

The Rate Constant for the Reaction $\text{H} + \text{C}_2\text{H}_5$ at $T = 295 - 150 \text{ K}$

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Abstract

The reaction between the hydrogen atom and the ethyl (C_2H_5) radical is predicted by photochemical modeling to be the most important loss process for C_2H_5 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 $H + C_2H_5$ (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 $H + C_2H_5$ 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 C_2H_5 radical in the presence of excess hydrogen was monitored by low-energy electron impact mass spectrometry under pseudo-first order conditions. H atoms and C_2H_5 radicals were generated rapidly and simultaneously by the reaction of fluorine atoms with H_2 and C_2H_6 , respectively. The total rate constant was found to be temperature and pressure independent. The measured total rate constant at each temperature are: $k_1(295K) = (1.02 \pm 0.24) \times 10^{-10}$, $k_1(202K) = (1.02 \pm 0.22) \times 10^{-10}$ and $k_1(150K) = (0.93 \pm 0.21) \times 10^{-10}$, all in units of $cm^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The total rate constant derived from all the combined measurements is $k_1 = (1.03 \pm 0.17) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. 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, C_2H_5 , Rate Coefficients, H atom reaction, Atom-Radical Reaction, Saturn, Jupiter, Atmosphere

Introduction

The ethyl radical, C_2H_5 , is predicted by photochemical modeling to be one of the most abundant C_2 radical species in the atmospheres of Jupiter¹ and Saturn^{2,3}. The $H + C_2H_5$ reaction is the most important loss process for C_2H_5 and a major source of CH_3 in these atmospheres along with the production from CH_4 photolysis (either directly to CH_3 or indirectly *via* 1CH_2)⁴. The column abundances of CH_3 on Saturn and Neptune were observed by the Infrared Space Observatory Satellite (ISO)^{5,6} to be lower than those predicted by atmospheric photochemical models^{1,2}. A suggested source for this discrepancy was the rate coefficient for the CH_3 self-recombination reaction. However, our previously study of the $CH_3 + CH_3$ reaction at $T = 155$ K showed that this reaction is not fast enough to completely solve the CH_3 overproduction problem in the photochemical models of Neptune and Saturn³. Therefore, it is logical to examine uncertainties in the rate coefficient for the $H + C_2H_5$ reaction as an important source of CH_3 .

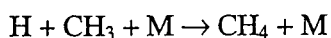
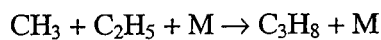
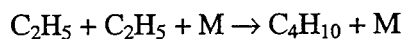
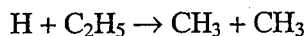
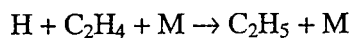
The thermodynamically accessible channels for the $H + C_2H_5$ reaction and the corresponding enthalpies of reaction at $T = 298$ K, ΔH_{298}^0 , are:



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 $k_1 = 6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = 298$ K. In what appears to be

the first direct (although not absolute) measurement, Kurylo *et al*⁷ employed flash photolysis-resonance fluorescence to derive the value $k_1 = 6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = 298 \text{ K}$ and $P = 50 \text{ Torr He}$.

In one of the two most recent studies, Pratt and Wood¹³ in 1984 performed discharge-flow experiments with final product analysis *via* gas chromatography at $P = 2\text{-}10 \text{ Torr Ar}$ and temperatures down to $T = 230 \text{ K}$, which is the lowest temperature at which this reaction has been studied. They derived a slightly negative temperature-dependent rate coefficient for reaction (1a), $k_{1a} = 8.0 \times 10^{-11} \exp(-127/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, based on the following series of reactions initiated by the reaction of atomic hydrogen with ethylene:



Pratt and Wood¹³ performed a complex multi-parameter fitting procedure for the formation of four products, which used rate constants for the reactions $\text{CH}_3 + \text{CH}_3$, $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5$, and $\text{CH}_3 + \text{C}_2\text{H}_5$, and a temperature-independent rate coefficient for the $\text{H} + \text{C}_2\text{H}_4$ reaction¹⁵. Their sensitivity analysis showed that the derived rate constant for the $\text{H} + \text{C}_2\text{H}_5$ reaction is highly dependent on the assumed rate constants for those reactions.

