1150 J. Phys. Chem. A **2004,** *108,* 1150−1159

Kinetics of the Cl(^2P_J) + C_2H_6 Reaction between 177 and 353 K

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Received: August 18, 2003; In Final Form: December 8, 2003

Absolute rate data for the Cl + $C_2H_6 \rightarrow$ HCl + C_2H_5 reaction have been measured from 177 to 353 K using a conventional discharge flow resonance fluorescence technique with helium as the diluent at a pressure of 1 Torr. The rate coefficient at 296 K was measured to be $(5.70 \pm 0.13) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The Arrhenius expression which describes the temperature dependence of the rate coefficient is $(7.32 \pm 0.39) \times 10^{-11} \exp[(-73.6 \pm 12.9)/T]$ cm^3 molecule^{-1} s^{-1}. The cited errors are at the level of two standard deviations. The results were checked for potential interferences from nonequilibration of atomic Cl spin states, impurities in the Cl atom source, and other secondary chemistry resulting from high reactant concentrations. There was no observed change in the rate coefficient upon the addition of a large concentration of efficient spin quencher, CF_4. The results were also found to be invariant to purification of the Cl atom precursor. Numerical simulations confirmed that at the low reactant concentrations used, secondary reactions did not affect the observed rate coefficients to a significant extent.

Introduction

Because of their importance in atmospheric chemistry, it is vital that we measure the rates of reaction of atomic chlorine with hydrocarbon species. The reactions of chlorine atoms with nonmethane hydrocarbons (NMHCs) become significantly more important at lower altitudes in the troposphere where elevated concentrations of certain hydrocarbons have been measured near their sources.[1] Ethane is the second most abundant organic trace species in the troposphere, and with concentrations ranging from a few hundred pptv to a few ppbv it is approximately 3 orders of magnitude less concentrated than methane.[2−5] The sources of ethane are of both nonanthropogenic (oceanic emissions and terrestrial biogenic sources) and anthropogenic origin (natural gas losses, motor vehicle evaporative emission, refinery emission and biomass burning) which have been estimated to combine to give an ethane source strength of 15.5 Tg/yr.[2d] Furthermore, as increased concentrations of active chlorine levels have also been reported in the marine boundary layer,[6,7] it has been postulated that at these low altitudes, approximately 25% of the total loss of ethane could be due to its reaction with atomic chlorine (eq 1).[8]

$$\mathrm{Cl}(^2P_J) + C_2H_6 \rightarrow \mathrm{HCl} + C_2H_5 \qquad (1)$$

Observations by the stratosphere−troposphere experiments by aircraft measurements (STREAM) II campaign have shown that the Cl + C_2H_6 reaction is also important in the lower stratosphere.[9] Here the CO/C_2H_6 ratio, which is known to be relatively invariant to oxidation by OH radicals, was seen to be significantly perturbed in the presence of ice crystals typical of thin cirrus clouds, an indication of chlorine activation through heterogeneous reactions of the reservoir species $ClONO_2$ and HCl in the middle and high-latitude lowermost stratosphere. At these altitudes, temperatures can fall as low as 180 K.

Previous studies of the reaction of Cl + C_2H_6 fall into three main categories. The first category comprises measurements that determined values for the rate coefficient of this reaction by absolute methods.[10−24] These studies used either the flash photolysis (FP)[10−12,16,17,20−24] or the discharge flow (DF)[13−15,18] techniques for radical initiation. Various techniques were used to follow the progress of the reaction including laser-induced fluorescence (LIF),[24] IR absorption,[16,20,22,23] resonance fluorescence (RF),[10,12−14,17−19,21] mass spectrometry (MS),[15] and gas chromatography (GC).[11] Only four of these studies[12,14,15,20] examined the temperature dependence of the reaction, covering the temperature range of 200−800 K among them, although the Arrhenius expressions proposed from the available data[25,26] have been recommended for use only above 220 K.

The second category comprises measurements made by relative methods.[27−31] Here we focus on those studies that used the technique of competitive chlorination to obtain the temperature dependence of the rate coefficient of the Cl + C_2H_6 reaction relative to that of Cl + CH_4 in the range of 198−500 K.

The final category of previous work consists of theoretical analyses of the Cl + C_2H_6 reaction, either by calculation[32,33] or by the use of structure activity relationships (SAR).[34]

The major motivation for undertaking the present study revolves around the disagreement between competitive chlorination and absolute measurements of the rate coefficient for the atmospherically important Cl + CH_4 reaction. Absolute Cl + CH_4 rate coefficients can be derived from the competitive chlorination results using the currently recommended Arrhenius parameters for the absolute Cl + C_2H_6 rate equation,[25] which results in the following Arrhenius expression: $k(\mathrm{Cl} + CH_4)_{\text{from relative data}} = 1.97 \times 10^{-11} \exp(-1535/T)$. When compared with the currently recommended absolute Cl + CH_4 Arrhenius expression from Atkinson et al.,[25] $k(\mathrm{Cl} + CH_4)_{\text{from absolute data}} = 6.6 \times 10^{-12} \exp(-1240/T)$, the relative rate results overpredict the Cl + CH_4 rate coefficient at 500 K by 65% and correspondingly underpredict the rate coefficient at 180 K by 42%. The Sander et al.[26] recommended expression

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10.1021/jp036458f CCC: $27.50

for the Cl + CH_4 reaction was not used in the comparison because it includes the relative rate measurements in the determination of the Cl + CH_4 Arrhenius parameters. As the Cl + C_2H_6 reaction was chosen as the reference reaction for the competitive chlorination experiments in the majority of previous work[27−31] there is a need to accurately obtain kinetic information on this system over a wide range of temperatures. Moreover, as there is only a single measurement of the Cl + C_2H_6 reaction at <200 K,[30] substantial errors in the rate coefficient for the Cl + CH_4 reaction could correspondingly be conferred at low temperatures. Furthermore, a recent detailed absolute experimental study of the Cl + CH_4 reaction[35] found no evidence of systematic error, which further suggests that either the error lies in the absolute value of the rate coefficient for the Cl + C_2H_6 reaction or in the relative rate measurements themselves, although rate coefficients for Cl + CH_4 obtained from relative measurements using Cl + H_2 as the reference reaction are also lower than the directly measured Cl + CH_4 rate coefficients.[28,36] In general, the agreement between measurements within each technique is good. At higher temperatures there is also considerable disagreement between rate coefficients obtained for the Cl + C_2H_6 reaction by absolute and relative methods, upward of 50% above room temperature with the relative rate measurements being generally lower.

