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The Rate Constant Ratio $k_1(Cl + C_2H_6)/k_2(Cl + CH_4)$ from 250 to 700 K

E. W. Kaiser* and T. J. Wallington

Ford Motor Company, Scientific Research Laboratories, Mail Drop 3083/SRL,
Dearborn, Michigan 48121-2053

Y. Hashikawa and M. Kawasaki

Department of Molecular Engineering and Graduate School of Global Environmental Studies,
Kyoto University, Kyoto 615-8510, Japan

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Knowledge of the rate constants of the reactions $Cl + C_2H_6$ (1) and $Cl + CH_4$ (2) is important to the modeling of atmospheric chemistry, particularly in marine environments and in the stratosphere. These rate constants are also used as reference reactions in the determination of rate constants of many other species with Cl atoms. In a recent publication, the results of previous relative rate measurements of k_1/k_2 have been called into question. The present experiments measure k_1/k_2 from 250 to 700 K using GC analysis and at 296 K using an FTIR smog chamber. These relative rate measurements are consistent with previous relative rate measurements and agree to within 15% with ratios of k_1 and k_2 determined in recent absolute rate experiments. Contrary to recent claims, we believe that the relative and absolute data provide a consistent picture of the reactivity of Cl atoms toward CH_4 and C_2H_6.

1. Introduction

In a recent publication, Hickson and Keyser[1] have measured the absolute rate constant (k_1) for the reaction of Cl atoms with ethane over the temperature range 177−353 K. They discuss the importance of reactions of Cl atoms with ethane and methane from the perspective of atmospheric chemistry in marine environments and the perspective of their importance as reference rate constants. To compare their measurement to the numerous relative rate measurements of k_1/k_2, they divided their temperature-dependent rate constant, k_1, by the temperature-dependent rate constant for Cl with methane (k_2) evaluated over the appropriate temperature range by the IUPAC data evaluation panel.[2]

$$Cl + C_2H_6 \rightarrow C_2H_5 + HCl \qquad (1)$$

$$Cl + CH_4 \rightarrow CH_3 + HCl \qquad (2)$$

Hickson and Keyser conclude that there is a serious disagreement over the temperature range 200−500 K between their data and the relative rate determinations and that the reason for the discrepancy lies in the relative rate data. Because of this apparent disagreement, we have undertaken a comprehensive study of k_1/k_2 using the relative rate method. Our experiments cover a wide temperature range (250−700 K), and the initial conditions (total pressure and initial reactant concentrations) were varied over large ranges. Finally, at ambient temperature, experiments were carried out using two very different experimental methods to verify that the rate constant ratio is not dependent on the reactor geometry or the analytical technique.

2. Experimental Section

The relative rate determinations were carried out in two different reactor/analysis systems. One system consisted of two temperature-controlled reactors, which measured k_1/k_2 over the temperature range 250−700 K. The concentrations of reactants and products were measured by gas chromatography (GC). The second system was a Fourier transform infrared (FTIR) smog chamber reactor operated only at ambient temperature. These two systems are discussed separately in the following sections.

2.1. FTIR Smog Chamber System. Experiments were performed to measure k_1/k_2 in 100 or 700 Torr of N_2 diluent at 296 K using a 140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer. The apparatus and techniques are described in detail elsewhere.[3] Initial reaction mixtures consisted of 39−150 mTorr of C_2H_6, 1000−5200 mTorr of CH_4, and 320−1500 mTorr of Cl_2 in 100 or 700 Torr of N_2. The reactor was surrounded by fluorescent black lamps (GE F15T8-BL), which were used to generate Cl atoms by photolysis of molecular chlorine

$$Cl_2 + h\nu \rightarrow 2Cl$$

$$Cl + C_2H_6 \rightarrow \text{products} \qquad (1)$$

$$Cl + CH_4 \rightarrow CH_3 + HCl \qquad (2)$$

$$CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$$

Reactant mixtures were prepared using calibrated volumes on an external gas-handling manifold and flushed into the chamber with N_2. Reactant and product compounds were monitored by FTIR spectroscopy using an infrared path length of 27.1 m and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added interferograms. All reactants were obtained from commercial sources at purities >99.9%.

