Absolute Rate Constant and Product Branching Ratios for the Reaction between H and C_2H_3 at T = 213 and 298 K

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The discharge-flow kinetic technique coupled to mass-spectrometric detection has been used to determine the variable-temperature dependence of the rate constant and product branching ratios for the reaction between H and C_2H_3 at 1 Torr nominal pressure (He). Atomic hydrogen was produced from the reaction between $F(^{2}P)$ and H_{2} while the vinyl radical was produced simultaneously from the reaction between $F(^{2}P)$ and ethylene, which gives both C_2H_3 and H. The reaction was studied at T = 213 and 298 K by monitoring the decay of C_2H_3 in the presence of a large excess of H. The rate constants were determined to be $k(H+C_2H_3)(298 \text{ K})$ $= (1.1 \pm 0.3) \times 10^{-10}$ and $k(H+C_2H_3)(213 \text{ K}) = (1.0 \pm 0.3) \times 10^{-10}$ both in the units cm³ molecule⁻¹ s⁻¹; the quoted uncertainty represents total errors. The activation energy for the reaction between H and C_2H_3 is therefore near zero over the temperature range studied. Further, the fractional product yields for the channels $H + C_2D_3 \rightarrow C_2D_3H$ (a) and $H + C_2D_3 \rightarrow C_2D_2 + HD$ (b) were determined by quantitatively measuring the yields of both C₂D₃H and HD independently. The derived fractional product yields were $\Gamma_a(298 \text{ K}) = 0.33$ ± 0.13 , $\Gamma_b(298 \text{ K}) = 0.67 \pm 0.18$, $\Gamma_a(213 \text{ K}) = 0.24 \pm 0.09$, and $\Gamma_b(213 \text{ K}) = 0.76 \pm 0.16$, where the quoted uncertainty represents total errors. Quantum RRK (QRRK) calculations have been undertaken to investigate the relationship between the observed kinetics, products, and possible mechanisms. With the available data and the QRRK calculations, a mechanism of the form $H + C_2H_3 + M \Leftrightarrow [H - C_2H_3]^* \rightarrow C_2H_4 + M$ (a) and $H + C_2H_3 \rightarrow H_2 + C_2H_2$ (b) is shown to be most likely. Further, Troe calculations have been undertaken in order to suggest values for the limiting low-pressure rate coefficients. A brief comparison is made between the results of the Troe and QRRK analyses. The implications for the conversion of C_2H_2 to C_2H_6 in the relatively low temperature conditions of planetary atmospheres are briefly discussed.

and C_2H_5 .¹⁸

Introduction

The kinetics of vinyl reactions have implicit importance in the observed chemistry of extraterrestrial planetary atmospheres,¹ combustion processes,² and dense interstellar clouds.³ The roles of small C₂ radicals such as ethynyl⁴ and vinyl⁵ are significant in such systems, as they can serve to interconvert hydrocarbon species. The radical species are produced in such systems by one of three methods: either thermal or vacuum ultraviolet dissociation from a stable precursor molecule or production *via* chemical reaction. In the atmosphere of Titan for example, C₂H₃ is produced by the reaction^{1,6}

$$\mathbf{H} + \mathbf{C}_2 \mathbf{H}_2 + \mathbf{M} \rightarrow \mathbf{C}_2 \mathbf{H}_3 + \mathbf{M} \tag{1}$$

Limited information is available on the spectroscopy and reaction kinetics of the vinyl radical. Electronic absorption spectroscopy has shown a weak system in the visible⁷ and a more intense absorption in the vacuum ultraviolet.⁸ The photoelectron spectrum of the vinyl radical has been measured, but it is difficult to get an accurate adiabatic ionization energy,

mann *et al.*¹⁷ derived a relative value for $H + C_2H_3$ normalized to the rate constant for the reference reaction $H + C_2H_5$.

as the threshold transition is very weak.⁹ Ab-initio,¹⁰ RRK-

(M),¹¹ and other theoretical calculations¹² have been used to

evaluate vinyl reaction rate constants. Absolute or relative rate

constants have been determined at T = 298 K for the reactions

of vinyl with Cl₂,¹³ O₂,^{8,14,15a} CH₃,¹⁶ O,¹⁷ H,^{16a,17} C₂H₃,¹⁶ HCl,¹⁵

 $H + C_2 H_3 \rightarrow C_2 H_4$ $\Delta H^{\circ}_{298} = -431 \text{ kJ mol}^{-1}$ (2a)

The reaction has the potential to be important in both the

relatively low temperatures of planetary atmospheres and the

elevated temperatures of combustion processes. There are two

recent direct, but not absolute, experimental determinations of

the room-temperature rate constant. Fahr et al.^{16a} used laser

 $\rightarrow C_2 H_2 + H_2$ $\Delta H^{\circ}_{298} = -255 \text{ kJ mol}^{-1}$ (2b)

the rate constant for the reaction between H and C_2H_3 .

To date there have been no direct absolute measurements of

In this paper we report the first absolute, direct, and variabletemperature determination of the rate constant and product

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branching ratios for the reaction between H and C_2H_3 . The measurements were undertaken using the discharge-flow kinetic technique coupled to mass-spectrometric detection at a nominal pressure of 1 Torr. Quantum RRK (QRRK) calculations are undertaken in order to investigate the relationship between the mechanism of the reaction between H and C_2H_3 and the observed kinetics and product branching ratios. A Troe analysis is subsequently applied to suggest a form for the implied pressure dependence of reaction 2. The planetary implications for the rate parameters and product branching ratios for H + C_2H_3 are discussed briefly.

Experimental Section

A. Discharge Flow Reactor. All experiments were performed in a Pyrex flow tube, ~ 60 cm long and 28 mm in diameter, the inner surface of the tube being lined with Teflon. The flow tube was used at ambient temperatures or cooled by circulating fluids from a reservoir through a jacket surrounding the flow tube. The flow tube was coupled via a two-stage stainless steel collision-free sampling system to a quadrupole mass spectrometer (Extrel, Inc.) that was operated at low electron energies (typically <20 eV) in order to minimize fragmentation. For example, a nominal ionization energy of 11 eV was employed to monitor the C_2H_3 radical, thereby minimizing formation of $C_2H_3^+$ via dissociative ionization of C_2H_4 ⁹ The stable products C_2D_3H and HD from the $H + C_2D_3$ reaction were monitored at ~ 20 eV. Ions were detected by an off axis channeltron multiplier (Galileo Electro Optics Corp.). Molecular reactants were admitted via a Pyrex movable injector, the position of which could be changed between a distance of 2 and 40 cm from the sampling point. This system has been described in detail previously.^{19,20}

Helium carrier gas was flowed at rates between 450 and 800 cm³ min⁻¹ (STP) into the reaction vessel. The linear flow velocity ranged from 1500 to 2700 cm s⁻¹ at nominal pressures in the region of 1 Torr (133.32 Pa). In calculating the linear flow velocity, the plug flow assumption was made. The flow velocity is calculated from the gas constant, temperature, cross-sectional area of the flow tube, total gas flow, and total pressure. Gas flows were measured and controlled by electronic flow meters (MKS). A side arm, at the upstream end of the flow tube, contained a microwave discharge (<70 W, 2450 MHz) for the production of atomic species.