All current evaluations[25,26] of the available Cl + C_2H_6 data recommend that only data at $T > 220$ K be included for evaluation purposes, a symptom of the lack of high-quality, low-temperature data for this reaction**.** The present study will reevaluate the rate coefficient for the Cl + C_2H_6 reaction using a conventional discharge flow technique with resonance fluorescence detection in the vacuum ultraviolet and will extend the temperature range of the currently available experimental data to temperatures significantly below 200 K in an attempt to discover the source of these discrepancies.

Experimental Section

The current study was performed using a fast discharge flow system with resonance fluorescence detection. The apparatus is similar to that used in a previous study[35] where a schematic diagram of the experimental setup can be found. In this section only important modifications will be discussed.

Reactor. The temperature-controlled reaction vessel used in this study was 60 cm in length and had an internal diameter of 5.04 cm. At the downstream end of the flow tube, a stainless steel resonance fluorescence cell was situated. A port connected between the resonance cell and the flow cell provided the means for pressure measurements to be made using a 10 Torr baratron (MKS). The upstream end of the flow system consisted of connections for various microwave discharge sources and two fixed inlets. The first inlet was used to admit the bulk of the carrier gas, helium, into the flow system and did not carry a microwave discharge source. The second inlet admitted Cl atoms into the flow system using a microwave discharge of Cl_2 in a small flow of helium. A 1.5 cm outer diameter moveable inlet was also located at the upstream end of the flow system, which allowed various radical species or coreagents to be added to the flow cell in a small flow of helium at varying distances from the detection region. The inner surface of the flow tube and the outer surface of the moveable inlet were coated with halocarbon wax (Series 15-00, Halocarbon Corp.) in order to minimize the heterogeneous loss of Cl atoms in the flow system. Typical helium flow rates between 1900 and 2500 $cm^3\ min^{-1}$ at standard temperature and pressure (STP) were used to give flow velocities of 1000−1500 cm s^{-1}. A trapped 38 L s^{-1} rotary pump provided the means for a sufficient throughput of gas to support the required flow velocities. A throttling valve before the pump allowed pressures of approximately 1 Torr to be maintained during the experiments. Ethane was added to the flow system through the moveable inlet at flow rates from 0.02 to 0.14 $cm^3\ min^{-1}$ at STP. Refrigerating/heating bath circulators (Neslab, ULT-80DD/RTE-110) containing pentane or water as the circulating medium, respectively, were used to vary the temperature of the gases in the flow cell through an external heat exchange jacket. The temperature in the external jacket was measured using two thermocouples (type E, chromel−constantan), each one being situated at either end of the flow tube. Temperatures could be maintained to within ± 2 K except at the lowest temperature investigated. At this temperature a gradient along the length of the external jacket of approximately 10 K was found to exist due to the slow flow of refrigerant. An average temperature of 177 K was used.

Atomic Chlorine Source. Chlorine atoms were generated in the flow tube through a 60 W microwave discharge (2.45 GHz) of dilute mixtures of Cl_2 in He (ca. 0.1%). A 1 cm internal diameter Suprasil quartz tube was used within the discharge source. Downstream from the discharge, the walls of the tube were coated with phosphoric acid to minimize loss of atomic chlorine through heterogeneous recombination. Typical flow rates of 500 $cm^3\ min^{-1}$ at STP were passed through the discharge. Dissociation efficiencies were found to be on the order of 10−18% for typical Cl atom concentrations of between 1.6×10^9 and 1.1×10^{10} atoms cm^{-3}.

Atomic Chlorine Detection. Relative intensities of atomic chlorine emission were observed downstream from the temperature-controlled portion of the flow system in the resonance cell. Atomic chlorine fluorescence was excited by radiation from a 50 W microwave discharge in a resonance lamp. A mixture of approximately 0.13% Cl_2 in He was passed through the lamp at a total pressure of approximately 1.5 Torr. Light emitted from the lamp was collimated using a series of concentric baffles, before being passed into the resonance cell. Fluorescence was emitted from the atomic chlorine within the illuminated portion of the cell on-resonance with the exciting radiation, mainly in the $(4s^13p^4)^4P_{3/2} \rightarrow (3p^5)^2P_{3/2}$ transition at 137.96 nm. The fluorescence was observed at right angles to the lamp using a channel photomultiplier (CPM) (Perkin-Elmer 1911P) which was sensitive to light between 120 and 200 nm. Immediately in front of the CPM, a 1 mm thick BaF_2 window was used as a cut-on filter to eliminate possible interference from oxygen and hydrogen atom emission. This was thought to potentially result from impurities in either the chlorine or helium flows. A second series of baffles was used in front of this window and Wood's horns were placed opposite the lamp and CPM in order to reduce further the detection of scattered light. The CPM output signal was passed to a photon-counting system, where typically, signals were integrated for 10 s and averaged over 5 iterations. During the experimental runs, background fluorescence signals were recorded with the Cl_2 flow through the fixed inlet switched off but with C_2H_6 flowing through the moveable inlet.

Atomic Chlorine Calibration. The sensitivity of the detection system to Cl atom concentrations in the flow cell was determined by generating a known concentration of Cl atoms via the reaction of F atoms with Cl_2 (eq 2).

$$F + Cl_2 \rightarrow Cl + FCl \qquad (k = 1.6 \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}\ at\ 298\ K) \quad (2)$$

TABLE 1: Atomic Chlorine Wall Loss Rates[a]

T/K	wall loss rate coefficient, s^{-1}
353	2.7 ± 2.0
324	2.8 ± 1.2
296	3.6 ± 0.3
276	3.7 ± 0.8
257	6.9 ± 2.7
237	10.4 ± 3.8
217	12.8 ± 3.6
197	14.2 ± 4.1
177	15.1 ± 4.5

[a] Errors are cited at the level of a single standard deviation.

F atoms were produced in a microwave discharge of a 1% mixture of F_2 in helium in the moveable inlet. An uncoated 1 cm i.d. alumina tube was used in the microwave source, which was operated at 20 W. Typical flow rates through the discharge were on the order of 300 cm^3 min^{-1} at STP. The concentration of F atoms used in the calibration measurements was kept in a large excess over the Cl_2 concentration. Background signals which consisted of scattered light and light from secondary sources of Cl atoms were determined by simply turning off the Cl_2 flow through the microwave discharge. Typical detection sensitivities were found to be in the region of 5.2×10^{-7} counts s^{-1}/(atoms cm^{-3}) with background signals at about 550 counts s^{-1}. For a 50 s counting time, this was equivalent to a minimum detectable Cl atom concentration of 9×10^6 atoms cm^{-3} at a signal-to-noise ratio of unity.