In the second recent study, Sillesen *et al.*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 literature¹⁵. 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.¹⁵ 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 $T = 298$ K¹⁶. 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 data⁷⁻¹⁴ 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 Jupiter¹ and Saturn².

Experimental Description

All experiments were performed in a Pyrex flow tube, ~100 cm long and 2.8 cm in diameter³. 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 nitrogen³. The temperature was continuously monitored using a thermocouple in the flow tube located at $d \approx 28$ 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 ± 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 F₂ (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 F₂ was dissociated in the discharge. The potential effect of residual F₂ on the C₂H₅ radical consumption was considered in the analysis of the kinetic data. The concentration of F atoms used to generate H atoms and C₂H₅ radicals was determined by measuring the consumption of Cl₂ in the fast titration reaction



where $k_2 = 6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ independent of temperature.¹⁸ The initial F atom concentration was determined by measuring the decrease in the Cl₂ signal ($m/z = 70$) when the microwave discharge was initiated. The dilute Cl₂/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 C₂H₅ reactant. Because Cl₂ has been observed³ 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.³ The F atom concentration is given by

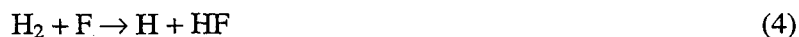
$[F]_0 \doteq [\text{Cl}_2]_{\text{disch,off}} - [\text{Cl}_2]_{\text{disch,on}} \equiv \Delta \text{Cl}_2 \text{ signal} \times [\text{Cl}_2]_{\text{disch,off}}$, where $\Delta \text{Cl}_2 \text{ signal}$ is the fractional decrease in the Cl₂ signal, $(S_{\text{disch,off}} - S_{\text{disch,on}}) / S_{\text{disch,off}}$. Under our experimental conditions, a

Cl₂ concentration greater than $2 \times 10^{13} \text{ molecule cm}^{-3}$ 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:

$$[F]_0^{\text{corrected}} = [F]_0 \times \left(1 + e^{\left(\frac{k_2 [Cl_2] d}{v} \right)} \right) \quad (3)$$

where d (cm) is the distance of the movable probe from the sampling pinhole, $[Cl_2]$ is the 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 C_2H_5 radicals were produced rapidly and simultaneously via the reactions:



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). H_2 and C_2H_6 were in large excess over F_2 with the ratio $[H_2 + C_2H_6]/[F_2] = 92/1$ to $9/1$. $[H_2]$ and $[C_2H_6]$ were adjusted to produce the desired $[H]_0/[C_2H_5]_0$ ratios, R , as shown in the expression:

$$R = \frac{[H]_0}{[C_2H_5]_0} = \frac{k_4 \times [H_2]_0}{k_5 \times [C_2H_6]_0} \quad (6)$$

Maricq and Szenté²⁰ 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 $[H]_0$ and $[C_2H_5]_0$ were calculated from the measured $[F]_0$ and the ratio R from equation 6 as given by

$$[H]_0 = [F]_0 \times \left(\frac{R}{1+R} \right) \quad (7)$$

$$[C_2H_5]_0 = [F]_0 - [H]_0 \quad (8)$$

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 ¹⁹. We use the direct result of Stevens *et al.*¹⁹, $k_4 = 1.20 \times 10^{-10} \exp(-470/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 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_2H_5 in our experiments. Neglecting mixing, formation of H and C_2H_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_2H_5 were complete within about 2 ms ($\approx 5 \text{ cm}$) due to the lower rate constants for reactions (4) and (5) at that temperature.

C_2H_5 radicals were detected at $m/z = 29$ following low-energy electron ionization to minimize any contribution to the C_2H_5 signal from dissociative ionization of C_2H_6 , which was present in large excess over C_2H_5 radicals. The observed C_2H_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_2H_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_2H_5 concentration of $\sim 1 \times 10^{11} \text{ molecule cm}^{-3}$ was detected with $S/B \geq 2$. Mass scans were initially recorded for the region $m/z = 27-31$, and C_2H_5 signals were taken as the integrated area of the $m/z = 29$ 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. F₂ (99.9%, Cryogenic Rare Gases, 5% in He) and H₂ (99.999%, Air Products UHP) were used as provided without further purification. Cl₂ (VLSI 4.8 grade, Air Products) and C₂H₆ (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 C₂H₅ 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:

