The Rate Constant for the Reaction H + C₂H₅ at T = 295 – 150 K

André S. Pimentel,¹ Walter A. Payne,¹ Fred L. Nesbitt,¹,² Regina J. Cody,¹,*

and Louis J. Stief ¹

¹Laboratory for Extraterrestrial Physics, NASA/Goddard Space Flight Center, Greenbelt, MD 20771.

²Department of Chemistry, Catholic University of America, Washington, DC. 20064. Also at Department of Natural Sciences, Coppin State College, Baltimore, MD 21216.

* Corresponding author:
Regina J. Cody
E-mail: Regina.Cody@nasa.gov
Tel: 301-286-3782
FAX: 301-286-1683
Abstract

The reaction between the hydrogen atom and the ethyl (C₂H₅) radical is predicted by photochemical modeling to be the most important loss process for C₂H₅ radicals in the atmospheres of Jupiter and Saturn. This reaction is also one of the major sources for the methyl radicals in these atmospheres. These two simplest hydrocarbon radicals are the initial species for the synthesis of larger hydrocarbons. Previous measurements of the rate constant for the H + C₂H₅ (1) reaction varied by a factor of five at room temperature, and some studies showed a dependence upon temperature while others showed no such dependence. In addition, the previous studies were at higher temperatures and generally higher pressures than that needed for use in planetary atmospheric models. The rate constant for the reaction H + C₂H₅ has been measured directly at T = 150, 202 and 295 K and at P = 1.0 Torr He for all temperatures and additionally at P = 0.5 and 2.0 Torr He at T = 202 K. The measurements were performed in a discharge - fast flow system. The decay of the C₂H₅ radical in the presence of excess hydrogen was monitored by low-energy electron impact mass spectrometry under pseudo-first order conditions. H atoms and C₂H₅ radicals were generated rapidly and simultaneously by the reaction of fluorine atoms with H₂ and C₂H₆, respectively. The total rate constant was found to be temperature and pressure independent. The measured total rate constant at each temperature are: k₁(295K) = (1.02±0.24)x10⁻¹⁰, k₁(202K) = (1.02±0.22)x10⁻¹⁰ and k₁(150K) = (0.93±0.21)x10⁻¹⁰, all in units of cm³ molecule⁻¹ s⁻¹. The total rate constant derived from all the combined measurements is k₁ = (1.03±0.17)x10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. At room temperature our results are about a factor of two higher than the recommended rate constant and a factor of three lower than the most recently published study.

KEYWORDS: Ethyl Radical, C₂H₅, Rate Coefficients, H atom reaction, Atom-Radical Reaction, Saturn, Jupiter, Atmosphere
Introduction

The ethyl radical, C₂H₅, is predicted by photochemical modeling to be one of the most abundant C₂ radical species in the atmospheres of Jupiter¹ and Saturn²,³. The H + C₂H₅ reaction is the most important loss process for C₂H₅ and a major source of CH₃ in these atmospheres along with the production from CH₄ photolysis (either directly to CH₃ or indirectly via ¹CH₂)⁴. The column abundances of CH₃ on Saturn and Neptune were observed by the Infrared Space Observatory Satellite (ISO)⁵,⁶ to be lower than those predicted by atmospheric photochemical models¹². A suggested source for this discrepancy was the rate coefficient for the CH₃ self-recombination reaction. However, our previously study of the CH₃ + CH₃ reaction at T = 155 K showed that this reaction is not fast enough to completely solve the CH₃ overproduction problem in the photochemical models of Neptune and Saturn³. Therefore, it is logical to examine uncertainties in the rate coefficient for the H + C₂H₅ reaction as an important source of CH₃.

The thermodynamically accessible channels for the H + C₂H₅ reaction and the corresponding enthalpies of reaction at T = 298 K, ΔH°₂₉₈, are:

\[
\begin{align*}
H + C₂H₅ &\rightarrow CH₃ + CH₃ & ΔH°₂₉₈ &= -44 \text{ kJ mol}^{-1} \quad (1a) \\
H + C₂H₅ + M &\rightarrow C₂H₆ + M & ΔH°₂₉₈ &= -419 \text{ kJ mol}^{-1} \quad (1b) \\
H + C₂H₅ &\rightarrow C₂H₄ + H₂ & ΔH°₂₉₈ &= -285 \text{ kJ mol}^{-1} \quad (1c)
\end{align*}
\]

Most of the available rate data for this reaction is derived from indirect experiments and/or fitting to a complex chemical mechanism⁷⁻¹⁴. The consensus is that the addition/decomposition channel (reaction 1a) dominates under the conditions of most of the experiments. A good evaluation for reactions (1a), (1b), and (1c) and their preferred rate constants is summarized in the review by Baulch et al.¹⁵. The recommended value for the total rate constant is \( k₁ = 6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at T = 298 K. In what appears to be
the first direct (although not absolute) measurement, Kurylo et al.\textsuperscript{7} employed flash photolysis-resonance fluorescence to derive the value $k_1 = 6.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at $T = 298$ K and $P = 50$ Torr He.