Chlorine Atom Wall Loss. As chlorine atoms were added to the flow through a fixed inlet position during the course of our experiments, wall losses were not observed directly. However, it was necessary to determine the magnitude of these wall losses in order to calculate the axial and radial diffusion corrections described below. Wall loss measurements were conducted under the same experimental conditions of flow velocities, temperatures, and pressures as the main $Cl + C_2H_6$ experiments, although no C_2H_6 was added to the flows. In these experiments, Cl atoms were generated in the moveable inlet of the flow system via the microwave discharge of a similarly dilute mixture of Cl_2 in He as used for the production of Cl atoms in the fixed inlet. The Cl atoms were then added at different points along the flow tube, and the fluorescence intensity was recorded using the identical averaging procedures as described earlier. The resultant semilog plots of fluorescence intensity versus reaction time clearly showed that the wall losses were first-order with respect to loss of Cl. A linear least-squares fit to the slope was then used to determine the rate coefficient for Cl atom wall loss at that temperature. The procedure was then repeated at all of the temperatures used. The measured values, after corrections for diffusional loss have been applied, are listed in Table 1.

Calibrations. The mass flow controllers and meters used during the course of the experiments were calibrated for the particular gas mixture to be flowed using a pressure drop/rise at constant volume method. An oil manometer was used to calibrate the pressure gauges. The thermocouples used to monitor the cell temperature were calibrated at 273 and 195 K using ice/water and $CO_2(s)$/ethanol mixtures, respectively. The internal temperature of the flow tube was measured at several positions using a thermocouple probe in place of the usual moveable inlet. At room temperature (296 K) and above, the probe temperature was within 0.1 K of the jacket thermocouple temperatures. At low temperatures the probe temperature and jacket thermocouple temperatures were within 1 K, the probe thermocouple reading the lower of the two. The reported temperatures are those measured using the probe thermocouple.

Corrections. The observed pseudo-first-order rate coefficients were corrected for axial and radial diffusion.[37] The diffusion coefficient for atomic chlorine in He is given by $0.0237 \times T^{1.75}$,[38] which gave rise to corrections to the pseudo-first-order rate coefficients of between 4.7% and 11.2%. No corrections were made for the viscous pressure drop between the reaction zone and the pressure measurement port because earlier observations using the present reactor showed that the corrections are less than 0.5%.

Reagents. Chromatographic grade He (99.9999%) and research grade Cl_2 (99.99%) were used in order to minimize the introduction of impurities into the flow. He was further purified prior to use by flowing through a molecular sieve (Linde 3A) trap held at 77 K. Molecular chlorine was also purified prior to use by freeze−pump−thaw cycles in order to prevent radicals such as H atoms from being generated in the discharge. These radicals could provide a means for Cl atom regeneration (eq 3).

$$H + Cl_2 \rightarrow HCl + Cl \tag{3}$$

Furthermore, a mixture of 1% research grade ethane (99.995%) in helium was also used in an attempt to exclude higher hydrocarbons from the reaction vessel. High-purity CF_4 (99.9%) and a 1% mixture of F_2 in He were also used during the experiments.

Results

The experiments described here were performed under pseudo-first-order conditions, with the coreagent ethane in excess over atomic chlorine. Data were collected at temperatures ranging from 177 to 353 K. Helium was used as the carrier gas for this study, at a total pressure of approximately 1 Torr. Molecular chlorine was added to the flow at concentrations ranging from 8×10^9 to 3×10^{10} molecules cm^{-3}. The subsequent discharge of Cl_2 resulted in concentrations of Cl in the flow ranging from 1.6×10^9 to 1.1×10^{10} atoms cm^{-3} calculated from the results of atomic chlorine calibration tests. Ethane concentrations ranging from 3×10^{11} to 3×10^{12} molecules cm^{-3} were added through the moveable inlet. Typical initial stoichiometric ratios, $[C_2H_6]/[Cl]_0$, ranged between 2.7×10^1 and 1.5×10^3. At these concentrations, the loss of atomic chlorine is well described by a pseudo-first-order loss equation

$$-d[Cl]/dt = k_1[Cl][C_2H_6] + k_L[Cl] \tag{4}$$

where k_1 represents the bimolecular rate coefficient for loss of Cl atoms through reaction with C_2H_6 (reaction 1) and k_L represents the rate coefficient for loss of Cl atoms in the flow tube via other loss mechanisms. These additional losses include Cl atom wall and injector loss and reaction of Cl with impurities or products in any of the flows. The atomic chlorine resonance fluorescence signal, I(Cl), was found to vary linearly with [Cl]. As such, it can be written that

$$k_+ \equiv -d\ln[I(Cl)]/dt = k_1[C_2H_6] + k_L \tag{5}$$

where k_+ represents the total pseudo-first-order rate coefficient for the loss of Cl atoms in the flow system. Values of k_+ were determined through a linear least-squares analysis of the slopes of $\ln[I(Cl)]$ versus reaction time, t, for various added $[C_2H_6]$. Under conditions of plug flow, t is given by the relationship $t = l/v$, where l is the reaction distance and v is the average flow velocity. Reaction times varied from 3 to 30 ms, given by reaction distances ranging from 4 to 39 cm. The extent of the