B. Production of C_2H_3 and **H.** Fluorine atoms were produced at the upstream end of the flow reactor by passing molecular F_2 (5% diluted in helium) through a microwave discharge; up to 95% of the F_2 was dissociated in the discharge. The discharge region consisted of a ${}^{3}/_{8}$ in. ceramic tube mounted inside the discharge arm. At the tip of the sliding injector both C_2H_3 and H were produced simultaneously *via* the reactions

$$\mathbf{F} + \mathbf{C}_2 \mathbf{H}_4 \rightarrow \mathbf{C}_2 \mathbf{H}_3 + \mathbf{HF} \qquad \Gamma = 0.35 \qquad (3a)$$

$$\rightarrow C_2 H_3 F + H \qquad \Gamma = 0.65 \qquad (3b)$$

$$k_3(298 \text{ K}) = 2.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 21)}$$

the branching ratio (Γ) having been determined by Slagle and Gutman, 22 and

$$\mathbf{F} + \mathbf{H}_2 \rightarrow \mathbf{H} + \mathbf{H}\mathbf{F} \tag{4}$$

$$k_4(298 \text{ K}) = 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 23)}$$

The ratio of [F] to $[H_2]$ and $[C_2H_4]$ was adjusted to produce the

requisite $[H]/[C_2H_3]$ (see Results for details). Formation of H and C_2H_3 was essentially complete within 2–3 cm of the injector tip.

C. Titration of F. Absolute F atom concentrations were determined by the fast titration reaction

$$\mathbf{F} + \mathbf{Cl}_2 \rightarrow \mathbf{Cl} + \mathbf{ClF} \tag{5}$$

$$k_{\rm 5}(298 \text{ K}) = 1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{ref } 24)$$

The F atom concentration was determined by measuring the decrease in the Cl_2^+ signal when the discharge was initiated. The absolute F concentration is given by $[F] = [Cl_2]_{disc off} - [Cl_2]_{disc on}$. As discussed previously for N atom studies,²⁵ a number of precautions were taken in order to avoid systematic errors in this type of measurement. Resultant fluorine atom concentrations were in the region $10^{12}-10^{13}$ molecule cm⁻³.

D. Materials. Helium (99.999%, Air Products) was dried by passage through a trap held at T = 77 K before entering the flow system. F₂ (99.9%, Cryogenic Rare Gases, 5% in He), H₂ (99.999%, Scientific Gas Products UHP), D₂ (99.5%, MSD Isotopes), and Cl₂ (99.9%, Matheson, 3.5% in He) were used as provided without further purification. C₂H₄ (99.999%, Matheson) and C₂D₄ (99.995%, MSD Isotopes) were degassed using repeated freeze-pump-thaw cycles at liquid nitrogen temperature.

Results

A. Kinetics. Rate coefficients for the reaction

$$H + C_2 H_3 \rightarrow \text{products}$$
 (2)

were measured under pseudo-first-order conditions by monitoring the decay of C_2H_3 as a function of contact time in the presence of excess H. With [H] > [C_2H_3], the decay of C_2H_3 is given by the expression

$$\ln[C_2H_3]_t = -k_{obs}(\frac{d}{v}) + \ln[C_2H_3]_0$$
(6)

where k_{obs} is the pseudo-first-order decay constant, d is the contact distance from the tip of the sliding injector to the sampling pinhole, and v is the linear flow velocity. Linear leastsquares analyses of plots of $\ln(C_2H_3 \text{ signal})$ at m/z = 27 vscontact distance yield the pseudo-first-order rate constants, k_{obs} . Corrections (3-12%) to k_{obs} to account for axial diffusion were made to give k_{corr} , according to the method described by Lewis et al.²⁶ The diffusion coefficient for C_2H_3 in He at T = 298 K was estimated to be $D = 592 \text{ cm}^2 \text{ s}^{-1}$ using the method in ref 26. At T = 213 K, D = 358 cm² s⁻¹ was calculated from the T = 298 K value by allowing for the $T^{3/2}$ dependence. Corrections for radial diffusion were not necessary, since they were always smaller than axial diffusion. As the ratio of $[H]/[C_2H_3]$ was large (156/1 to 28/1), no correction was made for the small depletion of H (0.6-4%) caused by reaction with C_2H_3 . The bimolecular rate coefficient, k_2 , is then related to $k_{\rm corr}$ through the expression

$$k_{\rm corr} = k_2[{\rm H}] + k_{\rm w} \tag{7}$$

where k_w is a first-order rate constant which accounts for the loss of C₂H₃ on the walls of the flow tube. The reaction between H and C₂H₃ was studied at both room temperature ($T = 298 \pm 2$ K) and subambient temperature ($T = 213 \pm 1$ K).

The ratio of $[H]/[C_2H_3]$ formed at the tip of the sliding injector can be ascertained from

$$\frac{[\mathrm{H}]}{[\mathrm{C}_{2}\mathrm{H}_{3}]} = \frac{\Gamma_{3b}k_{3}[\mathrm{C}_{2}\mathrm{H}_{4}] + k_{4}[\mathrm{H}_{2}]}{\Gamma_{3a}k_{3}[\mathrm{C}_{2}\mathrm{H}_{4}]}$$
(8)

Thus [H] and $[C_2H_3]$ are given by

$$[C_2H_3] = \frac{[F]}{1 + \frac{[H]}{[C_2H_2]}}$$
(9)

and

$$[H] = [F] - [C_2 H_3]$$
(10)

Resultant ratios of $[H]/[C_2H_3]$ were between 28-149 at T =298 K and 42-156 at T = 213 K. For each value of [H], separate experiments covered a range of $[C_2H_3]_0$. At T = 298K it was observed that the pseudo-first-order rate constant k_{obs} (see eq 6) was independent of the ratio $[H]/[C_2H_3]$ for values of the ratio between 28 and 149. However, k_{obs} increased for experiments with low values of $[H]/[C_2H_3] = 15$ and 26 due to contributions from the C_2H_3 self-reaction. In addition, experiments with $[C_2H_3]_0 \le 2 \times 10^{10}$ molecule cm⁻³ had too low a signal level to yield reliable pseudo-first-order decays. Both the low $[H]/[C_2H_3]$ and low $[C_2H_3]_0$ experiments, which were all in the lower range of [H] values, where it is difficult to achieve high pseudo-first-order ratios, were excluded from the data. On the basis of the experience at T = 298 K, we restricted the experiments at T = 213 K to those with $[H]/[C_2H_3] \ge 42$ and with $[C_2H_3]_0 \ge 2.5 \times 10^{10}$ molecule cm⁻³. Modeling studies showed that, under the time scales and concentration regimes of our experiments and with the ratio $[H]/[C_2H_3]$ restricted to the large values as discussed above, the contribution of the vinyl self-reaction (eq 11) was less than 3%.

$$C_2H_3 + C_2H_3 \rightarrow (E)-C_4H_6 (1,3 \text{ butadiene})$$
 (11a)

$$C_2H_3 + C_2H_3 \rightarrow C_2H_4 + C_2H_2 \tag{11b}$$

$$k_{11a}(298 \text{ K}) = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 16a)}$$

$$k_{11b}(298 \text{ K}) = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 16a)}$$

Possible contributions from the reactions

8

$$\mathbf{H} + \mathbf{C}_2 \mathbf{H}_2 + \mathbf{M} \rightarrow \mathbf{C}_2 \mathbf{H}_3 + \mathbf{M}$$
(12)

 $k_{12}(298 \text{ K}, 1 \text{ Torr of He}) =$

$$3.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 27)}$$

and

$$\mathbf{H} + \mathbf{C}_2 \mathbf{H}_4 + \mathbf{M} \rightarrow \mathbf{C}_2 \mathbf{H}_5 + \mathbf{M} \tag{13}$$

 $k_{13}(298 \text{ K}, 1 \text{ Torr of He}) =$

$$6.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 28)}$$

to the depletion of H or the reformation of C_2H_3 are negligible (<1%) under the conditions of the experiment.