$$\text{time } (t) = \text{distance } (d)/\text{velocity } (v) \quad (9)$$

Pseudo-first-order conditions were used with the hydrogen atoms in excess over ethyl radicals: $3.1 < [H]_0/[C_2H_5]_0 < 5.7$, as shown in Table 1. This lower than usual ratio is acceptable since the most likely complicating secondary reaction, the C₂H₅ self-reaction, is considerably slower¹⁵ 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

$$\ln[C_2H_5]_t = -k_{\text{obs}} (d/v) + \ln[C_2H_5]_0, \quad (10)$$

where [C₂H₅] is proportional to the mass spectrometer signal and *k*_{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*_{obs}. Plots of the decay of C₂H₅ 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_{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_{obs} were made to give k_{corr} :

$$k_{\text{corr}} = k_{\text{obs}} (1 + D k_{\text{obs}}/v^2) - k_{12} [\text{F}_2] \quad (11)$$

where D is the diffusion coefficient of C_2H_5 in He and k_{12} is the rate coefficient of the reaction of C_2H_5 with the remaining molecular fluorine from the microwave discharge. D was estimated to be $667 \text{ cm}^2 \text{ s}^{-1}$ at $T = 295 \text{ K}$ 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 $T = 295 \text{ K}$, 1-4 % at $T = 202 \text{ K}$ and 1-3 % at $T = 150 \text{ K}$.

The rate constant for the reaction $\text{C}_2\text{H}_5 + \text{F}_2$ has been measured²² relative to that for $\text{C}_2\text{H}_5 + \text{O}_2 + \text{M}$ at $T = 298 \text{ K}$ and $P = 1\text{-}15 \text{ Torr CO}_2$. The ratio $k(\text{C}_2\text{H}_5 + \text{F}_2) / k(\text{C}_2\text{H}_5 + \text{O}_2 + \text{M})$ 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 $T = 298 \text{ K}$ 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 CH_3 and C_2H_5 with F_2 and Cl_2 . The relevant reactions $\text{CH}_3 + \text{F}_2$ 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

$$k(\text{C}_2\text{H}_5 + \text{F}_2) = k(\text{CH}_3 + \text{F}_2) \times k(\text{C}_2\text{H}_5 + \text{Cl}_2) / k(\text{CH}_3 + \text{Cl}_2)$$

and using the data from the literature^{23,24}, we obtain the values for $k(\text{C}_2\text{H}_5 + \text{F}_2)$:



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

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

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

The $k_{j2} [\text{F}_2]$ correction to our k_{obs} in equation 11 was also small (< 9%).

Because of depletion of H atoms caused by reaction with C_2H_5 , calculated H atom concentrations, $[\text{H}]_0$, were corrected¹⁶ to yield $[\text{H}]_{\text{mean}}$ using the expression:

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

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 lower²⁵ 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_{corr} and $[\text{H}]_{\text{mean}}$ through the expression,

$$k_{\text{corr}} = k_1 [\text{H}]_{\text{mean}} + k_w, \quad (13)$$

where k_w is the first-order rate constant for heterogeneous loss of C_2H_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 9-10 had no effect on the reaction kinetics within experimental uncertainty.

Figure 2 shows a plot of k_{corr} vs $[\text{H}]_{\text{mean}}$ for the data at $P = 0.5, 1.0$ and 2.0 Torr He and $T = 202$ 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 $k_1(150 \text{ K}) = (0.93 \pm 0.11) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 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_{corr} vs $[\text{H}]_{\text{mean}}$ 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 $k_1 = (1.03 \pm 0.07) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and the k_w is $(216 \pm 30) \text{ s}^{-1}$, where the quoted uncertainty is statistical (1σ) only and is at the 95% confidence level. This k_w for C_2H_5 is larger than the one previously observed in our laboratory, $k_w = (80 \pm 90) \text{ s}^{-1}$, in the presence of N_2 for a study of the $\text{N} + \text{C}_2\text{H}_5$ reaction¹⁶. 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, $\approx 10 \text{ s}^{-1}$, and independent of temperature and pressure in the reaction $\text{CH}_3 + \text{CH}_3$ ^{3,26}; however, it was higher in studies of $\text{H} + \text{CH}_3$ ($\approx 25 \text{ s}^{-1}$)²⁷ and $\text{N} + \text{CH}_3$ ($\approx 67\text{-}109 \text{ s}^{-1}$ depending on temperature)^{28,29}. Therefore, the wall-loss variability of hydrocarbon radicals is expected but not completely understood²⁹.