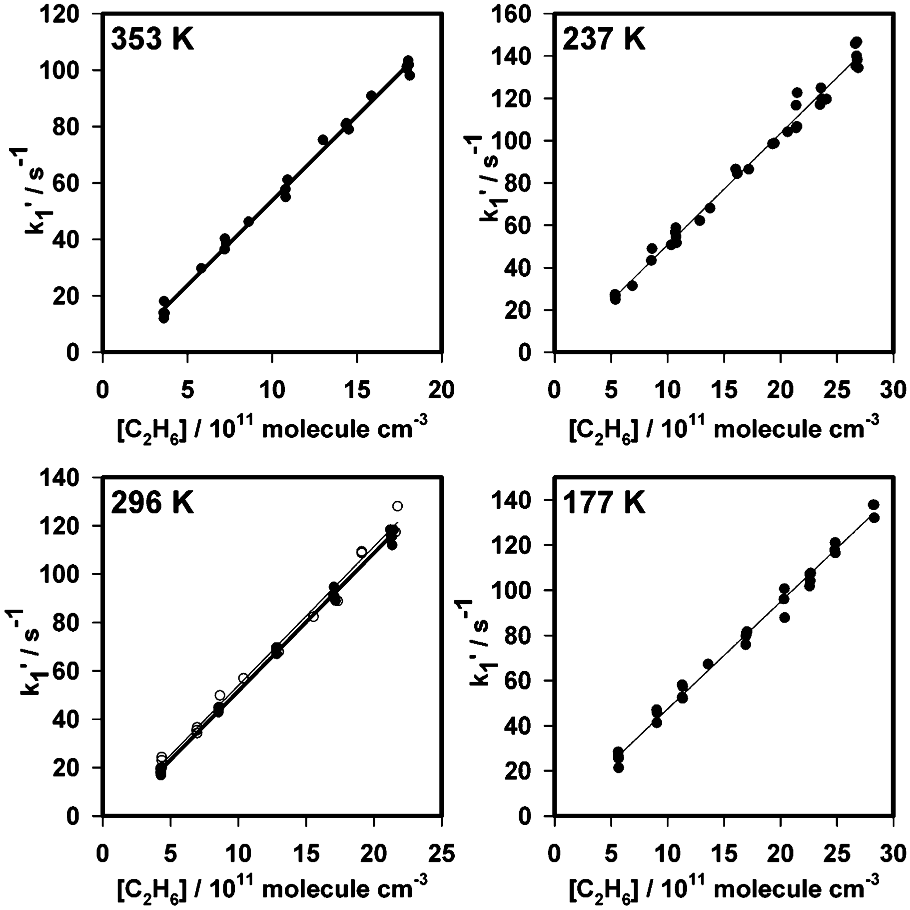

Figure 1. Plots of pseudo-first-order rate constants vs ethane concentrations at several temperatures. Open symbols in the 296 K plot are with spin quencher, CF_4, added.

Cl atom decays was highly dependent upon $[C_2H_6]$. Over the range of reaction times covered, the Cl atom decays had generally progressed between $e^{-1.4}$ to $e^{-3.4}$. Under these conditions, all of the plots of ln[I(Cl)] versus t were linear. The secondary loss rate coefficient for Cl, k_L, was determined from the linear least-squares analysis of the slopes of ln[I_0(Cl)] versus t with no C_2H_6 added to the flow. I_0(Cl) represents the Cl atom resonance fluorescence intensity in the absence of C_2H_6. In general, k_L comprised less than 13% of the total pseudo-first-order decay, k_+. From eq 5, the pseudo-first-order rate coefficient for loss of Cl solely through reaction 1, k_1', can be written as

$$k_1' = k_1[C_2H_6] = k_+ - k_L \quad (6)$$

The bimolecular rate coefficients measured in this study are listed in Table 2 and a representative selection of pseudo-first-order plots is presented in Figure 1. There is no significant difference between the rate coefficients obtained from the slopes and the averages. The values reported here are those obtained from the slopes.

A plot of the measured rate coefficients versus the reciprocal temperature is shown in Figure 2. Results from earlier measurements of the *absolute* rate coefficient for this reaction are included in the plot. An unweighted linear least-squares fit to our data results in the following Arrhenius expression:

$$k_1 = (7.32 \pm 0.39) \times 10^{-11} \times \exp[(-73.6 \pm 12.9)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (7)$$

TABLE 2: Summary of Observed Rate Coefficients for Cl + C_2H_6

		$k_1/10^{-11}$ cm^3 molecule^{-1} s^{-1}	
T /K	number of runs	average[a,b]	slope[a,c]
353	23	5.15 ± 1.44	6.00 ± 0.17
324	20	5.11 ± 0.99	5.73 ± 0.18
296	22	5.10 ± 0.96	5.70 ± 0.13
296[d]	15[d]	5.36 ± 0.70[d]	5.74 ± 0.30[d]
276	9	5.25 ± 0.48	5.69 ± 0.15
257	33	4.90 ± 0.86	5.44 ± 0.21
237	34	5.11 ± 0.54	5.27 ± 0.19
217	32	5.21 ± 0.53	5.33 ± 0.22
197	30	5.43 ± 0.50	5.12 ± 0.13
177	32	4.73 ± 0.54	4.75 ± 0.16

[a] Errors are cited at the level of two standard deviations. [b] Average of individual $k_1'/[C_2H_6]$. [c] Slopes of plots of $k_1' = k_1[C_2H_6]$ vs $[C_2H_6]$. [d] With added spin quencher, CF_4.

This expression applies to 177 ≤ T ≤ 353 K. The errors are cited at the level of two standard deviations.

Discussion

Numerical Simulations. Computer models were used to evaluate the sensitivity of the Cl + C_2H_6 reaction system to secondary chemistry. The effects of nonequilibrium spin excitation were also simulated and will be discussed in a separate section below. The simulations were carried out using the CHEMRXN program, which has been tested versus a standard differential equation integrator and a stochastic algorithm.[35] The reactions and rate coefficients listed in Table 3 were used to