Tables 1 and 2 summarize the rate data and experimental conditions for the reaction between H and C₂H₃ at T = 298 K and T = 213 K, respectively. Figures 1 and 2 show the variation in the pseudo-first-order rate constant k_{corr} with [H] at each temperature. A linear least-squares analysis of the data according to eq 7 gives bimolecular rate constants of $k_2(298 \text{ K}) = (1.06 \pm 0.11) \times 10^{-10}$ and $k_2(213 \text{ K}) = (0.99 \pm 0.15) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. The intercepts $k_w = 96 \pm 147$ and $67 \pm 134 \text{ s}^{-1}$ are consistent with a vinyl wall loss of 80 s⁻¹, as previously determined.²⁹ Quoted uncertainties include statistical errors at the 1σ level. If the neglected corrections to k_{obs} for radial diffusion and to [H] for depletion of H are included, the

TABLE 1: Summary of Rate Data for the Reaction H + C_2H_3 at T = 298 K

$[H]/10^{12}$ molecule cm ⁻³ a	no. of decays	$[C_2H_3]/10^{11}$ molecule cm ⁻³	[H]/[C ₂ H ₃]	average ^b k_{con}/s^{-1}
2.99	3	0.59-0.96	32-51	468 ± 104
5.03	3	0.64 - 1.24	40-79	662 ± 51
6.24	2	1.61, 2.05	30, 39	840 ± 98
6.91	3	0.67 - 1.10	62-103	744 ± 29
7.51	6	0.51 - 2.64	28-149	795 ± 104
10.1	4	1.31-2.52	40 - 78	1235 ± 158
11.0	7	0.75-2.82	39-149	1280 ± 204

^{*a*} Δ [H] for each set varies from ±0.3 to ±1.5%. ^{*b*} Quoted errors are statistical at one standard deviation. [H₂] = (9.22-9.95) × 10¹³ molecule cm⁻³. [C₂H₄] = (1.78-9.02) × 10¹¹ molecules cm⁻³. nominal pressure = 1 Torr (He).

TABLE 2: Summary of Rate Data for the Reaction $H + C_2H_3$ at T = 213 K

$[H]/10^{12}$ molecule cm ^{-3 a}	no. of decays	$[C_2H_3]/10^{11}$ molecule cm ⁻³	[H]/[C ₂ H ₃]	average ^b k_{corr}/s^{-1}
3.90	3	0.25-0.62	63-155	452 ± 117
7.22	3	0.47 - 1.37	52-156	816 ± 30
8.52	4	0.55 - 1.84	46-156	850 ± 133
9.94	3	1.26-1.87	53-79	955 ± 45
10.7	2	1.95, 2.56	42.55	1284 ± 197

^{*a*} Δ [H] for each set varies from ± 0.3 to $\pm 0.8\%$. ^{*b*} Quoted errors are statistical at one standard deviation. [H₂] = (1.28-1.35) × 10¹⁴ molecule cm⁻³. [C₂H₄] = (2.22-11.1) × 10¹¹ molecule cm⁻³. nominal pressure = 1 Torr (He).



Figure 1. Summary plot of the pseudo-first-order rate constant k_{corr} vs [H] for the reaction H + C₂H₃ at $T = 298 \pm 2$ K.

derived values for k_2 at both T = 298 and 213 K increase by less than the quoted 1σ levels. To allow for systematic errors, mostly in [H], we add an additional $\pm 15\%$ uncertainty to obtain the rate constants $k_2(298 \text{ K}) = (1.1 \pm 0.3) \times 10^{-10}$ and $k_2(213 \text{ K}) = (1.0 \pm 0.3) \times 10^{-10} \text{ cm}^3$ molecule⁻¹ s⁻¹. Given a consideration of the rate data within the error limits at T = 213and 298 K, the activation energy for reaction 2 is apparently near zero over the temperature range studied.

B. Products. In order to determine the product branching ratios at both T = 298 and T = 213 K, measurements were made on the absolute yields of both ethylene and molecular hydrogen. To discriminate between ethylene and H₂ used as precursors for vinyl and H production and ethylene and H₂ produced as products of reaction 2, isotopic labeling was used. C₂D₄ was used as a C₂D₃ source leading to

$$\mathbf{H} + \mathbf{C}_2 \mathbf{D}_3 \rightarrow \mathbf{C}_2 \mathbf{D}_3 \mathbf{H} \tag{2a}$$

$$\rightarrow C_2 D_2 + HD$$
 (2b)



[H] / 10¹² molecule cm⁻³

Figure 2. Summary plot of the pseudo-first-order rate constant k_{corr} vs [H] for the reaction H + C₂H₃ at $T = 213 \pm 1$ K.

where the branching fractions Γ are given by

$$\Gamma_{2a} = \frac{k_{2a}}{k_{2a} + k_{2b}} \tag{14}$$

and

$$\Gamma_{2b} = \frac{k_{2b}}{k_{2a} + k_{2b}}$$
(15)

$$\Gamma_{2b} = 1 - \Gamma_{2a} \tag{16}$$

This treatment assumes that substitution of C_2D_3 for C_2H_3 does not alter the branching fractions Γ_{2a} and Γ_{2b} within experimental uncertainty for a rapid reaction such as reaction 2 which occurs without an energy barrier. The typical conditions used were $[H] = 1 \times 10^{13}$ molecule cm⁻³ and $[C_2D_3] = 5 \times 10^{11}$ molecule cm^{-3} , insuring that reaction 2 went to completion in about 3 ms. The $[H]/[C_2D_3]$ ratio was maintained at about 20; this represents a compromise between keeping $[C_2D_3]$ small enough to minimize the vinyl self-reaction but large enough to quantitatively measure the products C_2D_3H and HD. These two products were chosen as they are not formed in the C_2D_3 + C_2D_3 self-reaction (as C_2D_2 is). Thus, the occurrence of the $C_2D_3 + C_2D_3$ self-reaction has no effect on the observed ratio of the products C_2D_3H/HD , which is identified with Γ_{2a}/Γ_{2b} ; it only affects the final absolute concentration of C₂D₃H and HD. In order to determine the product yield, the observed product signals were monitored as a function of distance (reaction time). The product profiles consisted of an increasing signal which leveled off, indicating that the $H + C_2D_3$ reaction had gone to completion. The final product signal levels were taken as the average of the signals in this plateau region. The magnitudes of the product signals were calibrated using a range of appropriate known concentrations of a reference compound under similar flow conditions. For C_2D_3H , the reference compound was C₂D₄, assuming the mass spectral sensitivities for the two isotopomers were the same. For HD, the system was calibrated for H_2 and D_2 and the average of these was taken as a composite signal calibration for HD. The fractional product branching ratios Γ were then calculated *via* the equations

$$\Gamma_{2a} = \frac{[C_2 D_3 H]}{[C_2 D_3 H] + [HD]}$$
(17)

$$\Gamma_{2b} = \frac{[\text{HD}]}{[\text{C}_2\text{D}_3\text{H}] + [\text{HD}]}$$
(18)

TABLE 3: Summary of the Experimentally Determined Product Branching Ratios Γ_{2a} and Γ_{2b} at T = 298 and T = 213 K for the Reactions $H + C_2D_3 \rightarrow C_2D_3H$ (2a) and $H+C_2D_3 \rightarrow C_2D_2 + HD$ (2b)