In one of the two most recent studies, Pratt and Wood\textsuperscript{13} in 1984 performed discharge-flow experiments with final product analysis via gas chromatography at $P = 2-10$ Torr Ar and temperatures down to $T = 230$ K, which is the lowest temperature at which this reaction has been studied. They derived a slightly negative temperature-dependent rate coefficient for reaction (1a), $k_{1a} = 8.0 \times 10^{-11} \exp(-127/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$, based on the following series of reactions initiated by the reaction of atomic hydrogen with ethylene:

$$
\begin{align*}
H + C_2H_4 + M &\rightarrow C_2H_5 + M \\
H + C_2H_5 &\rightarrow CH_3 + CH_3 \\
CH_3 + CH_3 + M &\rightarrow C_2H_6 + M \\
C_2H_5 + C_2H_5 + M &\rightarrow C_4H_{10} + M \\
CH_3 + C_2H_5 + M &\rightarrow C_3H_8 + M \\
H + CH_3 + M &\rightarrow CH_4 + M
\end{align*}
$$

Pratt and Wood\textsuperscript{13} performed a complex multi-parameter fitting procedure for the formation of four products, which used rate constants for the reactions $CH_3 + CH_3$, $C_2H_5 + C_2H_5$, and $CH_3 + C_2H_5$, and a temperature-independent rate coefficient for the $H + C_2H_4$ reaction\textsuperscript{15}. Their sensitivity analysis showed that the derived rate constant for the $H + C_2H_5$ reaction is highly dependent on the assumed rate constants for those reactions.

In the second recent study, Sillesen et al.\textsuperscript{14} in 1993 used pulse radiolysis experiments in which the reaction sequence was again initiated by the reaction of H with $C_2H_4$; the decay of $CH_3$ was monitored directly via IR absorption. They determined that the addition/stabilization
channel (reaction 1b) is slightly faster than the reaction (1a), $k_{1b}/k_{1a}=1.3$ at $P = 75$ Torr $H_2$ and $T = 298$ K. However, their total rate constant $k_1$ and that for the addition/decomposition channel $k_{1a}$ are about five times and two times higher, respectively, than the values recommended in the literature. As they also performed parameter fitting of the complex mechanism given above, their results could also be highly dependent on assumed model parameters. For instance, they used rate constants for the reactions $H + CH_3$, $CH_3 + CH_3$ and $C_2H_5 + CH_3$, which are not supported by Baulch et al. recommendations. This could affect the fitting analysis of the $CH_3$ signal.

In our laboratory we have previously measured the direct, absolute rate constant for the $N + C_2H_5$ reaction and its reaction channels at $T = 298$ K. We have now measured the total rate constant for the reaction $H + C_2H_5$ as a first step toward providing more appropriate data for the $H + C_2H_5$ reaction for models of the Jupiter's and Saturn's atmospheres. The motivation for this study is that the available data is mostly indirect and not isolated from secondary chemistry. This work represents the first measurement of the rate constant at low temperatures down to 150 K and low pressures between 0.5 and 2.0 Torr. These conditions are relevant to the photochemical models of Jupiter and Saturn.

**Experimental Description**

All experiments were performed in a Pyrex flow tube, ~100 cm long and 2.8 cm in diameter. The inner surface of the tube was lined with Teflon FEP which gave an effective diameter of 2.0 cm. 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 energy in order to minimize fragmentation. An off-axis channeltron multiplier (Galileo Electro Optics Corp.) was used to detect the ions. The molecular reactants $H_2$ and $C_2H_6$ were premixed in a mixing bulb and then introduced into the flow tube via a Pyrex...
movable injector. The position of the movable injector could be changed between a distance of 2 and 44 cm from the sampling pinhole to the mass spectrometer. This system has been described in detail previously [3,17].

The flow tube was used at room temperature or cooled to $T = 200$ K by circulating ethanol from a cooled reservoir through a jacket which surrounded the flow tube from 0 to 60 cm. In the experiments down to $T = 150$ K, a controlled flow of gaseous nitrogen was circulated through a copper coil immersed in liquid nitrogen [3]. The temperature was continuously monitored using a thermocouple in the flow tube located at $d = 28$ cm from the sampling pinhole to the mass spectrometer. The temperature profile of the flow tube was measured using another thermocouple in a movable probe to show that there is not a temperature gradient in the region $d = 2$ to 50 cm at $T = 202$ K and $d = 4$ to 44 cm at $T = 150$ K. In the experiments at $T = 295$ K, the temperature measured in the flow tube was controlled by room temperature, and the variation was about $\pm 2$ K. While the experiments at $T = 202$ K were well controlled ($\Delta T = \pm 0.5$ K), those at $T = 150$ K showed a larger variation, $\Delta T = \pm 4$ K.

Helium carrier gas was flowed at rates between 560 and 1800 sccm into the reaction flow tube through ports upstream in the flow tube. All gas flows were measured and controlled by mass flow controllers (MKS Instruments). The linear flow velocity ranged from 2310 to 2510 cm s$^{-1}$ for the kinetic experiments at nominal pressures of 0.5, 1.0, and 2.0 Torr. The pressure showed a very small variation ($\Delta P = \pm 0.02$ Torr) when the injector was moved to measure the $C_2H_5$ signal at different positions (reaction times) in the flow tube. The plug flow assumption was made in the calculation of the linear flow velocity. The flow velocity is calculated from the gas constant, temperature, cross-sectional area of the flow tube, total gas flow, and total pressure.
Fluorine atoms were produced at the upstream end of the flow tube in a side arm by passing molecular $\text{F}_2$ (5% diluted in He) through a microwave discharge (~50 Watts, 2450 MHz). The discharge region consisted of a 3/8-in. ceramic tube coupled via Teflon Swagelok connectors to a glass discharge arm. About 40-50% of the $\text{F}_2$ was dissociated in the discharge. The potential effect of residual $\text{F}_2$ on the $\text{C}_2\text{H}_5$ radical consumption was considered in the analysis of the kinetic data. The concentration of F atoms used to generate $\text{H}$ atoms and $\text{C}_2\text{H}_5$ radicals was determined by measuring the consumption of $\text{Cl}_2$ in the fast titration reaction