The uncertainties of the rate coefficients were statistically derived from the kinetic data. As shown in Figure 1, C_2H_5 decays consisted of 6-8 points, and each point was calculated by averaging 3-4 C_2H_5 signal measurements. The standard deviation of the C_2H_5 signal measurements was not considered in determining the measured pseudo-first-order rate constant (k_{corr}) in the least-square analysis. The statistical errors in the measured k_{corr} (σ ,

Δk_{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 . $[H]_{\text{mean}}$ had an uncertainty of about $\pm 5\%$, which was controlled by the uncertainty in $[F]_0$. 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 $k_1 = (1.03 \pm 0.17) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Discussion

The rate constant determined here for the atom-radical reaction $H + C_2H_5$ (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 $N + C_2H_5$ measured in our laboratory¹⁶, 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 $O(^3P) + C_2H_5$ measured by Slagle *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 *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 Method³¹ 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) $[\text{H}_2] = 1.40 \times 10^{14}$, $[\text{C}_2\text{H}_6] = 2.55 \times 10^{12}$, $[\text{F}_2] = 1.85 \times 10^{12}$, and $[\text{F}] = 3.97 \times 10^{12}$; and 2) $[\text{H}_2] = 1.38 \times 10^{14}$, $[\text{C}_2\text{H}_6] = 2.51 \times 10^{12}$, $[\text{F}_2] = 4.44 \times 10^{12}$, and $[\text{F}] = 8.89 \times 10^{12}$. To compare the graphical method with the numerical simulation, the C_2H_5 net signals were converted to absolute concentrations of C_2H_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 Hudgens³², 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 $\text{C}_2\text{H}_5 + \text{Cl}$ ³⁴ measured at $T = 218\text{-}297 \text{ K}$, 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_2H_5 while the C_2H_5 wall-loss contributed about 20-40%. The C_2H_5 self-reaction was negligible, contributing less than 1.7% or 2% depending on the value used for the C_2H_5 self-reaction rate constant. This shows that the result is not sensitive to the value used for $k(C_2H_5+C_2H_5)$ ^{32,33}. Most of the secondary chemistry contribution was due to the $C_2H_5 + F_2$ reaction along the decay (< 6%) and the $C_2H_5 + F$ reaction in the early stages (< 3 ms) of the C_2H_5 decay (< 4%). As the second contribution was limited in time and very small over the total C_2H_5 loss, the result is not sensitive to the estimated value of the $C_2H_5 + F$ rate constant used. The three secondary reactions ($C_2H_5 + C_2H_5$, $C_2H_5 + F_2$ and $C_2H_5 + F$) contributed less than 10 % to the observed C_2H_5 decay. It is important to note that the inclusion of the $C_2H_5 + F_2$ reaction in the model will decrease the estimated rate constant about 6 % while the inclusion of the $H + F_2$ reaction²⁵ 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 $H + C_2H_5$ 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 $[C_2H_5]$, we monitored the decay of C_2H_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 $H + C_2H_5$ are $k(295K) = (1.02 \pm 0.24) \times 10^{-10}$, $k(202K) = (1.02 \pm 0.22) \times 10^{-10}$, and $k(150 K) = (0.93 \pm 0.21) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The temperature independent rate constant derived from all the data is $k_1 = (1.03 \pm 0.17) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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Table 1. Summary of experimental results for the reaction $\text{H} + \text{C}_2\text{H}_5$ at $T = 295, 202,$ and 150