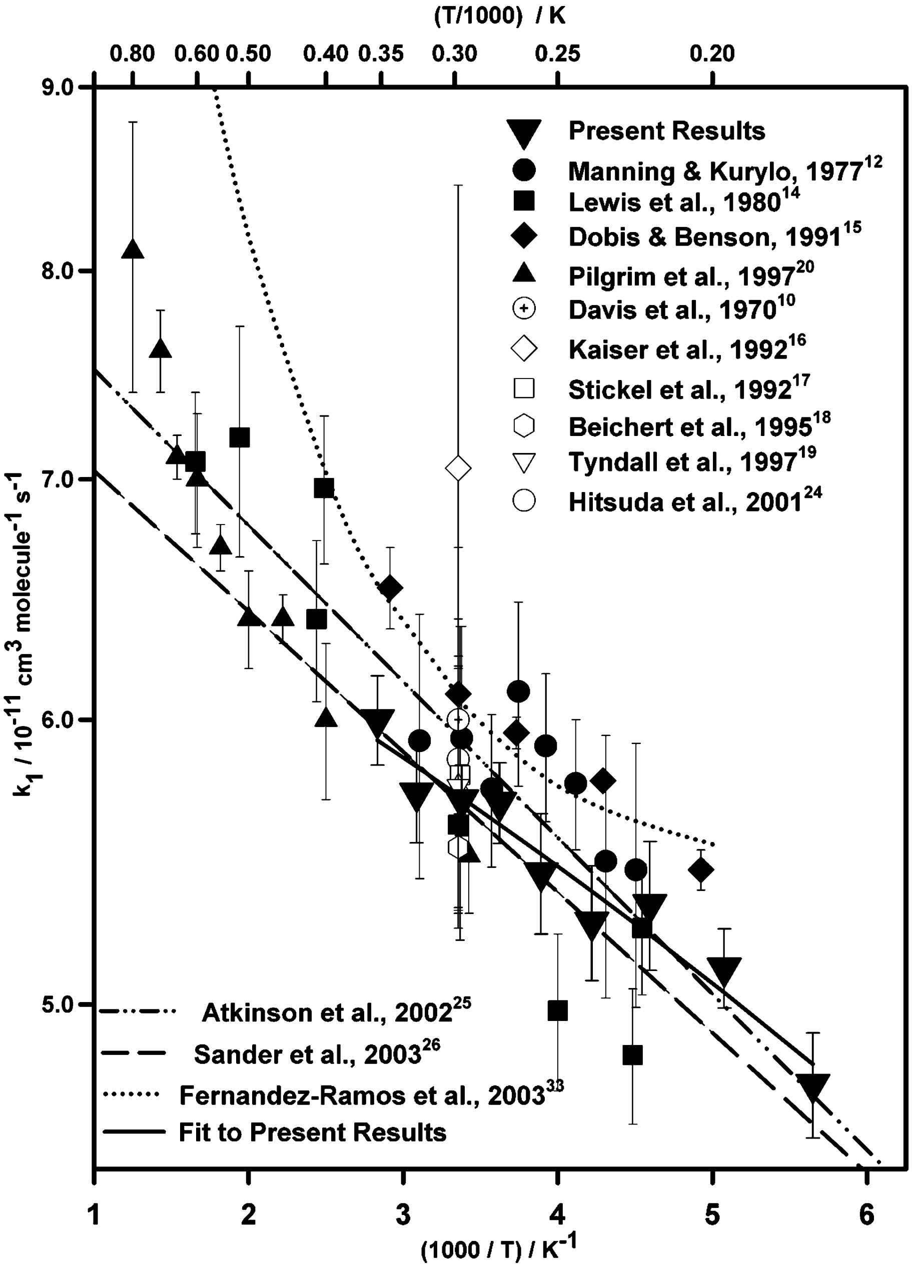

Figure 2. Arrhenius plot of present results compared to earlier absolute measurements. For clarity not all of the room temperature results have been included in the plot. The solid line is the unweighted linear least-squares fit to the present data only.

TABLE 3: Reactions Used in Numerical Simulations

reaction	rate coefficient[a,b]	ref
$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	$7.32 \times 10^{-11} \exp(-74/T)$	measured in this study
$Cl + C_2H_5 \rightarrow HCl + C_2H_4$	$7.57 \times 10^{-10} \exp(-290/T)$	Maricq et al., 1993[39]
$Cl + C_2H_4 \rightarrow C_2H_4Cl$	5.12×10^{-13}	Sander et al., 2003[26]
$Cl_2 + C_2H_5 \rightarrow Cl + C_2H_5Cl$	$1.26 \times 10^{-11} \exp(+152/T)$	Timonen and Gutman, 1986[40]
$C_2H_5 + C_2H_5 \rightarrow$ products	2.00×10^{-11}	Atkinson and Hudgens[41]
$HCl + C_2H_5 \rightarrow Cl + C_2H_6$	$8.32 \times 10^{-13} \exp(-1290/T)$	Manion and Louw, 1988[42]
$Cl + CCl_3 \rightarrow CCl_4$	6.5×10^{-11}	Ellermann, 1992[43]
$CCl_3 + CCl_3 \rightarrow CCl_3CCl_3$	$8.40 \times 10^{-12} \exp(+52/T)$	Cobos and Troe, 1985[44]
$Cl(^2P_{1/2}) + He \rightarrow Cl(^2P_{3/2}) + He$	6.0×10^{-14}	Tyndall et al., 1995[45]
$Cl(^2P_{1/2}) + CF_4 \rightarrow Cl(^2P_{3/2}) + CF_4$	2.3×10^{-11}	Tyndall et al., 1995[45]

[a] Units are cm^3 $molecule^{-1}$ s^{-1}. [b] Backward quenching rate coefficients were calculated from the forward coefficients using the principle of microscopic reversibility.

model the $Cl + C_2H_6$ system over the temperature range studied. Initial [Cl] and $[C_2H_6]$ were varied over a wide range. The input value for reaction 1, k_1(in), was the value observed in the present study. The model output consists of [Cl] versus reaction time profiles. These were treated in the same way as experimental data to obtain the model prediction of k_1: plots of ln[Cl] versus reaction time were fit by linear regression over time ranges similar to those used in the experiments; the slope gives a value for $k_1(\text{out})[C_2H_6]$. Knowing $[C_2H_6]$ we can obtain a value for k_1(out).

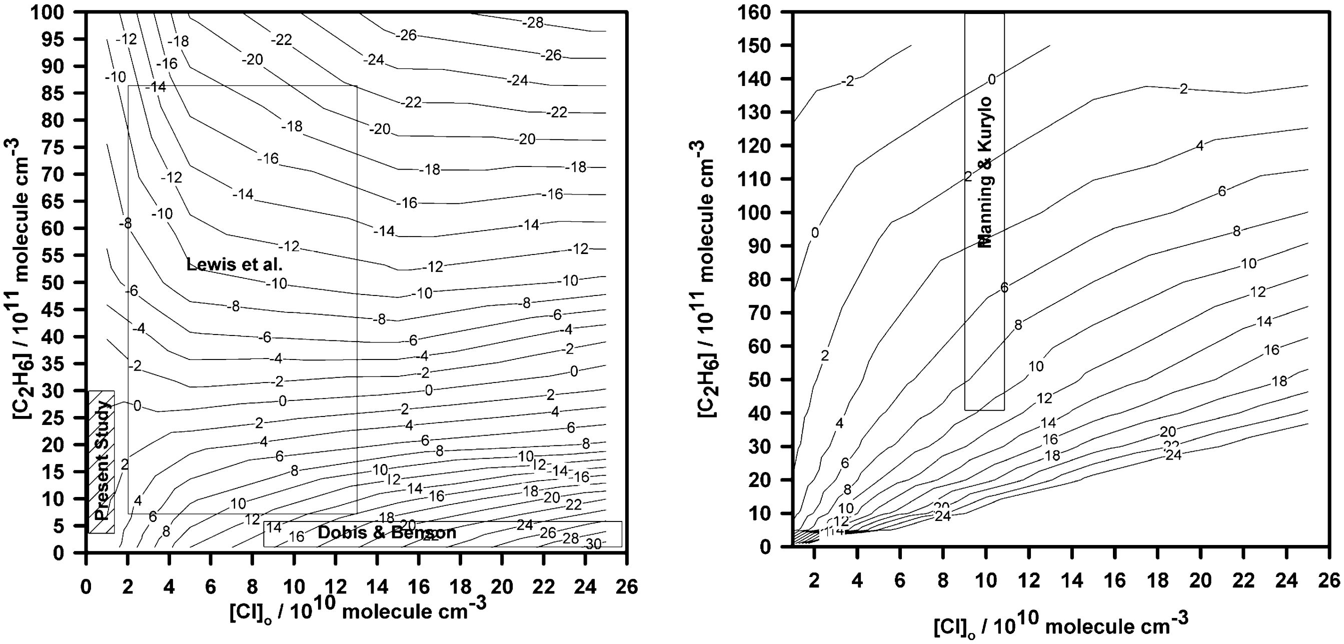

Figure 3. (a) Change in observed k_1 at 296 K due to secondary chemistry as predicted by numerical modeling. Atomic chlorine is produced from Cl_2. The contours are percent changes defined in the text. The boxes indicate the approximate concentration ranges used by Lewis et al.,[14] Dobis and Benson,[15] and the present study. (b) Same as part a, except atomic chlorine is produced from CCl_4. The box indicates the approximate concentration range used by Manning and Kurylo.[12]