$$\text{F} + \text{Cl}_2 \rightarrow \text{FCl} + \text{Cl}$$ (2)

where $k_2 = 6.0 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ independent of temperature. The initial F atom concentration was determined by measuring the decrease in the Cl$_2$ signal ($m/z = 70$) when the microwave discharge was initiated. The dilute Cl$_2$/He mixture (~5%) was admitted to the flow tube via the moveable injector. Separate experiments showed that [F] was constant along the flow tube from $d = 2$ to 44 cm. Nevertheless, the position of the injector was usually close to the middle of the decay range for the $\text{C}_2\text{H}_5$ reactant. Because Cl$_2$ has been observed to condense in the flow tube at temperatures lower than ~180 K, the initial F atom concentrations in the experiments at $T = 150$ K were determined by performing the titration at $T = 180$ K. The description of this procedure and a discussion of the validity of the approach have been given previously. The F atom concentration is given by

$$[\text{F}] = [\text{Cl}_2]_{\text{diss,off}} - [\text{Cl}_2]_{\text{diss,on}} = \Delta \text{Cl}_2\text{signal} \times [\text{Cl}_2]_{\text{diss,off}}$$

Under our experimental conditions, a Cl$_2$ concentration greater than $2 \times 10^{13}$ molecule cm$^{-3}$ is needed to ensure that reaction (2) went to completion with the injector at the usual position. Otherwise, the F atoms are undertitrated and the correction equation is used when needed.
where \( d \) (cm) is the distance of the movable probe from the sampling pinhole, \([\text{Cl}_2]\) is the \text{Cl}_2 concentration and \( v \) (cm s\(^{-1}\)) is the flow velocity. The correction equation showed excellent agreement with the F atoms concentration measured when the titration was performed at the position to ensure completion of reaction (2).

At the tip of the movable injector H atoms and \( \text{C}_2\text{H}_5 \) radicals were produced rapidly and simultaneously via the reactions:

\[
\begin{align*}
\text{H}_2 + \text{F} & \rightarrow \text{H} + \text{HF} \\
\text{C}_2\text{H}_6 + \text{F} & \rightarrow \text{C}_2\text{H}_5 + \text{HF}
\end{align*}
\]

(4)  
(5)

where \( k_4 = (1.20 \pm 0.1) \times 10^{-10} \exp(-470 \pm 28/T) \) (Ref. 19) and \( k_5 = (7.11 \pm 2.16) \times 10^{-10} \exp(-347 \pm 69/T) \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (Ref. 20). \( \text{H}_2 \) and \( \text{C}_2\text{H}_6 \) were in large excess over \( \text{F}_2 \) with the ratio \([\text{H}_2 + \text{C}_2\text{H}_6]/[\text{F}_2]\) = 92/1 to 9/1. \([\text{H}_2]\) and \([\text{C}_2\text{H}_6]\) were adjusted to produce the desired \([\text{H}]_0/[\text{C}_2\text{H}_5]_0\) ratios, \( R \), as shown in the expression:

\[
R = \frac{[\text{H}_0]}{[\text{C}_2\text{H}_5]_0} = \frac{k_4 \times [\text{H}_2]_0}{k_5 \times [\text{C}_2\text{H}_6]_0}
\]

(6)

Maricq and Szente \(^{20}\) measured \( k_5 \) relative to \( k_4 \) in the temperature range \( T = 210-363 \) K. Since reactions 4 and 5 compete for reaction with F in our experiments, their relative rate constant results and their temperature range are ideal for this calculation. However, they did not report values for the ratio of rate constants but values for \( k_5 \) based on a chosen value for \( k_4 \). From their reported value \( k_5 = 7.1 \times 10^{-10} \exp(-347/T) \) and their reference value \( k_4 = 1.7 \times 10^{-10} \exp(-550/T) \) we derived the expression \( k_5/k_4 = 4.2 \exp(203/T) \), where units of \( k_i \)'s are cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). The values for \([\text{H}]_0\) and \([\text{C}_2\text{H}_5]_0\) were calculated from the measured \([\text{F}]_0\) and the ratio \( R \) from equation 6 as given by
\[ [H]_b = [F]_b \times \left( \frac{R}{1 + R} \right) \]  

\[ [C_2H_5]_b = [F]_b - [H]_b \]  

Although not needed in equations 6-8, we can derive an Arrhenius expression for \( k_5 \) from the ratio \( k_5/k_4 \) using an absolute value for \( k_4 \). We use the direct result of Stevens et al., \( k_4 = 1.20 \times 10^{-10} \exp(-470/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), to obtain \( k_5 = 5.04 \times 10^{-10} \exp(-267/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). Using these rate constant values, we can calculate the formation time for H and C\(_2\)H\(_5\) in our experiments. Neglecting mixing, formation of H and C\(_2\)H\(_5\) were complete within 0.4-1.2 ms (1-3 cm from the injector tip) in most experiments. At \( T = 150 \text{ K} \) the formation of H and C\(_2\)H\(_5\) were complete within about 2 ms (= 5 cm) due to the lower rate constants for reactions (4) and (5) at that temperature.

C\(_2\)H\(_5\) radicals were detected at \( m/\ell = 29 \) following low-energy electron ionization to minimize any contribution to the C\(_2\)H\(_5\) signal from dissociative ionization of C\(_2\)H\(_6\), which was present in large excess over C\(_2\)H\(_5\) radicals. The observed C\(_2\)H\(_5\) signal was corrected to yield the net signal by subtracting the background signal measured with the microwave discharge off; the background signal includes both the instrument background and a small contribution from the dissociative ionization of C\(_2\)H\(_6\). An optimum ionization energy was sought to achieve maximum net signal to background (S/B) while still retaining an appreciable signal level. The optimum ionization energy was found to be 11.0 eV. Under these conditions, the lower limit C\(_2\)H\(_5\) concentration of \(-1 \times 10^{11} \text{ molecule cm}^{-3}\) was detected with S/B \( \geq 2 \). Mass scans were initially recorded for the region \( m/\ell = 27-31 \), and C\(_2\)H\(_5\) signals were taken as the integrated area of the \( m/\ell = 29 \) peak.

