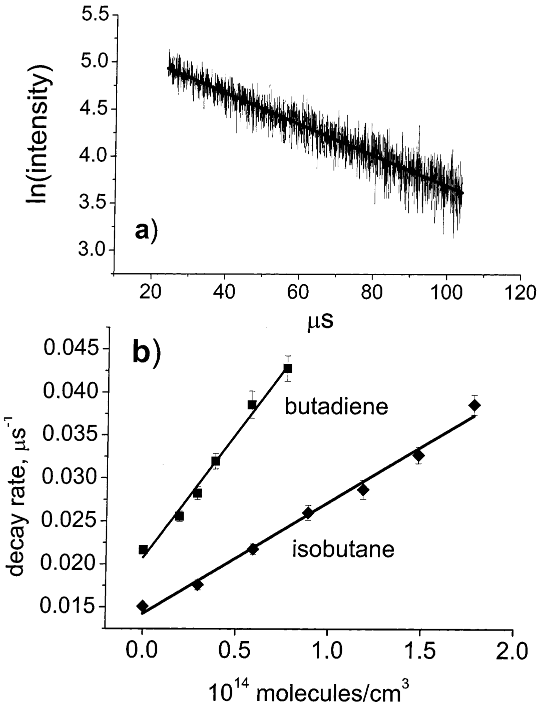

Figure 1. (a) Plot of the natural logarithm of the CH A → X 0−0 chemiluminescence signal vs time. The chemiluminescence signal is proportional to the C_2H concentration under the conditions of the experiment. (b) Plot of the first-order decay rate constants vs the reactant concentration for isobutane (♦) and 1,3-butadiene (■) at T = 104 K. The error bars on the experimental points are the standard deviations from the linear least-squares fitting. The straight lines are least-squares fits to the experimental points.

The pressure dependences of the rate constants at room temperature are investigated by measuring the k_3, k_5, k_6, and k_7 rate constants at several (2−3) values of total pressures. The pressure was varied in the 0.6−8.0 Torr (0.08−1.07 kPa) range, and no pressure dependence was observed within statistical uncertainty. The k_3, k_5, k_6, and k_7 rate constants for T = 296 K reported in Table 1 are the averages of such measurements.

The measured rate constants are summarized in Table 1 along with the uncertainties, which are reported as 2σ. The indicated uncertainties of the rate constants include both the statistical errors and the uncertainty associated with the inhomogeneity of the gas density and temperature profile along the flow axis. The statistical errors for the rate constants of C_2H reactions with the hydrocarbons are small, <5%, and the rate constants are the averages of two measurements. The statistical errors for the rate constants of C_2H reactions with the nitriles are significantly larger, 20−30%, because of relatively large statistical errors in the reactant concentration measurement. In this case, to reduce statistical error in the rate constant, 3−4 measurements are made.

The rate constant for the C_2H + CH_3CN reaction at room temperature from this work is in excellent agreement with the

TABLE 1: Rate Constants[a] for the C_2H Reactions with Hydrocarbons and Nitriles

reactant (k)	temperature, K	total gas density, 10^{16} cm^{-3}	[reactant], 10^{14} cm^{-3}	rate constant 10^{-10} cm^3 molecule^{-1} s^{-1}
isobutane, k_1	104 ± 5	2.1 ± 0.2	0−1.8	1.3 ± 0.3
	296 ± 2	7.87	0−2.0	1.0 ± 0.2
1-butene, k_2	104 ± 5	2.1 ± 0.2	0−0.9	2.1 ± 0.4
	296 ± 2	3.89	0−1.0	2.2 ± 0.4
isobutylene, k_3	104 ± 5	2.1 ± 0.2	0−1.4	1.4 ± 0.3
	296 ± 2	1.9−26	0−2.3	1.2 ± 0.2
1,3-butadiene, k_4	104 ± 5	2.1 ± 0.2	0−0.8	2.9 ± 0.6
	296 ± 2	6.57	0−2.0	3.3 ± 0.6
methyl cyanide, k_5	165 ± 15	5.7 ± 0.7	0−40	0.0015 ± 0.0004
	296 ± 2	1.9−26	0−300	0.0135 ± 0.003
ethyl cyanide, k_6	104 ± 5	2.1 ± 0.2	0−10	0.041 ± 0.008
	165 ± 15	5.7 ± 0.7	0−10	0.048 ± 0.009
	296 ± 2	1.9−26	0−60	0.105 ± 0.02
propyl cyanide, k_7	104 ± 5	2.1 ± 0.2	0−5.0	0.13 ± 0.04
	165 ± 15	5.7 ± 0.7	0−3.0	0.15 ± 0.04
	296 ± 2	0.19−26	0−2.5	0.18±0.03