K. $P = 1$ Torr He, except where noted.

T/K	$[\text{H}]_{\text{mean}}$ / 10^{12}	$[\text{C}_2\text{H}_5]_0$ molecule cm^{-3}	$[\text{F}_2]_{\text{rem}}^{\text{c}}$ cm^{-3}	$[\text{H}]_0/[\text{C}_2\text{H}_5]_0$	$k_{\text{corr}}/\text{s}^{-1}$
295	8.48	2.02	6.35	4.19	970
	6.32	1.23	4.50	5.12	805
	4.89	0.96	3.58	5.10	814
	7.10	1.39	5.24	5.09	953
	3.17	0.77	2.61	4.11	578
	1.96	0.47	2.26	4.13	399
	5.14	1.28	3.60	4.01	570
	1.47	0.37	1.76	4.01	361
202	4.30	1.23	3.47	3.49	644
	2.33	0.67	1.95	3.50	396
	0.95	0.27	1.00	3.50	207
	6.19	1.76	3.44	3.52	801
	7.43	2.11	5.01	3.53	860
	4.31	0.89	3.08	4.84	733
	3.29	0.68	2.03	4.84	536
	7.35	1.52	4.78	4.84	857
	3.19	0.66	2.60	4.81	692 ^a
	5.83	1.21	4.98	4.81	799 ^a
	1.03	0.21	0.99	4.81	310 ^a
	5.24	1.28	3.54	4.08	615 ^a
	3.17	0.73	2.57	4.35	520 ^b
	2.72	0.63	1.71	4.33	515 ^b
4.92	1.36	2.94	3.62	574 ^b	
150	4.58	1.49	3.55	3.06	509
	4.79	1.32	3.68	3.64	602
	1.73	0.45	1.24	3.89	328
	1.79	0.39	1.24	4.57	303
	1.13	0.27	0.92	4.24	278
	3.37	0.80	2.38	4.24	563
	7.20	1.26	4.47	5.69	784

^a $P = 2.0$ Torr He

^b $P = 0.5$ Torr He.

^c $[\text{F}_2]_{\text{rem}}$ 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.

Reaction Channel	k /cm ³ molecule ⁻¹ s ⁻¹	P /Torr (M) ^a	T/K	Technique ^b	Reference
Total	6.0×10 ⁻¹¹	50 (He)	298	FP-RF	[7]
1a	1.8×10 ⁻¹⁰ exp(-438/T)	1.2-2 (H ₂)	303-603	DF-GC	[8]
1a	8.3×10 ⁻¹¹	2-600 (He)	298	MSP-RA	[9]
1a	6.2×10 ⁻¹¹	8-16 (Ar)	503-753	DF-GC	[10]
1c	2.8×10 ⁻¹²	8-16 (Ar)	503-753	DF-GC	[10]
1a	1.1×10 ⁻¹⁰ exp(-112/T)	8 (He)	321-521	DF-MSFP	[11]
1a	7.1×10 ⁻¹¹	6-15 (He)	295	DF-MSFP	[12]
1a	8.0×10 ⁻¹¹ exp(-127/T)	2-10 (Ar)	230-568	DF-GC	[13]
Total	2.91×10 ⁻¹⁰	75 (H ₂)	298	PR-IR	[14]
1a	1.25×10 ⁻¹⁰	75 (H ₂)	298	PR-IR	[14]
Total	6.0×10 ⁻¹¹	—	300-2000	Review	[15] ^c
Total	(1.02±0.24)×10 ^{-10 d}	1 (He)	295	DF-MS	This work
Total	(1.02±0.22)×10 ^{-10 d}	0.5-2 (He)	202	DF-MS	This work
Total	(0.93±0.21)×10 ^{-10 d}	1 (He)	150	DF-MS	This work

^a M is the bath gas.

^b FP-RF: flash photolysis-resonance fluorescence; DF-GC: discharge flow-gas chromatography; MSP-RA: mercury sensitized photolysis-resonance absorption; DF-MSFP: discharge flow-mass spectrometry final products; PR-IR: pulse radiolysis-infrared absorption; DF-MS: discharge flow-mass spectrometry.

^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_2H_5 decays at $T = 202$ K.

Chemical Reaction	k (202 K) /cm ³ molecule ⁻¹ s ⁻¹	Reference
$F + H_2 \rightarrow H + HF$	1.12×10^{-11}	19
$F + C_2H_6 \rightarrow C_2H_5 + HF$	1.34×10^{-10}	20
$H + C_2H_5 \rightarrow$ products	1.0×10^{-10}	This work
$C_2H_5 + C_2H_5 \rightarrow$ products	2.0×10^{-11} ^a	32
$C_2H_5 + C_2H_5 \rightarrow$ products	2.8×10^{-11} ^b	33
$C_2H_5 + F_2 \rightarrow C_2H_5F + F$	1.2×10^{-11} ^c	23,24
$F + C_2H_5 \rightarrow C_2H_4 + HF$	1.8×10^{-10} ^d	34
$H + F_2 \rightarrow F + HF$	2.5×10^{-13}	25
$C_2H_5 \rightarrow$ products	216 ^e	This work

^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 $C_2H_5 + Cl$ reaction.