Helium (99.9995%, Air Products) was passed through a trap containing a molecular sieve before entering the flow system or before use in the preparation of mixtures. The molecular
sieve was periodically heated to about 220 °C under vacuum. F\textsubscript{2} (99.9\%, Cryogenic Rare Gases, 5\% in He) and H\textsubscript{2} (99.999\%, Air Products UHP) were used as provided without further purification. Cl\textsubscript{2} (VLSI 4.8 grade, Air Products) and C\textsubscript{2}H\textsubscript{6} (99.9\%, Air Products) were subjected to several freeze-pump-thaw cycles at liquid nitrogen temperature to remove impurities.

Results

The reaction of H atoms with C\textsubscript{2}H\textsubscript{5} radicals has been studied at T = 295, 202, and 150 K and P = 1.0 Torr He. At T = 202 K, some experiments were carried out at P = 0.5 and 2.0 Torr He. The decay of the ethyl radical was measured by observing the net signal (observed signal - background signal) at m/z = 29 as a function of the distance (d) from the tip of the movable injector to the sampling pinhole. From the known linear velocity (v) and d, the reaction time (t) is determined:

\[
time (t) = \text{distance (d)} / \text{velocity (v)} \tag{9}
\]

Pseudo-first-order conditions were used with the hydrogen atoms in excess over ethyl radicals: 3.1<[H]o/[C\textsubscript{2}H\textsubscript{5}]o<5.7, as shown in Table 1. This lower than usual ratio is acceptable since the most likely complicating secondary reaction, the C\textsubscript{2}H\textsubscript{5} self-reaction, is considerably slower\textsuperscript{15} than reaction (1). The correctness of this premise is confirmed by numerical simulation of the reaction system as described in the next section. Under these conditions, the decay of the ethyl radical is given by

\[
\ln[C\textsubscript{2}H\textsubscript{5}]_t = -k_{\text{obs}} (d/v) + \ln[C\textsubscript{2}H\textsubscript{5}]_0, \tag{10}
\]

where [C\textsubscript{2}H\textsubscript{5}] is proportional to the mass spectrometer signal and k\textsubscript{obs} is the measured pseudo-first-order rate constant. A plot of ln (net signal) vs reaction time should yield a straight line with slope equal to k\textsubscript{obs}. Plots of the decay of C\textsubscript{2}H\textsubscript{5} in the presence of three different concentrations of H atoms at T = 202 K and P = 1.0 Torr He are shown in Figure 1. Least-
squares analysis of these and similar plots yielded the rate constants \( k_{\text{obs}} \). In order to account for axial diffusion of the ethyl radical \(^{17,21}\) and its reaction with the remaining molecular fluorine from the microwave discharge, two corrections to \( k_{\text{obs}} \) were made to give \( k_{\text{corr}} \):

\[
k_{\text{corr}} = k_{\text{obs}} \left(1 + D \frac{k_{\text{obs}}}{v^2}ight) - k_{12} [F_2]
\]

(11)

where \( D \) is the diffusion coefficient of \( \text{C}_2\text{H}_5 \) in He and \( k_{12} \) is the rate coefficient of the reaction of \( \text{C}_2\text{H}_5 \) with the remaining molecular fluorine from the microwave discharge. \( D \) was estimated to be 667 cm\(^2\) s\(^{-1}\) at \( T = 295 \) K using the method of Lewis et al.\(^ {21}\) A \( T^{3/2} \) dependence was assumed to estimate \( D \) at \( T = 202 \) and 150 K. The diffusion correction was 4-11% at \( T = 295 \) K, 1-4% at \( T = 202 \) K and 1-3% at \( T = 150 \) K.

The rate constant for the reaction \( \text{C}_2\text{H}_5 + F_2 \) has been measured\(^ {22}\) relative to that for \( \text{C}_2\text{H}_5 + O_2 + M \) at \( T = 298 \) K and \( P = 1-15 \) Torr \( \text{CO}_2 \). The ratio \( k(\text{C}_2\text{H}_5 + F_2)/k(\text{C}_2\text{H}_5 + O_2 + M) \) is estimated to be about 3.3, independent of pressure over the range indicated. However this is a very indirect measurement based on heterogeneous initiation of the reaction and the measurement of a very small temperature rise. It is limited to \( T = 298 \) K and is complicated by being relative to a reaction whose rate constant under some conditions depends on both the pressure and the identity of the bath gas \( M \). We therefore prefer an estimated value based on a trend analysis in the reactions of \( \text{CH}_3 \) and \( \text{C}_2\text{H}_5 \) with \( F_2 \) and \( \text{Cl}_2 \). The relevant reactions \( \text{CH}_3 + F_2 \)\(^ {23}\), \( \text{C}_2\text{H}_5 + \text{Cl}_2 \)\(^ {24}\) and \( \text{CH}_3 + \text{Cl}_2 \)\(^ {24}\) have all been measured as a function of temperature in direct experiments. Assuming the relationship

\[
k(\text{C}_2\text{H}_5 + F_2) = k(\text{CH}_3 + F_2) \times k(\text{C}_2\text{H}_5 + \text{Cl}_2)/k(\text{CH}_3 + \text{Cl}_2)
\]

and using the data from the literature\(^ {23,24}\), we obtain the values for \( k(\text{C}_2\text{H}_5 + F_2) \):
\[ \text{C}_2\text{H}_5 + \text{F}_2 \rightarrow \text{C}_2\text{H}_5\text{F} + \text{F} \]  \hspace{1cm} (12)

\[ k_{12} = 1.35 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 295 \text{ K} \]

\[ k_{12} = 1.22 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 202 \text{ K} \]

\[ k_{12} = 1.07 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 150 \text{ K} \]

The \( k_{12} [\text{F}_2] \) correction to our \( k_{\text{obs}} \) in equation 11 was also small (< 9%).