<i>T/</i> K	$[H]/10^{12}$ molecule cm ⁻³	$[C_2D_3]/10^{11}$ molecule cm ⁻³	$\Gamma_{2\mathrm{a}}{}^a$	$\Gamma_{2b}{}^b$
298	8.29	4.96	0.27	0.73
298	2.45	1.18	0.44	0.56
298	11.0	5.34	0.27	0.73
298	4.65	2.25	0.35	0.65
			$\langle 0.33 \pm 0.08 \rangle^{c}$	$\langle 0.67 \pm 0.08 \rangle^{c}$
213	11.0	5.34	0.20	0.80
213	6.59	3.19	0.29	0.71
213	11.2	5.44	0.23	0.77
			$(0.24 \pm 0.05)^{\circ}$	$\langle 0.76 \pm 0.05 \rangle^c$

^{*a*} Γ_{2a} is the branching ratio for the product channel forming C₂D₃H. ^{*b*} Γ_{2b} is the branching ratio for the product channel forming C₂D₃ + HD. ^{*c*} Quoted errors are statistical at one standard deviation. [H₂] = 1.74 or 2.32 × 10¹⁴ molecule cm⁻³. [C₂D₄] = 3.14 × 10¹² molecule cm⁻³. nominal pressure = 1 Torr (He).

TABLE 4: Comparison of the Rate Constants Measured or Estimated for the Reaction $H + C_2H_3$ at T = 298 K

k_2/cm^3 molecule ⁻¹ s ⁻¹	pressure of He/Torr	technique ^a	ref
$(1.1 \pm 0.3) \times 10^{-10}$	1.1	DF-MS	this work
$(2.0 \pm 0.8) \times 10^{-10}$	100	LP-UVA	16a ^c
6.0×10^{-11}	100-800	estimate	30
$(5 \pm 3) \times 10^{-11}$	0.2 - 3.0	DF-MS ^b	17

^a DF-MS, discharge flow-mass spectrometry; LP-UVA, laser UV absorption. ^b Relative to $k(H+C_2H_5)$; temperature poorly defined. ^c A very recent remeasurement using the same LP-UVA technique yields $k_2 = (1.8 \pm 0.4) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ in excellent agreement with ref 16a but with reduced uncertainty: Fahr, A. *Int. J. Chem. Kinet.* **1995**, *27*, 769.

The fractional product yield results are summarized in Table 3 and give the following branching ratios: $\Gamma_{2a}(298 \text{ K}) = 0.33 \pm 0.13$, $\Gamma_{2a}(213 \text{ K}) = 0.24 \pm 0.09$, $\Gamma_{2b}(298 \text{ K}) = 0.67 \pm 0.18$, $\Gamma_{2b}(213 \text{ K}) = 0.76 \pm 0.16$, where the quoted uncertainties include statistical errors at the 1 σ level plus an additional 15% to allow for systematic errors in product signal calibration. One should consider the possibility of a contribution to the collisionally stabilized C₂D₃H, where the stabilization is provided by collision of C₂D₃H* with the walls of the flow tube. However, the time scale for stabilization by collision with He at 1 Torr pressure is more than 2 orders of magnitude faster than that for diffusion to the wall for a flow tube with a radius of 1.1 cm.

In order to put these branching ratios on an absolute basis, we also examined the ratio of $[C_2D_3H] + [HD]$ formed compared to initial $[C_2D_3]$. The value of the ratio was 1.05 at T = 298 K and 0.80 at T = 213 K but with rather large uncertainties (34% and 15%, respectively). This demonstrates that there was only minor occurrence of C_2D_3 self-reaction and little contribution from other possible channels of $H + C_2D_3$ which reduce the ($[C_2D_3H] + [HD]$)/ $[C_2D_3]$ ratio below the level of unity. Thus, reactions 2a and 2b are the only significant reaction channels.

Discussion

Our results at T = 213 and 298 K suggest that the activation energy for the reaction between H and C₂H₃ is essentially zero. This is not unexpected given the very large rate constants measured which are comparable to the collision rate. In Table 4 we summarize recent values of k_2 at T = 298 K; neglected are older values based on complex or uncertain analysis and values measured or estimated at very high temperatures. The list is thus reduced to two direct but not absolute measurements,^{16a,17} one estimated value,³⁰ and our direct, absolute determination. The measurements of k_2 summarized in Table 4 have been made over a wide range of pressures: 0.2-3.0Torr He in ref 17 (this is the range given in the abstract; the text gives 0.9-2.4 Torr He), 1.1 Torr He in our study, and 100 Torr He in ref 16a. Unfortunately, the quoted uncertainties in k_2 do not permit a definitive conclusion concerning a pressure dependence of the total rate constant k_2 . Our upper limit for k_2 overlaps with the lower limit at high pressure, ^{16a} and our lower limit just equals the upper limit from the lower pressure range studies.¹⁷ Thus, one interpretation would be that k_2 is pressure independent between 0.2 and 100 Torr with an average value of $k_2 = (1.2 \pm 0.8) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Equally plausible is the conclusion that k_2 increases from 0.5×10^{-10} to 2.0×10^{-10} cm³ molecule⁻¹ s⁻¹ between 0.2 and 100 Torr He. This apparent ambiguity concerning the effect of pressure on k_2 is resolved to a considerable extent in the following discussion concerning both experimental and theoretical results for the products of the $H + C_2H_3$ reaction.

A. Mechanistic Considerations. In the first instance, given the product information, the reaction between H and C_2H_3 could proceed *via* either of two mechanisms. The most probable mechanism (mechanism A) is one which is comprised of two separate competing parallel reactions

$$C_2H_3 + H + M \rightleftharpoons [H - C_2H_3]^* \rightarrow C_2H_4 + M \quad (A2a)$$

$$\mathbf{C}_{2}\mathbf{H}_{3} + \mathbf{H} \rightarrow \mathbf{H}_{2} + \mathbf{C}_{2}\mathbf{H}_{2} \tag{A2b}$$

Reaction channel A2a consists of the formation of an energized adduct which can redissociate to reactants or be stabilized to form ethylene. The rate constant for channel A2a may therefore display a pressure dependence. The second reaction channel (reaction A2b) is a direct abstraction process, and the rate constant for this channel will be invariant with pressure. The second possible mechanism (mechanism B) contains the elements

$$C_2H_3 + H \rightleftharpoons [H - C_2H_3]^* \rightarrow \begin{cases} C_2H_4 + M & (B2a) \\ H_2 + C_2H_2 & (B2b) \end{cases}$$

where an energized adduct is formed which can redissociate back to reactants, be stabilized to give ethylene (reaction B2a), or dissociate *via* a four-center intermediate to yield molecular hydrogen and acetylene (reaction B2b). An analogy for the decomposition of an energized complex of the type $[H-C_2H_3]^*$ can be found in the pyrolysis of ethylene, which produces a highly energized adduct. Studies of the pyrolysis of ethylene³¹⁻³³ have shown that decomposition of ethylene can occur both by a free radical mechanism, producing C₂H₃ and H, and by molecular elimination to produce H₂ and C₂H₂. Mechanism B is somewhat more complicated than mechanism A, but the possibility now exists for both k_{2a} and k_{2b} to display a pressure dependence.