2.2. GC Reactor System. The relative rate experiments using GC detection were carried out in two reactors: a high-temperature reactor for experiments between ambient and 700 K, and a low-temperature reactor for experiments between

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* Retired. Current address: 7 Windham Lane, Dearborn, MI 48120.

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ambient and 250 K. In both cases, the relative rate studies were performed using mixtures of Cl_2, C_2H_6, and CH_4 in He (all purities >99.99%). Each mixture was premixed in a Pyrex flask with a volume large enough to fill the reactor several times. As described already, Cl atoms were generated by irradiating the reactor with UV light from a Sylvania F6T5 BLB fluorescent lamp for temperatures of 600 K and below. For the data taken at 670−690 K, the thermal dissociation of Cl_2 was sufficiently fast that it dominated the irradiation process. Therefore, at these temperatures, the reaction was initiated thermally rather than by irradiation. After a chosen reaction time, the contents of the reactor were removed into a Pyrex transfer vessel and analyzed by gas chromatography. Each experiment represents one reaction time, unlike the FTIR experiments in which several reaction times can be sampled during a single experiment.

The gas samples were analyzed using a Hewlett-Packard model 6890/5973 GC/MS gas chromatograph. Most samples were analyzed using the flame-ionization detector (FID) in this instrument. For cases in which unknown peaks needed to be identified, the mass selective detector was used. A capillary column (J & W Scientific, DB1−30 m (0.32-mm i.d.) with 5-micron coating) separated the individual organic reactants and products. The temperature profile used in the GC analysis consisted of an initial temperature of 35 °C held for 6 min followed by a ramp at 8 °C/min to a final temperature of 180 °C.

The consumption of C_2H_6 was monitored directly by observing its decrease during the irradiation period. Because the rate of reaction of Cl with CH_4 is much slower than that of Cl with C_2H_6, the small (typically <2%) consumption of CH_4 could not be determined directly in most experiments. Instead, the formation of the major product CH_3Cl was measured to determine the consumption of CH_4. In certain cases where the CH_4 consumption was larger, the secondary product CH_2Cl_2, formed from Cl reaction with CH_3Cl, also needed to be included to obtain an accurate measurement of the CH_4 consumption.

Because product formation is an indirect measurement of the consumption of CH_4, experiments were carried out to verify that the sum of the chlorinated products (CH_3Cl with CH_2Cl_2, $CHCl_3$, and CCl_4 in experiments where CH_4 consumption was significant) does, in fact, equal the amount of CH_4 consumed to within experimental error. The GC (FID) response of each of these products was determined from calibration standards formed by partial-pressure mixing. In these carbon balance experiments, the unreacted mixture contained Cl_2, CH_4, and HFC-134a (CF_3CFH_2) in addition to He. In the relative rate experiments, the CH_4 consumed was always less than ∼5% of the initial CH_4 concentration. This was too small to measure the carbon balance accurately. Therefore, 5−10% of the CH_4 was consumed in the carbon balance measurements at ambient temperature, and 5−50% was consumed at 550 K. To improve the accuracy of the CH_4 measurement at lower percentage consumption (<10%), HFC-134a was added as an internal standard. HFC-134a reacts at a much slower rate than CH_4 (100 times slower at ambient temperature) and, therefore, can be used as an internal calibration by making corrections for the very small HFC-134a consumption (<1% for 10% CH_4 consumption at 550 K, no correction needed at ambient temperature). In these experiments, the carbon recovery was >97 ± 6% over the temperature range studied, indicating that product formation is an accurate method for deducing CH_4 consumption, as also observed in the FTIR experiments to be discussed.