Because of depletion of H atoms caused by reaction with \( \text{C}_2\text{H}_5 \), calculated H atom concentrations, \([\text{H}]_0\), were corrected \(^{16}\) to yield \([\text{H}]_{\text{mean}}\) using the expression:

\[ \text{[H]}_{\text{mean}} = \text{[H]}_0 - \text{[C}_2\text{H}_5\text{]}_0/2 \]  \hspace{1cm} (12)

This stoichiometric correction was \( \leq 14\% \). The H atoms may also react with the remaining molecular fluorine from the microwave discharge. However, the rate coefficient for this reaction is about 75 times lower \(^{25}\) at room temperature (and even lower at lower temperatures) than the \( \text{H} + \text{C}_2\text{H}_5 \) reaction studied here. The bimolecular rate constant, \( k_1 \), is then related to \( k_{\text{corr}} \) and \([\text{H}]_{\text{mean}}\) through the expression,

\[ k_{\text{corr}} = k_1 \text{[H]}_{\text{mean}} + k_w, \]  \hspace{1cm} (13)

where \( k_w \) is the first-order rate constant for heterogeneous loss of \( \text{C}_2\text{H}_5 \) on the wall, but could also include other first-order loss processes except for reaction with H atoms. Table 1 summarizes the results that comprise variations of several reaction parameters and conditions. Variation of \([\text{H}]_0/[\text{C}_2\text{H}_5]_0\) from 3.1 to 5.7 and variation of \([\text{H}]_{\text{mean}}\) and \([\text{C}_2\text{H}_5]_0\) by a factor of \( \times 10^{-10} \) had no effect on the reaction kinetics within experimental uncertainty.

Figure 2 shows a plot of \( k_{\text{corr}} \) vs \([\text{H}]_{\text{mean}}\) for the data at \( P = 0.5, 1.0 \) and 2.0 Torr He and \( T = 202 \text{ K} \). The absence of a pressure dependence on \( k_1 \) in the range covered is indicated by the fact that all the data lie on the same line. The bimolecular rate constant is determined from the slope of the line in Figure 2 using least-squares analysis. Similar plots were prepared using the
data at $T = 295$ and 150 K. The results for $k_1$ at each temperature are $k_1(295 \text{ K}) = (1.02 \pm 0.14) \times 10^{-10}$, $k_1(202 \text{ K}) = (1.02 \pm 0.12) \times 10^{-10}$, and $k_1(150 \text{ K}) = (0.93 \pm 0.11) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, where the quoted uncertainty is statistical (1σ) only and is at the 95% confidence level. As the rate coefficient $k_1$ does not appear to be temperature dependent, the least-squares analysis was performed for the complete data set. Figure 3 shows a plot of $k_{\text{corr}}$ vs [H]$_{\text{mean}}$ for all the data tabulated in Table 1. The least-squares analysis shows the rate constant for the entire data set is indistinguishable from those calculated separately for each temperature. Thus, the temperature independent rate constant $k_1 = (1.03 \pm 0.07) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, and the $k_w$ is $(216 \pm 30)$ s$^{-1}$, where the quoted uncertainty is statistical (1σ) only and is at the 95% confidence level. This $k_w$ for C$_2$H$_5$ is larger than the one previously observed in our laboratory, $k_w = (80 \pm 90)$ s$^{-1}$, in the presence of N$_2$ for a study of the N + C$_2$H$_5$ reaction. It may be noted that the hydrocarbon radical wall-losses may vary depending on many factors such as the condition of the wall and the presence of reagents. A good example is the methyl radical wall-loss measured in our flow tube studies. It was very small, = 10 s$^{-1}$, and independent of temperature and pressure in the reaction CH$_3$ + CH$_3$ \cite{3,26}; however, it was higher in studies of H + CH$_3$ (= 25 s$^{-1}$) \cite{27} and N + CH$_3$ (= 67-109 s$^{-1}$ depending on temperature) \cite{28,29}. Therefore, the wall-loss variability of hydrocarbon radicals is expected but not completely understood \cite{29}.

The uncertainties of the rate coefficients were statistically derived from the kinetic data. As shown in Figure 1, C$_2$H$_5$ decays consisted of 6-8 points, and each point was calculated by averaging 3-4 C$_2$H$_5$ signal measurements. The standard deviation of the C$_2$H$_5$ signal measurements was not considered in determining the measured pseudo-first-order rate constant ($k_{\text{corr}}$) in the least-square analysis. The statistical errors in the measured $k_{\text{corr}}$ (σ,
\(\Delta k_{\text{corr}}\) presented in Table 1 are relatively small. They did not affect the results when these statistical errors were included in a weighted least-square analysis to determine \(k_1\) and \(k_w\). 