[a] The indicated uncertainties are represented as $\pm 2\sigma$, where σ is the standard deviation uncertainty.

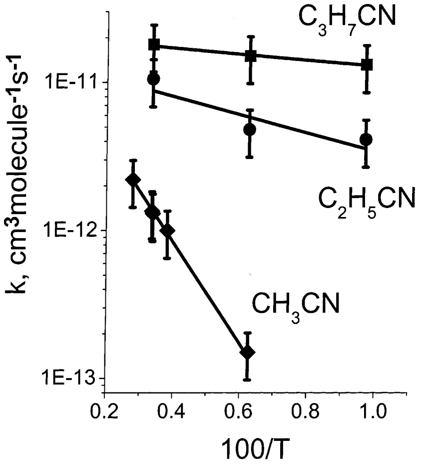

Figure 2. Arrhenius plot of the rate constants for C_2H reactions with methyl cyanide (♦), ethyl cyanide (●), and propyl cyanide (■). Two rate constants for the $C_2H + CH_3CN$ reaction at $T = 262$ and 360 K from the previous work[34] are added to the plot. The fit of the rate constants to an Arrhenius expression (straight lines) gives $k_5 = (1.8 \pm 0.35) \times 10^{-11} \exp(-766 \pm 38/T)$, $k_6 = (1.5 \pm 0.3) \times 10^{-11} \exp(-145 \pm 10/T)$, and $k_7 = (2.1 \pm 0.4) \times 10^{-11} \exp(-51 \pm 4/T)$ (in units of cm^3 molecule^{-1} s^{-1}, T is in Kelvin).

previous study of this reaction.[34] There is also excellent agreement of the rate constants for the C_2H + 1-butene reaction from this study with the rate constants reported in an earlier study.[18]

Figure 2 shows an Arrhenius plot of the rate constants of C_2H with methyl cyanide, ethyl cyanide, and propyl cyanide. The rate constants for the C_2H reaction with methyl cyanide at $T = 262$ and 360 K from an earlier study are added to this plot.[34] The fit of the rate constants to an Arrhenius expression gives $k_5 = (1.8 \pm 0.35) \times 10^{-11} \exp(-766 \pm 38/T)$, $k_6 = (1.5 \pm 0.3) \times 10^{-11} \exp(-145 \pm 10/T)$, and $k_7 = (2.1 \pm 0.4) \times 10^{-11} \exp(-51 \pm 4/T)$ (in units of cm^3 molecule^{-1} s^{-1}). All three reactions have a positive temperature dependence, and the activation energies decrease with an increase in the size of the alkyl group.