At ambient temperature, the percentage consumption of CH_4 was limited to a maximum of 10% in the carbon balance experiments. This limitation was imposed, because at ambient temperature, the rate of reaction of chlorinated methyl radicals with O_2 becomes much faster than with Cl_2 as the degree of chlorination increases (k_{O_2}/k_{Cl_2} = 0.8, 10, 200, and 25 000 for CH_3, CH_2Cl, $CHCl_2$, and CCl_3, respectively).[4] As the degree of CH_4 consumption increases, more highly chlorinated methyl radicals are formed via secondary consumption of products. A fraction of these radicals can be removed by very small amounts of oxygen contamination in the reactor, which are impossible to exclude, leading to an increasing underestimatation of the carbon balance as the percentage consumption of methane increases. At 550 K, the ratio k_{O_2}/k_{Cl_2} is much smaller for the highly chlorinated species (e.g., 67 for CCl_3), and larger methane consumption can be used.

In the relative rate experiments, the consumption of methane was small (typically 0.05−5.0%) and CH_3Cl was by far the principal product. Therefore, any reaction with an O_2 contaminant is negligible for these experiments.

2.2.1. High-Temperature Reactor. At temperatures from ambient to 690 K, experiments were carried out in a cylindrical Pyrex reactor with a volume of 40 cm^3 (i.d. = 2.5 cm, length = 8 cm). The temperature of the reactor was measured by placing a Chromel-Alumel thermocouple into a thermocouple well (7 cm long) located within the reactor along the cylinder axis. The temperature of the reactor varied by less than 3 K over the length of this thermocouple well at a temperature of 575 K. The reactor was placed in a high-temperature tube oven to heat the reactor. The hinged tube oven was propped open by approximately 0.8 cm on the side opposite the hinge to provide access for UV radiation to initiate the reaction.

2.2.2. Low-Temperature Reactor. Experiments below ambient temperature were carried out in a 200 cm^3 cylindrical Pyrex reactor (5-cm i.d.) enclosed within a Pyrex cooling jacket. Cooling was provided by circulating a 50−50 mixture of water and ethylene glycol through a temperature-controlled recirculating bath and then through the reactor cooling jacket. A test in which a thermocouple was placed inside the reactor showed that the temperature within the reactor was identical to that of the liquid in the reservoir of the recirculator at the flow rate used, and the reservoir temperature was used as the reactor temperature during irradiation experiments.

3. Results

3.1. FTIR Smog Chamber Measurement of k_1/k_2 at 296 K. Figure 1 shows IR spectra obtained before (panel A) and after (panel B) UV irradiation of a mixture of 76 mTorr of C_2H_6, 5200 mTorr of CH_4, and 1500 mTorr of Cl_2 in 700 Torr of N_2 at 296 K. The consumption of C_2H_6 was 75%. Comparison of the IR features in panel B with the reference spectrum of CH_3Cl in panel C shows the formation of this compound. Formation of C_2H_5Cl is evident from its characteristic absorption feature at 784 cm^{-1} indicated in panel B. The loss of CH_4 is too small to be observed directly but can be measured indirectly by virtue of the observed formation of CH_3Cl. For the experiment shown in Figure 1, the formation of CH_3Cl was 12.0 mTorr. If we assume that under the present experimental conditions each molecule of CH_4 consumed by reaction 2 leads to the formation of a molecule of CH_3Cl and that there is no loss of CH_3Cl in the system, then the observed CH_3Cl formation serves as a measurement of the CH_4 consumption. Hence, we would conclude that the loss of CH_4 in the experiment shown in Figure 1 is 12.0 mTorr (i.e., 0.23% of the initial concentration of 5200 mTorr).

Figure 2 shows a plot of the loss of C_2H_6 versus that of CH_4 for all experiments conducted using the FTIR smog chamber.