The results show that reactions of the ethyl radical, C_2H_5, (eqs 8 and 9)

$$Cl + C_2H_5 \rightarrow HCl + C_2H_4 \tag{8}$$

$$Cl_2 + C_2H_5 \rightarrow Cl + C_2H_5Cl \tag{9}$$

can interfere with the measurements over certain concentration ranges of Cl and C_2H_6. The results at 296 K are shown in Figure 3, where the percent changes in k_1 induced by the secondary chemistry are plotted versus $[Cl]_o$ and $[C_2H_6]$. The percent change in k_1 is calculated using the relation del% $\equiv \{[k_1(\text{out})/k_1(\text{in})] - 1\} \times 100$. The results show that to keep the interference less than 10% over the range of $[C_2H_6]$ used in the present study ($3 \times 10^{11} - 3 \times 10^{12}$ molecules cm^{-3}), $[Cl]_o$ should be less than about 5×10^{10} atoms cm^{-3}. The range of concentrations used in the present study is superposed on the plot in Figure 3a. The modeling results indicate that, under these conditions, interference from secondary chemistry in the present study should be less than 3%. Similar results were obtained at lower temperatures. These estimates of interference from secondary chemistry are upper limits since the wall loss of C_2H_5 radicals was set to zero in the models. As such, any added loss of C_2H_5 in the system would make the system less sensitive to reactions 8 and 9.

Spin Equilibrium. Ground state chlorine atoms are partitioned between two spin−orbit levels of the atom, namely the $^2P_{3/2}$ and $^2P_{1/2}$ states.

$$Cl(^2P_{3/2}) + C_2H_6 \rightarrow HCl + C_2H_5 \tag{1a}$$

$$Cl(^2P_{1/2}) + C_2H_6 \rightarrow HCl + C_2H_5 \tag{1b}$$

The $^2P_{1/2}$ state is higher in energy by 882 cm^{-1}.[45,46] These spin states are expected to be at thermal equilibrium in the troposphere and stratosphere,[45] where interconversion between the two states is rapid and the total rate coefficient, k_1, is given by

$$k_1 = (k_{1a} + (Kk_{1b}))/(1 + K) \tag{10}$$

The equilibrium constant for interconversion between the two spin states, K, is given by $0.5 \exp(-2520/RT)$. If interconversion is slow with respect to reaction, then the two spin−orbit states will decay with distinct rate coefficients k_{1a} and k_{1b}. It is then dependent upon the sensitivity of the resonance lamp to fluorescence from each of these states as to which of these decays is predominantly observed.

In the flow system it is possible that quenching rates may not be sufficient to maintain equilibrium over the entire course of the reaction. Equilibration at the start of the reaction is likely because any Cl atoms formed in a non-Boltzmann distribution of states will be collisionally quenched by the helium carrier gas during the 50 ms delay between Cl formation and C_2H_6 addition (see below). At 298 K, only 0.7% of the Cl atoms occupy the upper $^2P_{1/2}$ state at equilibrium. As such, if $Cl(^2P_{1/2})$ reacts with C_2H_6 at a significantly faster rate than $Cl(^2P_{3/2})$, then an elevated population in the upper state could enhance the measured rate coefficient over and above the rate of reaction under equilibrium conditions, which apply to the atmosphere. Furthermore, if reaction 1b occurs at a fast enough rate, then the upper state might become depleted with respect to the lower state. It is therefore important to check for spin equilibration in the flow system. Model calculations and experimental measurements were performed to evaluate the possible effect of nonequilibration.

Model calculations were performed at 200 and 296 K using the CHEMRXN program. The helium carrier acts as an efficient quencher (eq 11) in this system: $k_{11}(\text{forward}) = 6.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.[45]

$$Cl(^2P_{1/2}) + He \leftrightarrow Cl(^2P_{3/2}) + He \tag{11}$$

At 1 Torr of He, this gives a quenching rate of 1940 s^{-1} at 296 K and 2900 s^{-1} at 200 K. Thus, the system should be fully equilibrated during the 50 ms between Cl atom formation and the start of the Cl + C_2H_6 reaction, and this was assumed in the model calculations. In addition to He, the effect of an added spin quencher, CF_4, was investigated (eq 12), where k_{12}(forward) = 2.3 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.[45]

$$Cl(^2P_{1/2}) + CF_4 \leftrightarrow Cl(^2P_{3/2}) + CF_4 \qquad (12)$$

Several parameters were varied in the model: the concentration of added spin quencher was changed by more than a factor of 15, the rate coefficient, k_{1b}, for the loss of $Cl(^2P_{1/2})$ was varied up to an assumed "gas kinetic" limit of 3 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, and the sensitivity of the resonance lamp to fluorescence from the different spin−orbit levels of Cl was also varied by a factor of 10. The results indicate that even if the rate coefficient, k_{1b}, is at the gas kinetic limit, the effect of spin nonequilibrium is negligible. With no added quencher in addition to He, the rate constant for reaction 1 obtained from the model agrees with the input value within 2% even though the population ratio of the two spin states is 20% to 40% lower than the equilibrium value. Addition of CF_4 in the model at a concentration of 1 × 10^{15} molecules cm^{-3} brings and maintains the population ratio within 2% of equilibrium. No significant effect is observed when the lamp sensitivity for the two states is varied over a factor of 10. The conclusion of the modeling work is that spin has no effect on the observed rate constant for reaction 1. This is because of the low population in the upper state and the fast rate constant of the reaction.

In addition to the modeling work, rate constant measurements were carried out to check the effect of an added spin quencher. The experiments comprised the addition of CF_4 at a concentration of approximately 1 × 10^{15} molecules cm^{-3} to the flow of gases used in typical experimental runs. These measurements were performed at 296 K only. The results are shown in Figure 1, where the open and closed symbols are the measurements with and without added CF_4, respectively. The results are also summarized in Table 2. It can be seen that there is no significant difference in the observed rate coefficients with and without added spin quencher, thus supporting the finding of the numerical simulations.