Insight into the probable mechanism can be gained from examination of the experimental product analyses. The results of the product study show that $([HD] + [C_2D_3H])/[C_2D_3]_0 = 1.0$ at T = 298 K. If the reaction proceeds via mechanism B, the decomposition of the energized adduct $[H-C_2D_3]^*$ would give both HD and D₂; viz,

$$[C_2D_3 - H]^* \rightarrow C_2D_2 + HD$$
(19a)

$$\rightarrow C_2 DH + D_2$$
 (19b)

Assuming to a first approximation that equal amounts of HD and D_2 are formed, the observed product yield would be somewhat less than unity (*ca.* 0.7). There is then already

experimental evidence to suggest that mechanism A is favored over mechanism B. There remains the possibility of a minor D_2 -producing channel from the addition-elimination channel, *i.e.* from decomposition of the energized adduct. It should also be recognized that the isotopic changes made in the branching ratio experiments may favor HD elimination over D_2 elimination.

In order to further investigate the possible mechanisms in relation to the observed kinetics and products for the reaction between H and C₂H₃, QRRK calculations were performed. The QRRK method is an alternative to full RRKM calculations, from which it is possible to obtain semiquantitative information concerning the relative rates of reaction for the various channels accessible to the newly formed energized adduct. According to RRK theory, the unimolecular rate constant for a dissociation of the type AB \rightarrow A + B can be expressed as

$$k = \nu \left(\frac{E - E_{\rm c}}{E}\right)^{s-1} \tag{20}$$

where E is the total energy, E_c is the critical energy for the breaking of the A-B bond, ν is the dissociation rate of the complex, and s is the number of oscillators. In the QRRK method, as suggested by Dean,³⁴ the limiting high-pressure Arrhenius pre-exponential factor (A') for the particular reaction i is used to stand in place of the transition-state information of the RRKM formulation; E_c for the reaction is taken either as the dissociation energy of the appropriate (stabilized) complex or as the measured activation barrier for the formation of new products. First, the geometric mean frequency $\langle \nu \rangle_g$ is calculated using

$$\langle \nu \rangle_{g} = \left(\prod_{i}^{s} \nu_{i}\right)^{1/s} \tag{21}$$

where s is the number of vibrational degrees of freedom of the adduct (s = 12 for the adduct under consideration here). The geometric mean frequency (or energy) is the quantum for the energized complex. The energy of the complex can be determined from a consideration of the $\Delta H_{\rm f}$ of the radical reactants. In order to determine the first populated quantum state (n), the formula

$$n = \frac{(\Delta H_{\rm f}(A) + \Delta H_{\rm f}(B) - \Delta H_{\rm f}(AB))}{\langle \nu \rangle_{\rm g}}$$
(22)

is applied. Now having determined the energy and minimum quantum number (n), the rates of the individual channels i available to the energized adduct can be expressed as

$$k_i(E) = A^i_{\infty} \frac{n!(n-m_i+s-1)!}{(n-m_i)!(n+s-1)!}$$
(23)

In essence one calculates via the QRRK method the probability that, following randomization, enough energy will end up in the critical oscillator. The A factor reflects the tightness or looseness of the dissociation process. Dean³⁴ has suggested that, in order to calculate the contribution of the stabilization channel, we simply take the gas kinetic collision frequency, modified by the bath gas, and the pressure to determine a rate of stabilization. The next step is to calculate the Boltzmann distribution of states in the complex and then calculate the microcanonical rate constants from these states into the various channels.³⁴ From this form of calculation we can determine the partitioning of the various channels.

TABLE 5: Data Used for QRRK Calculations

fate of energized complex	A/s^{-1}	E/kJ mol ^{−1}	$\langle v \rangle_{gal}$ cm ⁻¹	ref
$\overline{[C_2H_3-H]^* \rightarrow C_2H_3 + H}$	2.0×10^{16}	464	1633	2, 35
$[C_2H_3-H]^* \rightarrow C_2H_2 + H_2$	7.0×10^{12} to	391	1633	see text
	1.0×10^{14}			

^a Reference 36.

TABLE 6: Fractional Contribution of Different Channels Obtained in the QRRK Calculations on the $H + C_2H_3$ System at T = 298 K and 213 K

		P/Torr				
process	T/K	0	1	10	100	1000
	Μ	lechanis	m A			
$C_2H_4 \rightarrow H + C_2H_3$	298	1.00	0.79	0.27	0.04	0.00
C_2H_4 (stabilized)	298	0.00	0.21	0.73	0.96	1.00
$C_2H_4 \rightarrow H + C_2H_3$	213	1.00	0.69	0.19	0.02	0.00
C ₂ H ₄ (stabilized)	213	0.00	0.31	0.81	0.98	1.00
	M	lechanis	m B			
$C_2H_4 \rightarrow H + C_2H_3$	298	0.11	0.11	0.10	0.03	0.00
$C_2H_4 \rightarrow C_2H_2 + H_2$	298	0.89	0.85	0.65	0.20	0.03
C ₂ H ₄ (stabilized)	298	0.00	0.04	0.25	0.77	0.97
$C_2H_4 \rightarrow H + C_2H_3$	213	0.12	0.10	0.08	0.02	0.00
$C_2H_4 \rightarrow C_2H_2 + H_2$	213	0.88	0.83	0.56	0.13	0.02
C ₂ H ₄ (stabilized)	213	0.00	0.05	0.36	0.85	0.98

^a For details of the mechanism, see text.

TABLE 7: Summary of Derived Rate Constants from the
QRRK Calculations Using Mechanism A^a

	$k_2(1 \text{ Torr})^b$ T = 298 K	$k_2 \infty^c$ $T = 298 \text{ K}$	$k_2(1 \text{ Torr})^b$ T = 213 K	$k_{2}\infty^{c}$ $T = 213 \text{ K}$
k_{2a} k_{2b} total	$\begin{array}{c} 3.6 \times 10^{-11} \\ 7.4 \times 10^{-11} \\ 1.1 \times 10^{-10} \end{array}$	$\begin{array}{c} 1.7 \times 10^{-10 \ c} \\ 7.4 \times 10^{-11 \ b} \\ 2.4 \times 10^{-10 \ d} \end{array}$	$\begin{array}{c} 2.4 \times 10^{-11} \\ 7.6 \times 10^{-11} \\ 1.0 \times 10^{-10} \end{array}$	$\begin{array}{c} 8.0 \times 10^{-11} \ c \\ 7.6 \times 10^{-11} \ b \\ 1.6 \times 10^{-10} \ d \end{array}$

^{*a*} All units cm³ molecule⁻¹ s⁻¹. ^{*b*} This experimental work. ^{*c*} From QRRK calculations, see text. ^{*d*} Extrapolated values, as sum of $k_{2a} + k_{2b}$.

The relevant data^{2,35,36} used in the QRRK calculations are summarized in Table 5. Table 6 summarizes the results of the QRRK calculations for mechanisms A and B. For mechanism A, since the energized adduct can either redissociate or be stabilized, the QRRK calculations do not provide any information about the abstraction channel (reaction A2b); hence, only the ratio $k_{2a}(P)/k_{2a}(P\infty)$ can be obtained, where P is the pressure in Torr. For mechanism B, since both product channels arise from the energized adduct, the relative partitioning of these channels can be compared directly with the experimentally determined yields.