\(\text{[H]}_{\text{mean}}\) had an uncertainty of about \(\pm 5\%\), which was controlled by the uncertainty in \([\text{F}]_0\). In addition to these errors, the experimental procedure allowed for systematic errors that added an additional \(\pm 10\%\) uncertainty to the rate constants measured in this study. The rate constants \(k_1\) at \(T = 295, 202\) and \(150\) K, with their total uncertainties, are presented in Table 2.

The temperature independent rate constant derived from all the data, with its total uncertainty, is \(k_1 = (1.03\pm0.17) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

**Discussion**

The rate constant determined here for the atom-radical reaction \(\text{H} + \text{C}_2\text{H}_5\) (1) is very fast as expected, \(k_1 = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at \(T = 295\) K and \(P = 1.0\) Torr He. It is as fast as that for \(\text{N} + \text{C}_2\text{H}_5\) measured in our laboratory\(^{16}\), which is \(1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at the same temperature and pressure. The rate constant is also found to be temperature and pressure independent, \(k_1 = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at \(T = 295-150\) K and \(P = 0.5-2.0\) Torr He.

This is about one-half the value of the rate constant for \(\text{O}(^{3}\text{P}) + \text{C}_2\text{H}_5\) measured by Slagle \textit{et al.}\(^ {30}\), which is \(2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and is also temperature and pressure independent in the ranges of \(T = 295-600\) K and \(P = 1.0-4.0\) Torr He.

In Table 2 we summarize the previous as well as the present measurements of \(k_1\) which have been made over a range of pressures and temperatures and with a variety of experimental techniques. Our results for \(k_1\) are only in moderate to poor agreement with previous studies or reviews, being in general either about a factor of two higher\(^{7,13,15}\) or three lower.\(^ {14}\) We do note that the value of the rate constant for the addition/decomposition channel from the direct and most recent study by Sillesen \textit{et al.}\(^ {14}\), \(k_{1a} = 1.25 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at \(T = 298\) K and \(P\).
= 75 Torr H₂, is coincidentally in agreement with our value for the total rate constant, \( k_1 = 1.03 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at \( T = 295 \text{ K} \) and \( P = 1.0 \text{ Torr He} \). This could support the hypothesis that channel 1a is the major channel for the \( \text{H} + \text{C}_2\text{H}_5 \) reaction.

We conclude our discussion of the \( \text{H} + \text{C}_2\text{H}_5 \) reaction with the results of the numerical simulation of this reaction system. Two numerical simulations of the reaction system at \( T = 202 \text{ K} \) and \( P = 1.0 \text{ Torr} \) were performed using Gear's Method to check the premise that the simple graphical method (equation 13) determined a valid rate constant \( k_1 \). The initial concentrations in molecule cm⁻³ used in these two simulations were as follows: 1) \([\text{H}_2] = 1.40 \times 10^{14}, [\text{C}_2\text{H}_5] = 2.55 \times 10^{12}, [\text{F}_2] = 1.85 \times 10^{12}, \) and \([\text{F}] = 3.97 \times 10^{12} \); and 2) \([\text{H}_2] = 1.38 \times 10^{14}, [\text{C}_2\text{H}_5] = 2.51 \times 10^{12}, [\text{F}_2] = 4.44 \times 10^{12}, \) and \([\text{F}] = 8.89 \times 10^{12} \). To compare the graphical method with the numerical simulation, the \( \text{C}_2\text{H}_5 \) net signals were converted to absolute concentrations of \( \text{C}_2\text{H}_5 \) by multiplication with a scaling factor. The latter was calculated from \([\text{C}_2\text{H}_5]_0 \) derived from equation 8 and the intercept (signal at \( t = 0 \)) of the decay curves similar to the ones shown in Figure 1. The reaction mechanism and the rate constants used in the numerical simulation are presented in Table 3. The rate constant for the reaction \( \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \) is known to be essentially pressure and temperature independent in the range of our experiments, with \( k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (Ref. 32) or \( 2.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (Ref. 33). Shafir et al. 33 pointed out potential complications in the experiments of Atkinson and Hudgens 32, which may possibly explain the difference. We employed both values in the simulation. Since the reaction \( \text{C}_2\text{H}_5 + \text{F} \) has not been studied previously, we used as an estimate the rate constant for the related reaction \( \text{C}_2\text{H}_5 + \text{Cl} \) measured at \( T = 218-297 \text{ K} \), i.e. \( k(\text{C}_2\text{H}_5 + \text{F}) = 1.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at \( T = 202 \text{ K} \).

According to our numerical simulation and depending on \([\text{H}] \), reaction (1) accounted for
about 55-75% of the loss of C$_2$H$_5$ while the C$_2$H$_5$ wall-loss contributed about 20-40%. The C$_2$H$_5$ self-reaction was negligible, contributing less than 1.7% or 2% depending on the value used for the C$_2$H$_5$ self-reaction rate constant. This shows that the result is not sensitive to the value used for k(C$_2$H$_5$+C$_2$H$_5$)$_{32,33}$. Most of the secondary chemistry contribution was due to the C$_2$H$_5$ + F$_2$ reaction along the decay (< 6%) and the C$_2$H$_5$ + F reaction in the early stages (< 3 ms) of the C$_2$H$_5$ decay (< 4%). As the second contribution was limited in time and very small over the total C$_2$H$_5$ loss, the result is not sensitive to the estimated value of the C$_2$H$_5$ + F rate constant used. The three secondary reactions (C$_2$H$_5$ + C$_2$H$_5$, C$_2$H$_5$ + F$_2$ and C$_2$H$_5$ + F) contributed less than 10% to the observed C$_2$H$_5$ decay. It is important to note that the inclusion of the C$_2$H$_5$ + F$_2$ reaction in the model will decrease the estimated rate constant about 6% while the inclusion of the H + F$_2$ reaction$^{25}$ will increase the estimated rate constant about 4%. Thus, the presence of these two secondary reactions has little effect on the measurement of the rate constant for the H + C$_2$H$_5$ reaction.