^e Units are s⁻¹.

Figure Captions

Figure 1. Typical first-order logarithmic decay plots of C_2H_5 signal (arbitrary units) vs time (ms) in the presence of three excess concentrations of hydrogen atoms: $[H]_{\text{mean}} = 0.82 \times 10^{12}$ (\square); $[H]_{\text{mean}} = 2.98 \times 10^{12}$ (\blacklozenge); and $[H]_{\text{mean}} = 6.66 \times 10^{12}$ 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 (\blacktriangle), 1.0 Torr (\triangle), and 2.0 Torr (\bullet).

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 (\square); $T = 202$ K and $P = 0.5$ Torr (\blacktriangle); $T = 202$ K and $P = 1.0$ Torr (\triangle); $T = 202$ K and $P = 2.0$ Torr (\bullet); $T = 150$ K and $P = 1.0$ Torr (\times)).

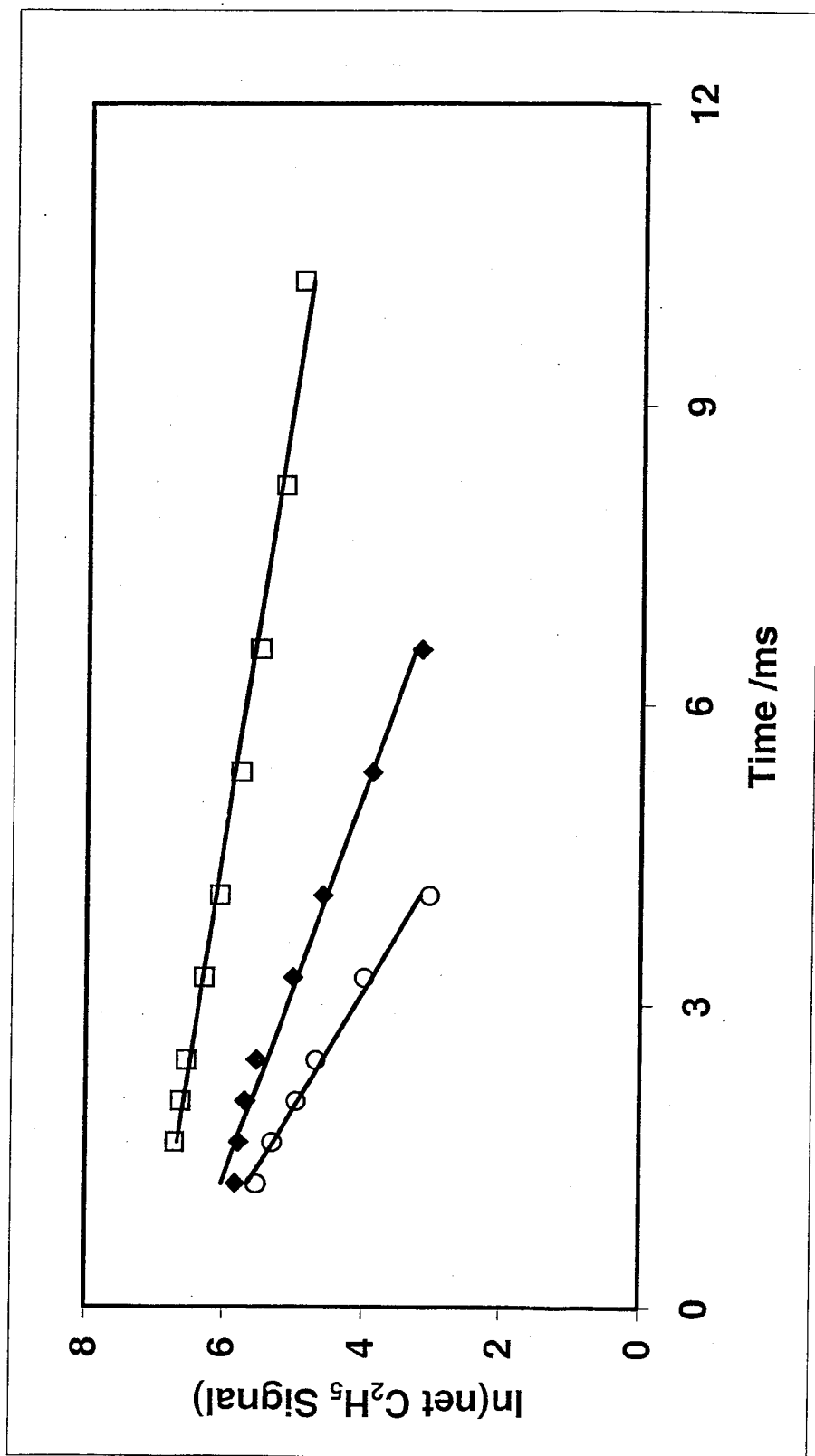


Figure 1

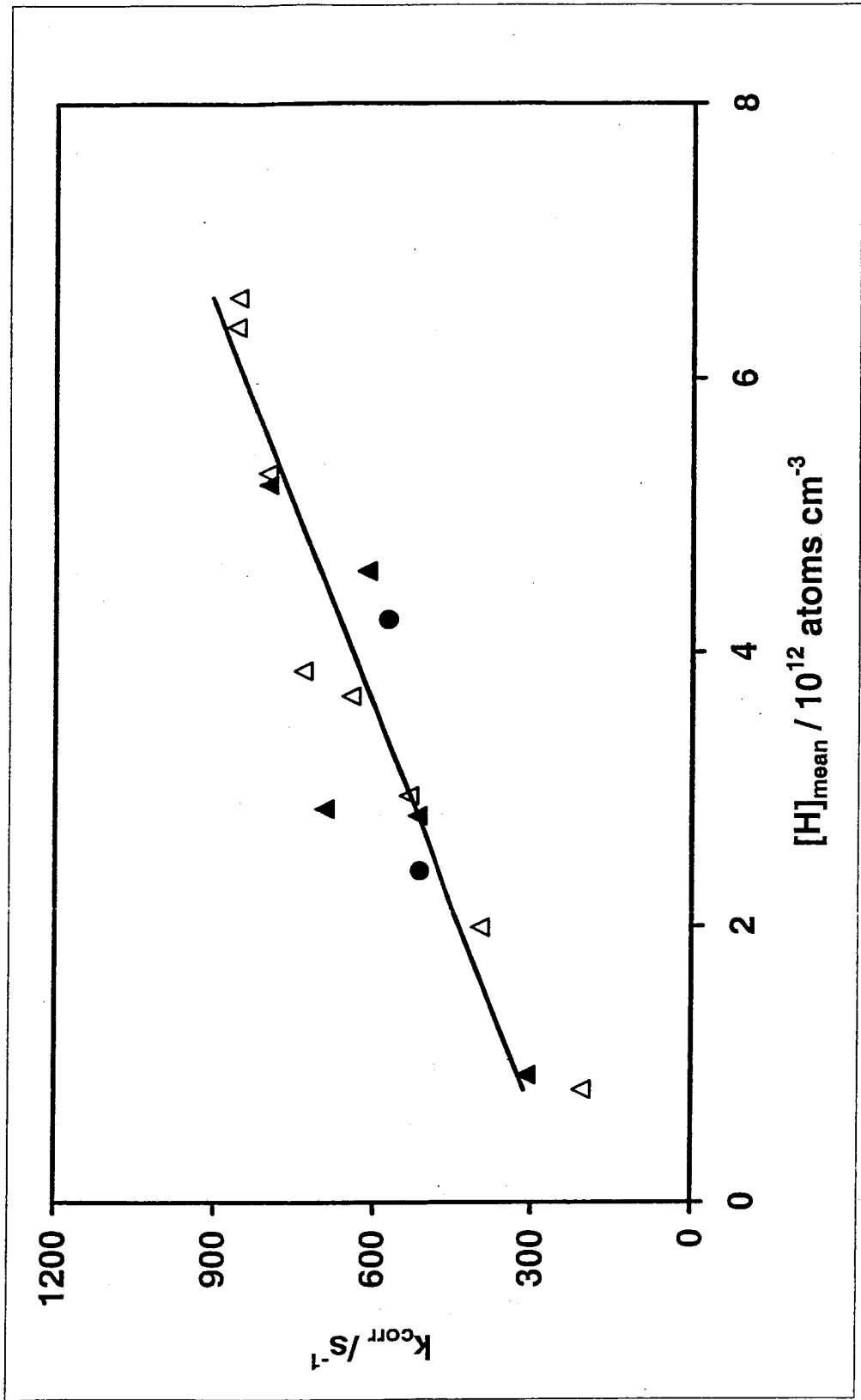


Figure 2

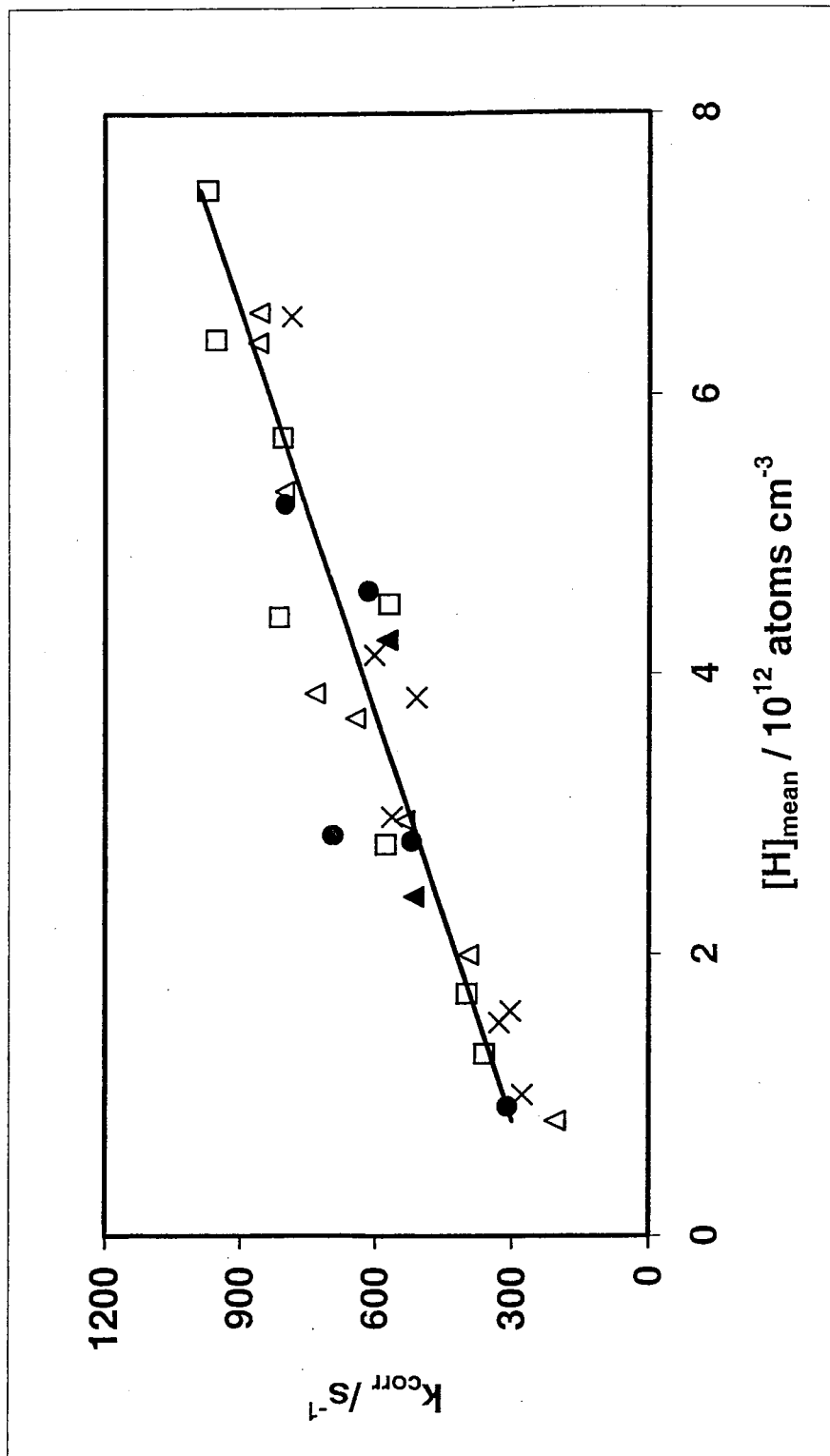


Figure 3