Mechanism A. At T = 298 K the QRRK results show that $k_{2a}/k_{2\infty}$ is 0.21 at P = 1 Torr, increasing to near unity (0.96) at P = 100 Torr. The experimentally determined value for k_{2a} at P = 1 Torr and T = 298 K is 3.6×10^{-11} cm³ molecule⁻¹ s⁻¹, which, when coupled with the ratio determined by the QRRK calculation, provides an estimate for the high-pressure limiting rate constant $k_{2a}\infty$ of 1.7×10^{-10} cm³ molecule⁻¹ s⁻¹ (see Table 7). Therefore, at P = 100 Torr, using the ratio $k_{2a}(100 \text{ Torr})/k_{2a}\infty$ (=0.96) and the estimate for $k_{2a}\infty$, $k_{2a}(100 \text{ Torr}) = 1.7 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. Since k_{2b} will be invariant with pressure according to mechanism A, $k_2(100 \text{ Torr}) = 1.7 \times 10^{-10}$ + $7.4 \times 10^{-11} = 2.4 \times 10^{-10}$ (all cm³ molecule⁻¹ s⁻¹). This calculation is in good agreement with $k_2(100 \text{ Torr})$, $(2.0 \pm 0.8) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ derived by Fahr *et al.*, ^{16a} where the bath gas was helium.

A similar treatment for these data at T = 213 K, *i.e.* combining the experimentally determined value for k_{2a} at 1 Torr with the QRRK ratio $k_{2a}/k_{2a}\infty$ at 1 Torr, provides an estimate for $k_{2a}\infty = 8.0 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (see Table 7). These

estimates compare favorably with estimates from the work of Duran *et al.*, ¹⁰ where $k_{2a} \approx (298 \text{ K}) \approx 1.7 \times 10^{-10}$ and $k_{2a} \approx (213 \text{ K}) \approx 8.8 \times 10^{-11}$ (both cm³ molecule⁻¹ s⁻¹).

Therefore, if mechanism A is in operation, k_{2b} is independent of pressure and within experimental error independent of temperature whereas k_{2a} is pressure dependent in the range 1-100 Torr and the high-pressure limit $k_{2a}\infty$ decreases with decreasing temperature.

Mechanism B. The values (see Table 5) for $A \infty$ for channel B2b

$$[C_2HD_3]^* \rightarrow C_2D_2 + HD \tag{19a}$$

were taken from Tsang and Hampson's recommendation² (10¹⁴ s^{-1}), and the value for the energy E was taken from an estimate of Raghavarchi et al.³⁵ derived from an *ab-initio* study (E =391 kJ mol⁻¹). The results of the QRRK analysis (see Table 6) are clearly in disagreement with the experimental data derived in this study. At P = 1 Torr and T = 298 K the QRRK calculations predict the relative yields of (C_2H_4) : $(C_2H_2 + H_2)$ = 0.04:0.85 as opposed to the experimental values 0.33:0.67. Since both the A factor and activation energy are taken from estimates for channel B2b, it is possible to obtain better agreement at T = 298 K between theory and experiment by lowering the A factor. Using a lower A factor of 7×10^{12} increases agreement between the calculations and the experimentally determined branching ratios at room temperature but leads to discrepancies at lower temperatures, as the calculated yield follows the wrong trend, *i.e.* at T = 298 K, Γ_{2a} : $\Gamma_{2b} \sim$ 0.37:0.63 but at T = 213 K, Γ_{2a} : $\Gamma_{2b} = 0.48:0.52$ compared to the experimentally determined ratios of 0.33:0.67 at T = 298K and 0.24:0.76 at T = 213 K.

Westmoreland *et al.*³⁷ have used the QRRK method to fit high-temperature data for the $H + C_2H_3$ system. These workers adopted mechanism B, *i.e.* that the reaction proceeds via an energized adduct C_2H_4 *, which can redissociate back to reactants H and C_2H_3 , be stabilized to give C_2H_4 , or isomerize to produce C_2H_2 and H_2 . However we have used their suggested parameters and calculated the product ratios they produce at 1 Torr pressure for the two temperatures, 298 and 213 K. For both temperatures the formation of C_2H_2 and H_2 dominates; *i.e.*, Γ_{2b} is approximately one and Γ_{2a} is zero, which is in disagreement with our experimental results. We cannot rule out the possibility that at high temperature isomerization of the energized adduct $[C_2H_3-H]^*$ to form C_2H_2 and H_2 may become significant, but at low temperatures this process appears to be unimportant.

In summary, it would seem that mechanism A is the most likely. The experimentally determined rate constants coupled with the QRRK calculations show good agreement with the high-pressure data of Fahr *et al.*^{16a} and the estimates of Duran *et al.*¹⁰ (Table 8). The QRRK calculations suggest that if mechanism B operates, then the yield of channel B2b dominates totally at low pressures, which is contrary to observations. Lowering the *A* factor for channel A2b (from 10¹⁴ to 7×10^{12} s⁻¹) provides better agreement at T = 298 K, but a large discrepancy still exists at T = 213 K. In conjunction with the experimental yield ([HD] + [C₂D₃H])/[C₂D₃]₀ = 1.0 at T = 298 K, it is unlikely that mechanism B occurs.

B. Pressure Dependence. As an extension to the coupling of the QRRK calculations and experimental data, it is useful to derive a pressure dependent expression for atmospheric modeling purposes. Given the data available, the following calculations must be adjudged to be estimates at best. Though a simple expression could be derived using the calculated QRRK ratios, it is more customary to express falloff curves in terms of the Troe formalism.^{38,39} The Troe formalism is based on the Lindemann-Hinshelwood expression multiplied by a broaden-

 TABLE 8: Comparison of Experimentally Determined and Calculated (QRRK) Branching Ratios and Rate Constants

quantity ^a	QRRK calculation ^b	experimental ^c
Γ _{2a} (298 K, 1 Torr)	0.21	0.33
k _{2a} (298 K, 1 Torr)	3.1×10^{-11}	3.6×10^{-11}
k _{2b} (298 K)		7.4×10^{-11}
k ₂ (298 K, 1 Torr)	$1.0_5 \times 10^{-10}$	1.1×10^{-10}
k _{2a} (298 K, 100 Torr)	1.4×10^{-10}	
k ₂ (298 K, 100 Torr)	2.1×10^{-10}	$2.0 \times 10^{-10 \ d}$
<i>k</i> ₂ ∞(298 K)	2.4×10^{-10}	$1.7 \times 10^{-10} e$
Γ _{2a} (213 K, 1 Torr)	0.24	0.24
k _{2a} (213 K, 1 Torr)	2.2×10^{-11}	2.4×10^{-11}
$k_{2b}(213 \text{ K})$		7.6×10^{-11}
k ₂ (213 K, 1 Torr)	9.8×10^{-11}	10.0×10^{-11}
$k_{2a}(213 \text{ K}, 100 \text{ Torr})$	8.9×10^{-11}	
k ₂ (213 K, 100 Torr)	$1.6_5 \times 10^{-10}$	
$k_2 \infty (213 \text{ K})$	1.8×10^{-10}	$8.8 \times 10^{-11} e$

^{*a*} All *k* units are cm³ molecule⁻¹ s⁻¹. ^{*b*} QRRK calculations assume mechanism A (see text). ^{*c*} This work, except where noted. ^{*d*} Reference 16a. ^{*e*} Calculated value from ref 10.

ing parameter, which allows for the energy dependence of k(E). So, the pressure dependence of k_{2a} can be described by the threeparameter equation

$$k = \frac{k_{\infty}k_0[\mathbf{M}]}{k_{\infty} + k_0[\mathbf{M}]} F_{c}^{\{1 + \lceil \log(k_0[\mathbf{M}]/k_{\infty}) \rceil^2\}^{-1}}$$
(24)

where k_0 is the low-pressure limiting rate coefficient, k_{∞} is the high-pressure limiting rate coefficient, and F_c is a coefficient which characterizes the broadening of the falloff curve, induced by the energy dependence of the rate coefficient for unimolecular dissociation of the energized adduct. Values for F_c are given by the product of the strong and weak collision factors

$$F_{\rm c} = F_{\rm c}^{\rm SC} F_{\rm c}^{\rm WC} \tag{25}$$

 F_c^{SC} can be estimated from the structural parameters of the adduct while F_c^{WC} is related to the efficiency of energy transfer between the energized adduct and the bath gas.