Summary and Conclusions

The title rate constant has been measured at low temperatures, T = 150, 202 and 295 K, and low pressures, P = 0.5, 1.0 and 2.0 Torr He, using the discharge-flow kinetic technique with low-energy electron impact mass spectrometry. With [H] in excess over [C$_2$H$_5$], we monitored the decay of C$_2$H$_5$ at m/z = 29. The results of this study show the primary reaction was essentially isolated from secondary reactions. Our results suggest a negligible temperature and pressure dependence over the ranges studied. The absolute rate constants for the reaction H + C$_2$H$_5$ are $k_{395K} = (1.02\pm0.24)\times10^{-10}$, $k_{202K} = (1.02\pm0.22)\times10^{-10}$, and $k_{150K} = (0.93\pm0.21)\times10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The temperature independent rate constant derived from all the data is $k_1 = (1.03\pm0.17)\times10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. 
Acknowledgements. The NASA Planetary Atmospheres Research Program supported this work. ASP thanks the National Academy of Science for the award of a research associateship. FLN acknowledges support under a NASA cooperative agreement with the Catholic University of America.
References


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(31) Gear, C. W. *Numerical initial value problems in ordinary differential equations*, Prentice


Table 1. Summary of experimental results for the reaction H + C₂H₅ at T = 295, 202, and 150 K. P = 1 Torr He, except where noted.

<table>
<thead>
<tr>
<th>T/K</th>
<th>([\text{H}]_{\text{mean}}/10^{12}) molecule cm⁻³</th>
<th>[C₂H₅]₀</th>
<th>[F₂]rem</th>
<th>([\text{H}]₀/\text{[C₂H₅]}₀)</th>
<th>(k_{\text{corr}}) s⁻¹</th>
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<tbody>
<tr>
<td>295</td>
<td>8.48</td>
<td>2.02</td>
<td>6.35</td>
<td>4.19</td>
<td>970</td>
</tr>
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<td></td>
<td>6.32</td>
<td>1.23</td>
<td>4.50</td>
<td>5.12</td>
<td>805</td>
</tr>
<tr>
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<td>4.89</td>
<td>0.96</td>
<td>3.58</td>
<td>5.10</td>
<td>814</td>
</tr>
<tr>
<td></td>
<td>7.10</td>
<td>1.39</td>
<td>5.24</td>
<td>5.09</td>
<td>953</td>
</tr>
<tr>
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<td>3.17</td>
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<td>2.61</td>
<td>4.11</td>
<td>578</td>
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<tr>
<td></td>
<td>1.96</td>
<td>0.47</td>
<td>2.26</td>
<td>4.13</td>
<td>399</td>
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<td>5.14</td>
<td>1.28</td>
<td>3.60</td>
<td>4.01</td>
<td>570</td>
</tr>
<tr>
<td></td>
<td>1.47</td>
<td>0.37</td>
<td>1.76</td>
<td>4.01</td>
<td>361</td>
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<tr>
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<td>4.30</td>
<td>1.23</td>
<td>3.47</td>
<td>3.49</td>
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<td>2.33</td>
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<td>5.01</td>
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<td>860</td>
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<td>4.31</td>
<td>0.89</td>
<td>3.08</td>
<td>4.84</td>
<td>733</td>
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<td>4.84</td>
<td>536</td>
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<td>202</td>
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<td>4.78</td>
<td>4.84</td>
<td>857</td>
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<td>0.99</td>
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<td>1.71</td>
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<td>515ᵇ</td>
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<tr>
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<td>4.92</td>
<td>1.36</td>
<td>2.94</td>
<td>3.62</td>
<td>574ᵇ</td>
</tr>
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<td>1.49</td>
<td>3.55</td>
<td>3.06</td>
<td>509</td>
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<td>1.32</td>
<td>3.68</td>
<td>3.64</td>
<td>602</td>
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<td>0.45</td>
<td>1.24</td>
<td>3.89</td>
<td>328</td>
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<td>150</td>
<td>1.79</td>
<td>0.39</td>
<td>1.24</td>
<td>4.57</td>
<td>303</td>
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<td>1.13</td>
<td>0.27</td>
<td>0.92</td>
<td>4.24</td>
<td>278</td>
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<td>3.37</td>
<td>0.80</td>
<td>2.38</td>
<td>4.24</td>
<td>563</td>
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<td>7.20</td>
<td>1.26</td>
<td>4.47</td>
<td>5.69</td>
<td>784</td>
</tr>
</tbody>
</table>

ᵃ P = 2.0 Torr He
ᵇ P = 0.5 Torr He.
ᶜ \([\text{F₂}]_{\text{rem}}\) is the remaining molecular fluorine when the microwave discharge is on.
Table 2. Comparison of the rate coefficients measured for the H + C₂H₅ reaction at different temperatures and pressures.