Comparison with Earlier Absolute Rate Data and Calculations. Previous absolute room temperature determinations of the rate coefficient for the Cl + C_2H_6 reaction are too numerous to be mentioned individually, although most of these data are presented in Figure 2. The reviews by Atkinson et al.[25] and Sander et al.[26] which provide an evaluation of the available data show reasonable agreement at 298 K, with values of (5.9 ± 0.9) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} and (5.7 ± 0.6) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} having been reached, respectively. These numbers agree favorably with the 296 K determination of the present study, which gives k_1(296 K) = (5.7 ± 0.1) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. As several different techniques have been used to study this reaction at room temperature with good agreement, especially between the later studies, it seems that a downward revision of the proposed value of Atkinson et al.[25] is required.

Conversely, the temperature-dependent behavior of the Cl + C_2H_6 reaction is not particularly well established, especially at high ($T > 500$ K) and low ($T < 220$ K) temperatures with only four previous absolute determinations of the Arrhenius parameters of the Cl + C_2H_6 rate equation. Manning and Kurylo,[12] using a FP-RF technique with CCl_4 as the Cl atom precursor, performed the earliest absolute determination of the temperature dependence of this reaction over a temperature range of $222 \leq T \leq 322$ K. When considered alongside the present study, this earlier determination is found to give comparatively high values for the Cl + C_2H_6 rate coefficient, k_1. Our modeling calculations shown in Figure 3b suggest that Manning and Kurylo[12] could have been operating in a reactant concentration region where the observed rate coefficients were potentially high. Two other studies, namely those by Lewis et al.[14] and Dobis and Benson,[15] used Cl_2 as the precursor for Cl atom formation. Lewis et al.[14] used a conventional DF-RF technique similar to that used in this study over a temperature range of $220 \leq T \leq 604$ K, whereas Dobis and Benson[15] employed a DF-MS technique coupled with a very low-pressure reactor (VLPR) over a temperature range of $203 \leq T \leq 343$ K. Modeling calculations shown in Figure 3a clearly show that the range of reactant concentrations used by Dobis and Benson[15] may have been appropriate for a substantial deviation in the observed k_1 to occur: up to as much as 30%. Correspondingly, it can be seen in Figure 2 that the values of Dobis and Benson[15] are consistently higher than those determined in the present study. It can be seen in Figure 3a that Lewis et al.[14] used a range of reactant concentrations that was large in comparison with this study and that of Dobis and Benson[15] and operated in a regime where both upward and downward deviation of k_1 could occur. Consequently, it is more difficult to predict whether they may have observed high or low (or both) values of k_1. This seems to be borne out in Figure 2, where these data are seemingly high at $T > 400$ K and low at $T < 250$ K. The most recent temperature-dependent evaluation of k_1 was performed by Pilgrim et al.[20] They used a FP-IR absorption technique to monitor the progress of the Cl + C_2H_6 reaction by observing the time dependence of the growth of the HCl product. No modeling calculations were performed upon this system, although it can be seen in Figure 2 that there is good agreement between the high-temperature data of the present study ($T > 296$ K) and the low-temperature data of the Pilgrim et al.[20] work ($T < 400$ K). All of the Arrhenius parameters derived in these studies are presented in Table 4 alongside the most recent evaluations. The preexponential factor and activation energy determined by Manning and Kurylo[12] are close to those derived in this study with the error bars on the activation energies bringing the two numbers into agreement. Lewis et al.,[14] Dobis and Benson,[15] and Pilgrim et al.[20] all show preexponential factors of the rate equation which are higher than the value determined in this study. The Sander et al.[26] evaluation of this preexponential factor lies within the error bars cited in the present study; however, the Atkinson et al.[25] evaluation of this parameter lies outside our error limits. The activation energies determined by these studies all lie close together, although the value derived in the present work is within the error bars of all of the cited references except for Lewis et al.,[14] Pilgrim et al.,[20] and Sander et al.[26]

Above 600 K the combined absolute data appear to show a marked deviation from linearity as can be seen in Figure 2,

TABLE 4: Absolute Arrhenius Parameters[a]

study	$A_{ethane}/10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}	(E_{ethane}/R)/K
Manning and Kurylo[12]	(7.3 ± 1.2)	(61 ± 44)
Lewis et al.[14]	(9.0 ± 1.0)	(133 ± 30)
Dobis and Benson[15]	(8.2 ± 0.2)	(86 ± 20)
Pilgrim et al.[20]	(8.6 ± 0.5)	(135 ± 26)
Atkinson et al.[25]	8.3	(100 ± 100)
Sander et al.[26]	7.7	90
present study	(7.3 ± 0.4)	(74 ± 13)

[a] Errors are cited at the level of two standard deviations.