The details of a Troe type analysis are given elsewhere.³⁸⁻⁴¹ The molecular parameters^{36,42-46} used in the calculations are given in Table 9, and the derived values of F_c^{SC} are shown in Table 10. A value for F_c^{WC} is given to a good approximation by the expression

$$F_{\rm c}^{\rm WC} = \beta_{\rm c}^{0.14} \tag{26}$$

where $\beta_c(\text{He})$ is the collision efficiency derived from $k_{(0)}/k_0^{\text{SC}}$. Values for $\beta_c(\text{He})$ range between 0.05 and 0.25. At T = 298 K a value for $\beta_c(\text{He})$ of 0.08 has been used in accordance with the study of Frost and Smith.⁴⁷ At T = 213 K a value for β_c -(He) of 0.09 was used.

It should be noted that for an association reaction, such as that between H and C_2H_3 , it has been shown by Troe⁴⁸ that k_0^{SC} , the low-pressure strong collision coefficient, is

$$k_0^{\rm SC} = \frac{Q(C_2H_4)}{Q(C_2H_3) Q(H)} Z_{\rm LJ} \rho(E_0) RTF_E F_{\rm anh} F_{\rm rot} F_{\rm rot \ int} \quad (27)$$

where Q represents the relevant partition functions, Z_{LJ} is the Lennard-Jones collision frequency, $\rho(E_0)$ is the harmonic vibrational density of states at the critical energy E_0 , and F_E , F_{anh} , F_{rot} , and $F_{rot int}$ are coefficients that account for the energy dependence of the density of states, for anharmonicity, for rotational contributions, and for hindered internal rotations, respectively. The various formulas and methods used to calculate these parameters are detailed in refs 38-41 and 48.

 TABLE 9: Molecular Parameters Used in the Troe

 Calculation

	$C_2H_4^a$	$C_2H_3^b$
	Vibrational Frequenc	ies (cm ⁻¹)
ν_1	3153	3265
ν_2	1655	3192
ν_3	1397	3116
ν_4	1044	1670
V 5	3232	1444
ν_6	1245	1185
ν_7	969	918
ν_8	959	827
ν_9	3235	783
ν_{10}	842	
ν_{11}	3147	
ν_{12}	1473	
	Rotational Constant	s (cm ⁻¹)
Α	4.83	7.91
В	1.00	1.08
С	0.83	0.95
	Lennard-Jones Para	meters ^{c,d}
	$\sigma(C_2H_4) = 0.4136 \text{ nm}$	$\sigma(\text{He}) = 0.2608 \text{ nm}$
	$\epsilon/k(C_2H_4) = 224.7 \text{ K}$	$\epsilon/k(\text{He}) = 10.22 \text{ K}$

^{*a*} Vibrational frequencies from ref 36; rotational constants from ref 43. ^{*b*} Vibrational frequencies from ref 42; rotational constants from ref 44. ^{*c*} Reference 45. ^{*d*} Reference 46.

TABLE 10: Values of $F_c(SC)$ as a Function of T and ΔS

	$F_{\rm c}({\rm s})$	SC)	
T/K	$\Delta S = 1$	$\Delta S = 2$	
213	0.99	0.75	
298	0.94	0.70	

TABLE 11: Results and Parameters Used in the Calculation of $k_0(SC)$

<i>T/</i> K	М	Z_{LJ}^{a}	$F_{\rm E}$	$F_{\rm rot}$	$F_{\rm rotint}$	$ ho(E_0)^b$	F_{anh}	$k_0(\mathbf{SC})^c$
213	He	3.96	1.05	32.1	1.0	4.24	1.15	7.3
298	He	4.37	1.07	22.3	1.0	4.24	1.15	4.6

^{*a*} Units are 10^{-10} cm³ molecule⁻¹ s⁻¹. ^{*b*} Units are 10^3 states cm⁻¹. ^{*c*} Units are 10^{-26} molecule⁻² cm⁶ s⁻¹.

TABLE 12: Falloff Parameters for the Reaction C_2H_3+H + $M \rightarrow C_2H_4$ + M

$F_{\rm c} = F_{\rm c}({\rm WC}) F_{\rm c}({\rm SC})$						k	2a ^C	
<i>T/</i> K	М	$\Delta S = 1$	$\Delta S = 2$	$k_0(\mathrm{He})^a$	β_{c}	k∞ ^b	$\Delta S = 1$	$\Delta S = 2$
213 298	He He	0.71 0.66	0.54 0.49	5.4 3.5	0.09 0.08	5 16	3.4 4.2	2.8 3.1

^{*a*} Units of k_0 are 10^{-27} molecule⁻² cm⁶ s⁻¹. ^{*b*} Units of k_{∞} are 10^{-11} cm³ molecule⁻¹ s⁻¹. ^{*c*} Units of k_{2a} are 10^{-11} cm³ molecule⁻¹ s⁻¹ at P = 1 Torr.

Table 11 shows the calculated values for a number of these parameters as well as the derived values of k_0^{SC} at the temperatures used in this study. From the derived value of k_0^{SC} at a given temperature, a value for $k_{2a(0)}$ (He) can be gained *via* the simple relationship

$$k_{2a(0)}(\text{He}) = k_0^{\text{SC}} \beta_c \tag{28}$$

Using eq 24 and the derived parameters $k_{2a(0)}$ (He) (constrained by eqs 27 and 28) and F_c (constrained by eqs 25 and 26 and the values for $F_c(SC)$ listed in Table 10), the experimental values can be fitted using $k_{2a}\infty$ as the fitting parameter. The fitting was performed for both $\Delta S = 1$ and $\Delta S = 2$ (see ref 41). Better fits to the experimental data were gained using $\Delta S = 2$. The derived falloff parameters are listed in Table 12. Figure 3 shows the derived fits in the falloff region ((0-30) × 10¹⁶ molecule cm⁻³) at T = 298 K for both the Troe expression and one derived from the QRRK analysis with our experimental point



Figure 3. Pressure dependence of k_{2a} at T = 298 K over the range [M] = 0 to 30×10^{16} molecule cm⁻³ (the falloff region) for M = He. The upper curve (solid line) is the QRRK calculation, and the lower curve (dashed line) is the Troe fit ($\Delta S = 2$). The circle is the value of k_{2a} at 1 Torr (this work), and the vertical line is the uncertainty in that value.