<table>
<thead>
<tr>
<th>Reaction Channel</th>
<th>k /cm³ molecule⁻¹ s⁻¹</th>
<th>P /Torr (M)ᵃ</th>
<th>T/K</th>
<th>Techniqueᵇ</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>6.0x10⁻¹¹</td>
<td>50 (He)</td>
<td>298</td>
<td>FP-RF</td>
<td>[7]</td>
</tr>
<tr>
<td>1a</td>
<td>1.8x10⁻¹⁰ exp(-438/T)</td>
<td>1.2-2 (H₂)</td>
<td>303-603</td>
<td>DF-GC</td>
<td>[8]</td>
</tr>
<tr>
<td>1a</td>
<td>8.3x10⁻¹¹</td>
<td>2-600 (He)</td>
<td>298</td>
<td>MSP-RA</td>
<td>[9]</td>
</tr>
<tr>
<td>1a</td>
<td>6.2x10⁻¹¹</td>
<td>8-16 (Ar)</td>
<td>503-753</td>
<td>DF-GC</td>
<td>[10]</td>
</tr>
<tr>
<td>1c</td>
<td>2.8x10⁻¹²</td>
<td>8-16 (Ar)</td>
<td>503-753</td>
<td>DF-GC</td>
<td>[10]</td>
</tr>
<tr>
<td>1a</td>
<td>1.1x10⁻¹⁰ exp(-112/T)</td>
<td>8 (He)</td>
<td>321-521</td>
<td>DF-MSFP</td>
<td>[11]</td>
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<td>1a</td>
<td>7.1x10⁻¹¹</td>
<td>6-15 (He)</td>
<td>295</td>
<td>DF-MSFP</td>
<td>[12]</td>
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<tr>
<td>1a</td>
<td>8.0x10⁻¹¹ exp(-127/T)</td>
<td>2-10 (Ar)</td>
<td>230-568</td>
<td>DF-GC</td>
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<tr>
<td>Total</td>
<td>2.91x10⁻¹⁰</td>
<td>75 (H₂)</td>
<td>298</td>
<td>PR-IR</td>
<td>[14]</td>
</tr>
<tr>
<td>1a</td>
<td>1.25x10⁻¹⁰</td>
<td>75 (H₂)</td>
<td>298</td>
<td>PR-IR</td>
<td>[14]</td>
</tr>
<tr>
<td>Total</td>
<td>(1.02±0.24)x10⁻¹⁰ᵈ</td>
<td>1 (He)</td>
<td>295</td>
<td>DF-MS</td>
<td>This work</td>
</tr>
<tr>
<td>Total</td>
<td>(1.02±0.22)x10⁻¹⁰ᵈ</td>
<td>0.5-2 (He)</td>
<td>202</td>
<td>DF-MS</td>
<td>This work</td>
</tr>
<tr>
<td>Total</td>
<td>(0.93±0.21)x10⁻¹⁰ᵈ</td>
<td>1 (He)</td>
<td>150</td>
<td>DF-MS</td>
<td>This work</td>
</tr>
</tbody>
</table>

ᵃ M is the bath gas.
ᶜ Extensive literature review where the major process is recommended to be the reaction 1a.
ᵈ Total uncertainty is 1σ statistical plus 10 % systematic.
Table 3. Chemical mechanism and rate constants used in the numerical simulations of the 
C$_2$H$_5$ decays at T = 202 K.

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>$k$ (202 K) /cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>F + H$_2$ → H + HF</td>
<td>1.12×10$^{-11}$</td>
<td>19</td>
</tr>
<tr>
<td>F + C$_2$H$_6$ → C$_2$H$_5$ + HF</td>
<td>1.34×10$^{-10}$</td>
<td>20</td>
</tr>
<tr>
<td>H + C$_2$H$_5$ → products</td>
<td>1.0×10$^{-10}$</td>
<td>This work</td>
</tr>
<tr>
<td>C$_2$H$_5$ + C$_2$H$_5$ → products</td>
<td>2.0×10$^{-11}$</td>
<td>32</td>
</tr>
<tr>
<td>C$_2$H$_5$ + C$_2$H$_5$ → products</td>
<td>2.8×10$^{-11}$</td>
<td>33</td>
</tr>
<tr>
<td>C$_2$H$_5$ + F$_2$ → C$_2$H$_3$F + F</td>
<td>1.2×10$^{-11}$</td>
<td>23, 24</td>
</tr>
<tr>
<td>F + C$_2$H$_5$ → C$_2$H$_4$ + HF</td>
<td>1.8×10$^{-10}$</td>
<td>34</td>
</tr>
<tr>
<td>H + F$_2$ → F + HF</td>
<td>2.5×10$^{-13}$</td>
<td>25</td>
</tr>
<tr>
<td>C$_2$H$_5$ → products</td>
<td>216</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^a$ Rate constant at T = 295 K; no T dependence expected at lower temperatures.

$^b$ Rate constant at T = 300, 400 K; no T dependence expected at lower temperatures.

$^c$ Rate constant estimated by trend analysis; see text.

$^d$ Rate constant for the analogous C$_2$H$_5$ + Cl reaction.

$^e$ Units are s$^{-1}$.

Figure Captions

Figure 1. Typical first-order logarithmic decay plots of C$_2$H$_5$ signal (arbitrary units) vs time (ms) in the presence of three excess concentrations of hydrogen atoms: [H]$_{mean}$ = 0.82×10$^{12}$ (□); [H]$_{mean}$ = 2.98×10$^{12}$ (○); and [H]$_{mean}$ = 6.66×10$^{12}$ molecule cm$^{-3}$ (O) at T = 202 K.

Figure 2. Plot of corrected pseudo-first-order rate constant $k_{corr}$ vs the mean hydrogen atom concentration at T = 202 K and P = 0.5 Torr (▲), 1.0 Torr (△), and 2.0 Torr (●).

Figure 3. Summary plot of corrected pseudo-first-order rate constant $k_{corr}$ vs the mean hydrogen atom concentration at different temperatures and pressures (T = 295 K and P = 1 Torr (□); T = 202 K and P = 0.5 Torr (▲); T = 202 K and P = 1.0 Torr (△); T = 202 K and P = 2.0 Torr (●); T = 150 K and P = 1.0 Torr (×)).