4. Discussion

4a. C_2H + Hydrocarbons and Comparison to Previous Work. In this work, the rate coefficients for C_2H reactions with hydrocarbons are measured for two temperatures, $T = 104$ and 296 K, and the rate coefficients for C_2H reactions with nitriles are measured for three temperatures, $T = 104$, 165, and 296 K. Below, the results from this work are compared to the results of previous studies to determine whether the observed temperature dependencies of the rate coefficients are consistent with what is known from the other studies of similar reactions. Out of the four hydrocarbons studied, isobutane is a saturated hydrocarbon (alkane), and the other three hydrocarbons (1-butene, isobutylene, and 1,3-butadiene) are unsaturated hydrocarbons (alkenes). Results of this work for the C_2H reaction with isobutane can be compared to the results from the previous studies of C_2H reactions with isobutane, *n*-butane, and other alkanes.[19,25] In one of the studies of C_2H reactions with alkanes at low temperature, the rate constant for C_2H reaction with isobutane was measured over the 177−298 K temperature range.[25] The rate constants for the C_2H reaction with isobutane from this work are in excellent agreement with the results of previous work,[25] and this work extends the temperature range over which this rate constant is measured down to 104 K. In the other previous study, the rate constants for C_2H reactions with ethane, propane, and *n*-butane were measured in the $104 < T/\mathrm{K} < 298$ temperature range and were fit to an Arrhenius expression; the trend of a decrease in the activation energies with an increase in the size of the hydrocarbon chain was observed.[19] For the C_2H reaction with isobutane, the activation energy for the temperature range $177 < T/\mathrm{K} < 298$ was reported to be $E_a = -28$ K (−0.23 kJ/mol).[25] For the C_2H reaction with *n*-butane, the activation energy for the temperature range $104 < T/\mathrm{K} < 298$ was reported to be zero within experimental uncertainty.[19] As can be seen from Table 1, the activation energy for the C_2H reaction with isobutane is also very close to zero. The rate constants for the C_2H reactions with *n*-butane ($k = (1.3 \pm 0.4) \times 10^{-10}$)[19] and isobutane ($k_1 = (1.3 \pm 0.3) \times 10^{-10}$, this work at $T = 104$ K) are essentially identical. In an earlier study,[19] it was concluded that the C_2H reaction with alkanes proceeds via a hydrogen-atom abstraction mechanism based on the experimental results and available theoretical work.[27,28] Results of this work support this conclusion.

The mechanisms of the C_2H reactions with saturated and unsaturated hydrocarbons are different. As noted above, at low temperatures C_2H reacts with saturated hydrocarbons via the H-atom abstraction mechanism. Reactions of C_2H with unsaturated hydrocarbons can proceed either via the H-atom abstraction mechanism or via the addition/elimination mechanism. 1-Butene, isobutylene, and 1,3-butadiene have both double bonds and alkyl groups, and these molecules can react via both mechanisms. Reactions of these three unsaturated hydrocarbons with C_2H can be compared to reactions of ethene with C_2H to investigate the relative importance of the addition/elimination and the H-atom abstraction mechanisms. In another previous work,[18] the rate constants for C_2H with ethene were measured at $T = 104$ and 296 K. At $T = 104$ and 296 K, the values of the rate constants for the C_2H reaction with ethene are $(1.4 \pm 0.4) \times 10^{-10}$ and $(1.13 \pm 0.14) \times 10^{-10}$ (in units of cm^3 $molecule^{-1}$ s^{-1}), respectively. The values of the rate constants for C_2H reactions at $T = 104$ K with 1-butene ($(2.1 \pm 0.4) \times 10^{-10}$), isobutylene ($(1.4 \pm 0.3) \times 10^{-10}$) and 1,3-butadiene ($(2.9 \pm 0.6) \times 10^{-10}$) are consistent with the expectation that the rate constants for these reactions should be comparable to the value of the rate constant for the $C_2H + C_2H_4$ reaction because at least the addition/elimination channel is open for all of these reactions. Because the temperature dependencies of the rate constants for C_2H radical reactions with large alkanes (*n*-butane and isobutane) and ethene are very similar, it is not possible to distinguish the relative contribution of the two mechanisms on the basis of the temperature dependence of the rate constants for C_2H reactions with 1-butene, isobutylene, and 1,3-butadiene. The Arrhenius activation energies for the C_2H reactions with large alkanes (four carbon atoms or more) are zero or negative, and the rate constants for these reactions are large, comparable to the rate constants for the $C_2H + C_2H_4$ reaction, which also has a negligible activation energy. It is possible that both mechanisms operate with similar efficiencies, and it will be an important task for future studies to quantify the branching ratios for these different mechanisms.