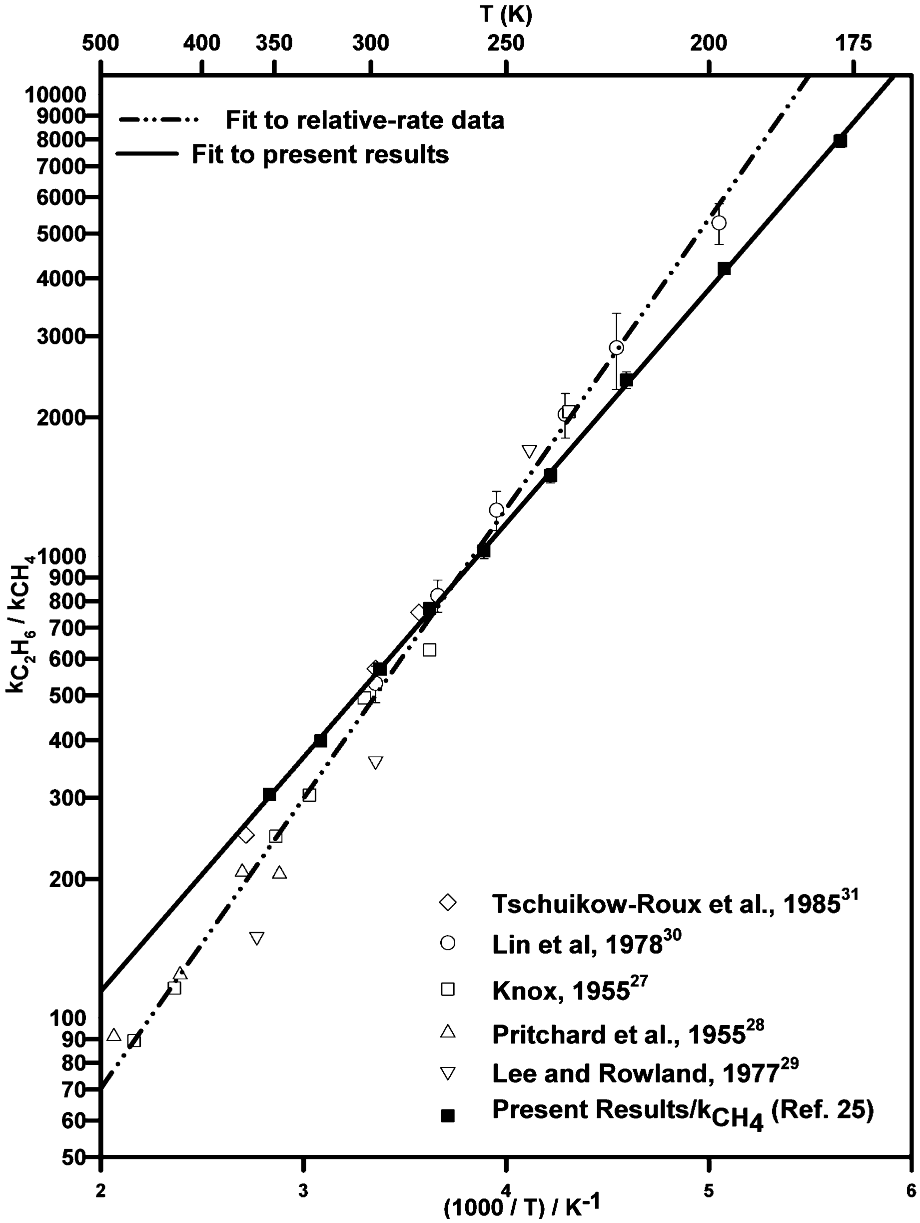

Figure 4. Arrhenius plot of relative rate results compared to the present absolute results. The present results have been transformed to relative values using the current recommended evaluation for the Arrhenius parameters for Cl + CH_4 given by Atkinson et al.[25]

although further experimental studies are required in this region to determine whether this is a real deviation from Arrhenius behavior or simply indicative of a more difficult region in which to collect data. A recent theoretical study by Fernández-Ramos et al.,[33] however, qualitatively predicts this deviation at higher temperatures. They calculated rate coefficients using microcanonical variational transition state theory on a high-level ab initio potential energy surface. Using a loosely constrained transition state for the Cl + C_2H_6 reaction coordinate, these authors ascribed the increasing rate coefficient at high temperatures to the displacement of the reaction bottleneck toward the transition state, an effect that they attributed to the increasing entropic contribution to the Gibbs free energy. At lower temperatures, however, Fernández-Ramos et al.[33] predict a slight upturn in the rate coefficient due to the small but increasing influence of tunneling, an effect not observed in the present study. Despite the considerable scatter in the absolute data at temperatures below 298 K, it is evident that there is little or no deviation from linear Arrhenius behavior at $180 \leq T \leq 600$ K as had been previously suggested by Michelsen and Simpson.[47] These authors used the nonlinear Arrhenius expression: $k(T) = 4.21 \times 10^{-11} (T/298)^{0.492} \exp(94.85/T)$ to fit the existing absolute data. This fit leads to a pronounced plateau region in the temperature dependence of the rate coefficient at $T < 250$ K which is contradictory to the present results.

Comparison with Earlier Relative Rate Data. Previous temperature-dependent relative rate measurements of the Cl + C_2H_6 rate coefficient relative to the rate coefficient for the Cl + CH_4 reaction consist of five studies.[27-31] These data have been plotted in Figure 4. Alongside these values, the absolute numbers from the present study have been plotted after being converted to relative numbers using the most recent evaluation of the Arrhenius parameters for the Cl + CH_4 rate equation.[25] It can be seen that there are large discrepancies at $T > 350$ K and also at $T < 220$ K between the relative rate measurements and the converted absolute numbers and also among the relative rate values themselves at higher temperatures.

The present study agrees well with the relative results obtained by Tschuikow-Roux et al.[31] in the overlapping temperature region, from 296 to 400 K, of the two studies. The

TABLE 5: Relative Arrhenius Parameters[a]

study	$A_{\text{ethane}}/A_{\text{methane}}$	$(E_{\text{methane}} - E_{\text{ethane}})/R$/K
sum of relative studies (refs 27−31)	3.9 ± 0.8	1450 ± 80
present study (relative to ref 25)	7.6 ± 0.2	1290 ± 20

[a] Errors are cited at the level of two standard deviations.

agreement between the values determined by Lee and Rowland[29] and the present study is poor, especially above room temperature. All of the other relative rate studies seem to be in reasonable agreement with the present results at intermediate temperatures, although the slopes of the fits to the two data sets are significantly different, giving values which vary by as much as 30% at 500 K and 19% at 180 K. The relative Arrhenius parameters derived from a linear least-squares fit to the available data are shown in Table 5.

It is apparent from Table 5 that the discrepancy between the fits to the two data sets derives predominantly from the preexponential factors, which differ by almost a factor of 2. The difference activation energies lie reasonably close to one another although they remain outside the error limits of both sets of measurements.

Clearly, the discrepancy between relative rate results and the absolute measurements does not lie with the measured Arrhenius parameters for either the Cl + CH_4 or Cl + C_2H_6 reactions at $180 \leq T \leq 500$ K as both of these reactions have been comprehensively studied over this temperature range. It seems likely, therefore, that the discrepancy now lies in the relative rate measurements themselves.

Summary

The present discharge flow resonance fluorescence study clearly shows that the temperature dependence of the Cl + C_2H_6 reaction is best described by a conventional linear Arrhenius expression and extends the temperature range of the currently available data to 177 K. Furthermore, it has been demonstrated that these measurements are not subject to systematic errors arising from either nonequilibration of Cl atom spin−orbit states or from secondary reactions. Addition of CF_4 at concentrations sufficient to bring and maintain the spin−orbit states to within 2% of their equilibrium values showed no observable change in the Cl + C_2H_6 rate coefficient. These findings agreed with the results from numerical simulations of the system. Secondary reactions brought about by impurities in the Cl atom source were eliminated by using freeze−pump−thaw cycles to purify Cl_2 prior to use. No significant differences were found to occur when purification procedures were not used. Secondary reactions brought about by the reaction of product molecules with other atoms or molecules in the system were minimized by using low reactant concentrations. This result was borne out by the fact that only minor deviations of the observed rate coefficients were predicted by numerical simulations. Absolute and relative rate coefficients for this reaction (after conversion of the absolute values to relative numbers using the latest evaluation of the absolute Cl + CH_4 kinetic expression) are seen to differ significantly. Comprehensive absolute kinetic measurements of the reactions of both Cl + C_2H_6 and Cl + CH_4 have now been performed, and these systems have been shown to follow a conventional linear Arrhenius temperature dependence at temperatures below 350 K. This conclusion casts doubt on the accuracy of the measured relative rate values.

Acknowledgment. The research described in this article was performed at the Jet Propulsion Laboratory, California Institute of Technology under a contract with the National Aeronautics and Space Administration.

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