Figure 4. Pressure dependence of k_{2a} at T = 298 K over the range [M] = 0 to 500×10^{16} molecule cm⁻³ for M = He. The upper curve (solid line) is the result of the QRRK calculation scaled to the data point at 1 Torr, and the lower curve (dashed line) is the result of the Troe calculation ($\Delta S = 2$). The circle is the value of k_{2a} at 100 Torr derived from the values of k_2 (ref 16a) and k_{2b} (this work). The uncertainty in k_{2a} at 100 Torr is quite large and difficult to define; the arrows on the vertical line are meant to indicate this.

at 1 Torr. Similarly, Figure 4 shows the same fits over the $(0-500) \times 10^{16}$ molecule cm⁻³ region at T = 298 K with a point from the study of Fahr *et al.*^{16a} ($k_2 - k_{2b}$) at P = 100 Torr. At T = 213 K, there is only one experimental point (this work); thus, only the falloff region and therefore the limiting low-pressure rate coefficient for k_{2a} can be adequately constrained in the fitting procedure (see Figure 5). At T = 213 K, the calculated value for $k_{2(0)}$ (He) = 6.6×10^{-27} cm⁶ molecule⁻² s⁻¹, but for the best fit (*i.e.* nearer to the center experimental value of k_{2a} at P = 1 Torr) a value of $k_{2(0)}$ (He) = 5.4×10^{-27} cm⁶ molecule⁻² s⁻¹ was used. Therefore, from the Troe analysis an expression for the limiting low-pressure rate coefficient of

$$k_{2a(0)} = (3.5 \times 10^{-27})(T/298)^{-1.3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$
 (29)

can be suggested for helium as the bath gas (see lower curve in Figure 4). For the limiting high-pressure rate coefficient it is not possible to derive a temperature dependent expression given the paucity of the data available. Thus, at T = 298 K, the QRRK analysis ($k_{2a} \approx 1.7 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹), the analysis of Duran *et al.*¹⁰ ($k_{2a} \approx 1.7 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹), and the Troe analysis ($k_{2a} \approx 1.6 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹) suggest a value of approximately

$$k_{2a} \approx (298 \text{ K}) = 1.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (30)

Table 13 gives a comparison of values for $k_{2a(0)}$ (He) and $k_{2a} \infty$



Figure 5. Pressure dependence of k_{2a} at T = 213 K over the range [M] = 0 to 30×10^{16} molecule cm⁻³ (the falloff region) for M = He. The upper curve (solid line) is the QRRK calculation, and the lower curve (dashed line) is the Troe fit ($\Delta S = 2$). The circle is the value of k_{2a} at 1 Torr (this work), and the vertical line is the uncertainty in that value.

TABLE 13: Comparison of Values for $k_{2a(0)}$ (He) and $k_{2a} \infty$ Derived from the Troe and QRRK Analyses

T/K	$k_{2a(0)}(\text{He})/\text{QRRK}^a$	$k_{2a(0)}(He)/Troe^a$	$k_{2a}\infty/QRRK^b$	$k_{2a}\infty/\mathrm{Troe}^b$
213	1.1	5.4	8	5
298	1.4	3.5	17	16

 a All k_0 values are in the units 10^{-27} cm 6 molecule 2 s $^{-1}$. b All $k\infty$ values are in the units 10^{-11} cm 3 molecule $^{-1}$ s $^{-1}$.

derived from the Troe and QRRK analyses. The derived expressions for both $k_{2a(0)}(He)$ and $k_{2a}\infty$ must be treated with considerable caution, as they represent at best an estimate given the data set used to derive them, but they are nonetheless useful. Further measurements over a larger pressure and temperature range are obviously required to constrain the falloff curve better for the reaction $H + C_2H_3 + M \rightarrow C_2H_4 + M$.

Planetary Implications

Reactions of the vinyl radical, C_2H_3 , are important in determining the relative abundances of such molecules as C_2H_2 , C_2H_4 , and C_2H_6 in the atmospheres of Jupiter, Saturn, Titan, and Neptune.⁴⁹ Also, reactions of the vinyl radical on Titan and Neptune can lead to the formation of nitrile compounds,²⁹ which are thought to be important prebiotic molecules.⁵⁰ As previously discussed the reaction between H and C_2H_3 can occur *via* two possible reaction channels

$$\mathbf{H} + \mathbf{C}_2 \mathbf{H}_3 + \mathbf{M} \rightarrow \mathbf{C}_2 \mathbf{H}_4 + \mathbf{M}$$
(2a)

$$\mathbf{H} + \mathbf{C}_2 \mathbf{H}_3 \rightarrow \mathbf{C}_2 \mathbf{H}_2 + \mathbf{H}_2 \tag{2b}$$

The vinyl is produced from reaction 1 and can convert C_2H_2 *via* C_2H_3 to C_2H_4 by reaction 2a or simultaneously recycle C_2H_3 back to C_2H_2 by reaction 2b. An example of the potential importance of this reaction may be found in the work of Allen et al.51 Central to matching both ground-based data52 and Voyager IRIS spectra⁵³ of the C₂H₆/C₂H₂ abundance ratio on Jupiter to a photochemical model is the conversion of C₂H₃ to C_2H_4 (and subsequently to C_2H_6). Allen et al.⁵¹ use the relatively slow reaction between C_2H_3 and H_2 (ca. 10^{-17} cm³ molecule⁻¹ s⁻¹ at T = 298 K) in their photochemical model in order to convert the vinyl into ethylene; they point out that this reaction is the "key" in getting the model and observational data to converge. Recent measurements by Fahr et al.54 have shown that the $C_2H_3 + H_2$ reaction is probably 2-3 orders of magnitude slower than previously thought and thus less important. In contrast, the rate constant $k(H+C_2H_3)$ is now known to be greater than the value used in current models and

all present models assume reaction 2 yields only C_2H_2 and H_2 at the relatively low pressures and temperatures of planetary atmospheres. The reaction between H and C_2H_3 could provide a potentially important means of converting C_2H_2 to C_2H_4 and alter the hydrocarbon abundances not provided for in present models of the hydrocarbon chemistry of the outer planets. However, detailed laboratory measurements of the pressure and temperature dependence of reaction 2a need to be performed before firm conclusions can be drawn about the importance of this reaction in models of planetary atmospheres.

Conclusions

The rate coefficients for the reaction between $H(^{2}S)$ and $C_{2}H_{3}$ have been determined at both room temperature (T = 298 K) and subambient (T = 213 K) temperature using the dischargeflow kinetic technique coupled to mass-spectrometric detection. The rate coefficients are $k(H+C_2H_3)(298 \text{ K}) = (1.1 \pm 0.3) \times$ 10^{-10} cm³ molecule⁻¹ s⁻¹ and $k(H+C_2H_3)(213 \text{ K}) = (1.0 \pm$ 0.3) $\times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. Therefore, the activation energy for the reaction between H and C_2H_3 is near zero. Quantitative determinations of the fractional product yields have shown that $\Gamma(H+C_2D_3 \rightarrow C_2D_3H) = 0.33 \pm 0.13$ at T = 298 K and 0.24 \pm 0.09 at T = 213 K, as well as $\Gamma(H+C_2D_3 \rightarrow$ C_2D_2 +HD) = 0.67 ± 0.18 at T = 298 K and 0.76 ± 0.16 at T = 213 K. This work has demonstrated that the reaction between H and C_2H_3 has a significant yield of ethylene; this in turn has ramifications for both combustion and planetary studies. The experimental data has been used in conjunction with QRRK calculations to suggest a mechanism of the following type for the reaction

$$\mathbf{H} + \mathbf{C}_2 \mathbf{H}_3 + \mathbf{M} \rightleftharpoons [\mathbf{H} - \mathbf{C}_2 \mathbf{H}_3]^* \rightarrow \mathbf{C}_2 \mathbf{H}_4 + \mathbf{M} \quad (2a)$$

$$\mathbf{H} + \mathbf{C}_2 \mathbf{H}_3 \rightarrow \mathbf{C}_2 \mathbf{H}_2 + \mathbf{H}_2 \tag{2b}$$

A comparison between experimental and calculated QRRK results is given in Table 8. Further, a Troe analysis was used to suggest a limiting low-pressure rate coefficient for k_{2a} . This study has highlighted the importance of studying not only the primary rate coefficient for a reaction but also quantitative product yields over a range of temperatures.

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