As was mentioned above, the rate coefficients for the C_2H reactions with isobutylene (k_3) and all three nitriles (k_5-k_7) do not show any pressure dependence in the 0.6−8.0 Torr pressure range ($(0.19-2.6) \times 10^{17}$ cm^{-3} density range) of nitrogen at room temperature. The absence of a pressure dependence for k_3 in this pressure range is consistent with previous investigations of the pressure dependence of the rate constants for the reactions of C_2H with hydrocarbons. In one of the previous studies, no pressure dependence of the rate constants for the C_2H + *n*-butane and C_2H + isobutane reactions was observed in the $(0.32-2.9) \times 10^{18}$ cm^{-3} density range of He.[25] In the other work,[23] the pressure dependencies of the rate constants for the $C_2H + C_2H_4$ and $C_2H + C_2H_6$ reactions were investigated in the $(0.5-2.7) \times 10^{18}$ cm^{-3} density range of He, and the rate constants were found to be constant as a function of buffer gas density. The pressure dependence of the rate constant for the $C_2H + C_2H_6$ reaction was investigated in a number of works, and no pressure dependence was observed for gas densities less than 10^{18} cm^{-3}.[19,23,28,38] Lander et al.[38] observed a pressure dependence of the rate constant for the $C_2H + C_2H_6$ reaction for densities of He buffer gas higher than 10^{18} cm^{-3}, which was attributed to the addition channel.

For the C_2H + isobutylene reaction, the lack of a pressure dependence and the small negative temperature dependence of the rate constants are attributed to the formation of a collision complex that undergoes a unimolecular reaction to form final products before it can be stabilized by collisions. The same explanation is also offered for the pressure dependence of the k_5-k_7 rate constants, assuming that the reactions of the larger alkyl cyanides (C_3H_7CN and larger) are similar to those of the corresponding alkanes. It is possible that there is a weak pressure dependence of the C_2H reactions with smaller alkyl cyanides that could not be observed because of the limited pressure range and relatively large (∼25%) statistical errors, or possibly there is only a small difference in the rate constants at the zero and high-pressure limits.

4b. C_2H Reactions with Nitriles. Methyl cyanide and the larger alkyl cyanides can react via both hydrogen-atom abstraction and the addition/elimination mechanisms; both channels are thermodynamically possible, as can be seen by the example of the $C_2H + CH_3CN$ reaction:

$$C_2H + CH_3CN \rightarrow C_2H_2 + CH_2CN \qquad \Delta H_{rxn} = -180 \text{ kJ/mol}$$

$$C_2H + CH_3CN \rightarrow HCCCN + CH_3 \qquad \Delta H_{rxn} = -150 \text{ kJ/mol}$$

The rate constant of the $C_2H + CH_3CN$ reaction, k_5, was measured previously over the 262−320 K temperature range.[34] This work extends the temperature range over which this rate constant is measured down to 165 K. Measuring k_5 at 104 K using a Mach 3 nozzle was not possible because the value of k_5 at this temperature would be too small to be obtained with the Laval method. It is still a relatively large extrapolation from the current lowest temperature point (165 K) to the temperature range important for Titan, but this extrapolation is more reliable than that from the previous lowest temperature, 262 K.

A comparison can be made between the C_2H reaction with the alkyl cyanides, R−CN, and the C_2H reactions with the corresponding alkanes, R−H, on the basis of the temperature dependence of the rate constants. It is expected that the contribution of the H-atom abstraction channel to the rate constant for the C_2H + R−CN reaction becomes larger than the contribution from the addition/elimination channel as the size of R increases. The number of possible transition states for the H-atom abstraction channel (the number of C−H bonds from which C_2H can abstract hydrogen) will increase, and the activation energies for the H-atom abstraction will decrease as the size of R increases. This is expected because the influence of the cyanide group on the properties of the transition states of the alkyl radical, R, is limited to that part of the R−CN molecule adjacent to the cyanide group, and the rest of the molecule will react similarly to the R−H molecule. At the same time, the number of transition states for the addition/elimination channel that produces cyanoacetylene stays constant, and the activation energies for this channel will likely remain positive as the size of R increases. The activation energies for reactions with alkyl cyanides versus the activation energies for reactions with the corresponding alkanes are 6.4 kJ/mol versus 4.1 kJ/mol, 1.2 kJ/mol versus 0.63 kJ/mol, and 0.59 kJ/mol versus 0.42 kJ/mol for R = CH_3, C_2H_5, and C_3H_7, respectively.[22,23] As expected, the activation energies for C_2H reactions with R−CN and R−H become increasingly more equal as the size of R increases. For R = C_3H_7, the temperature dependencies of the rate constants for $C_2H + C_3H_7CN$ and $C_2H + C_3H_8$ are essentially identical. Overall, the rate constants for the C_2H reactions with R−H are larger than the rate constants for the C_2H reactions with R−CN. For the largest R = C_3H_7 studied, the rate constant for the C_2H reaction with C_3H_8 is about 4.5 times larger than the rate constant for the C_2H reaction with C_3H_7CN over the 104−296 K temperature range. This difference is likely to be related to the number of H-atom abstraction sites that have small barriers and contribute most to the rate constant. The cyanide group affects the barriers for the abstraction of hydrogen atoms from CH bonds on the carbon atoms adjacent to the cyanide group, possibly by withdrawing electrons. In a related study, it was found that the rate constant for the C_2H reaction with C_2H_5Cl is approximately 6 times smaller than the rate constant for the C_2H reaction with C_2H_5Br, in agreement with an expectation based on the relative electronegativities of the Cl and Br atoms.[39] Unfortunately, in this earlier study of the C_2H reactions with alkanes only the relative rate constants were measured,[39] and a comparison of the rate constants for the C_2H reactions with C_2H_5CN, C_2H_5Cl, and C_2H_5Br is not possible.

The photochemical models of Titan's atmosphere include CH_3CN, but they limit the loss processes of the species to photolysis and condensation. Because the rate constant for the $C_2H + CH_3CN$ reaction is small relative to the rate constants for C_2H reactions with more abundant hydrocarbons and because the concentration of CH_3CN is low in Titan's atmosphere, C_2H reactions with CH_3CN account for a very small fraction of the C_2H removal by chemical reactions. However, there is a possibility that the reaction $C_2H + CH_3CN \rightarrow HC_3N + CH_3$ may contribute to the synthesis of cyanoacetylene, HC_3N. Currently, there are no theoretical or experimental investigations of the products of the $C_2H + CH_3CN$ reaction to answer the question of whether this reaction contributes significantly to the synthesis of cyanoacetylene. For a related reaction, $C_2H + HCN$, it is suggested that because the calculated barrier for the H-atom abstraction (66 kJ/mol) is higher than the barrier for the addition/elimination (16 kJ/mol) for this reaction the addition/elimination channel could be more important than the H-atom abstraction channel.[34] The agreement between the calculated barriers and the experimentally determined activation energy (6.4 kJ/mol) for the $C_2H + HCN$ reaction is qualitative;[34] however, the conclusion that both channels may contribute to the reaction mechanism seems reasonable. It is difficult to predict how replacing the H atom in HCN with a CH_3 group changes the relative importance of the H-atom abstraction and the addition/elimination channels in the overall reaction mechanism for the $C_2H + CH_3CN$ reaction; however, currently there is no evidence that the addition/elimination channel that produces cyanoacetylene does not occur. Further theoretical and experimental studies are needed to answer the question about the products of the $C_2H + CH_3CN$ reaction.

An attempt was made to study the reaction of C_2H with acrylonitrile (propenenitrile), C_2H_3CN. Although acrylonitrile has not been observed yet in Titan's atmosphere, it is likely to be present, and it is included in current photochemical models.[9,10] Acrylonitrile has been observed in a previous study that examined the overall product photochemistry of acetylene and hydrogen cyanide mixtures to simulate the chemical evolution of a N_2/CH_4 atmosphere.[40] In that study, 5:1 mixtures of HCN/C_2H_2 were exposed to 85-nm light from a low-pressure mercury lamp (10^7 photon/s) for 2 min, and then products of the photolysis were analyzed by gas chromatography/mass spectrometry. Interestingly enough, a significant amount of acrylonitrile was observed among the photolysis products. One of the reactions that controls the concentration profiles of acrylonitrile in Titan's atmosphere is its reaction with C_2H; therefore, an experiment was tried to measure the rate constant for the $C_2H + C_2H_3CN$ reaction. Unfortunately, the absorption cross section of acrylonitrile at 193 nm is large, and for the concentrations of acrylonitrile necessary to produce a measurable change in the first-order rate constant, k_{obs}, a significant fraction of the photolysis beam is absorbed by this reactant. Because it is necessary for the kinetic measurements that the photolysis produces a uniform initial concentration of the C_2H radical along the length of the supersonic flow, it was not possible to study this important reaction.

4c. Progress in the Measurement of Rate Coefficients for C_2H Reactions Relevant to the Photochemistry of Titan and the Outer Planets. Thus far, the rate constants for C_2H reactions with hydrocarbon molecules in the temperature range important for Titan have been measured for all hydrocarbons with three carbon atoms (C_3 hydrocarbons) or less and now for five hydrocarbons (*n*-butane, isobutane, 1-butene, isobutylene, 1,3-butadiene) with four carbon atoms (C_4 hydrocarbons). Currently, the photochemical models of Titan's atmosphere include C_2H reactions with hydrocarbons up to C_3 and polyynes (C_4H_2, C_6H_2). C_4 hydrocarbons except for C_4H_2 are not included in the photochemical models because of their low vapor pressure at low temperatures. However, as the models become more accurate and more detailed laboratory measurements of the rate constants and branching ratios become available, the inclusion of such hydrocarbons into the models may become warranted. Reactions of C_2H with larger hydrocarbons may be important in environments other than Titan's atmosphere. Gladstone et al.[41] urged that there be more rate determinations with C_3 and larger hydrocarbon species, and they indicated that these rates will be important in understanding carbon partitioning in Jupiter. Some of the important reactions in hydrocarbon chemistry that are included in the photochemical models but have not been studied experimentally include the $C_2H + C_4H_2$ and $C_2H + C_6H_2$ reactions and radical−radical reactions. Current photochemical models assume that the values for the rate constants of the $C_2H + C_4H_2$ and $C_2H + C_6H_2$ reactions are the same as for the $C_2H + C_2H_2$ reaction. Experimental measurements of the branching ratios for C_2H reactions with hydrocarbons at low temperatures are scarce, and such measurements are important when it is not obvious from theoretical calculations or other considerations what the reaction products are.

There has been very little work on the kinetics of C_2H reactions with nitrogen-containing species relevant to the photochemistry of Titan and the outer planets. The number of C_2H reactions with nitrogen-containing species for which the rate constants are measured is significantly less than the number of such reactions that are important for the photochemistry of Titan and the outer planets. The continuation of the current work on low-temperature gas-phase chemistry is important for the practical purpose of understanding chemistry in the atmospheres of the outer planets and the chemistry of interstellar clouds and for the understanding of chemical dynamics at low collision energies.

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