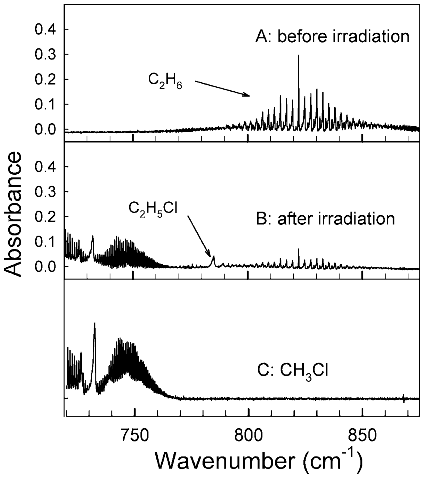

Figure 1. IR spectra obtained before (panel A) and after (panel B) UV irradiation of a mixture of 76 mTorr of C_2H_6, 5200 mTorr of CH_4, and 1500 Torr of Cl_2 in 700 Torr of N_2 at 296 K. Panel C shows a reference spectrum of CH_3Cl.

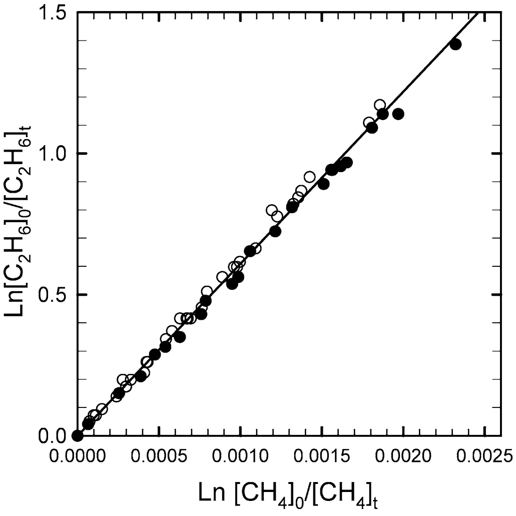

Figure 2. Loss of C_2H_6 vs CH_4 following exposure to Cl atoms in 100 (●) or 700 Torr (○) of N_2 diluent at 296 K.

As seen from Figure 2, the data obtained at 100 and 700 Torr total pressure were indistinguishable. Individual variation of $[Cl_2]_0$ and the $[C_2H_6]_0/[CH_4]_0$ ratio by a factor of four had no discernible effect on the relative decay rate of C_2H_6 and CH_4. The line through the data in Figure 2 is a linear least-squares fit to the combined data set which gives a slope equal to $k_1/k_2 = 609 \pm 45$. The quoted error represents two standard deviations from the regression analysis. We estimate that uncertainties associated with calibration of the CH_3Cl reference spectrum contribute an additional 5% of systematic uncertainty. Propagation of this uncertainty leads to our final value of $k_1/k_2 = 609 \pm 54$ in 100−700 Torr of N_2 at 296 K; the quoted error represents the accuracy of the measurement.

As discussed already, we assume that the formation of CH_3Cl can be equated to the loss of CH_4. To test this assumption, product experiments were conducted using mixtures of 19 mTorr of CH_4 and 470 mTorr of Cl_2 in 700 Torr of N_2 diluent. These product experiments employed much lower $[CH_4]_0$ than the kinetic experiments described already. In contrast to the kinetic experiments where the loss of CH_4 was typically 0.05−0.5%, in the product experiments, the loss of CH_4 was substantial (5−25%) and could be measured directly and compared to the formation of CH_3Cl. In the product experiments, within the experimental uncertainties, the observed formation of CH_3Cl, when corrected for loss via reaction with Cl atoms (necessary in experiments with conversions of CH_4 greater than a few percent), accounted for 100% of the loss of CH_4. This observation shows that it is reasonable in the kinetic experiments to equate the formation of CH_3Cl with the loss of CH_4.

TABLE 1: Initial Test Conditions and Results for the GC Study of k_1/k_2

T (K)	data points	P (Torr)	Cl_2 (Torr)	C_2H_6 (Torr)	ΔC_2H_6[a]	CH_4 (Torr)	k_1/k_2
690	3	840	1.16	0.82	75%	8.4	34.0
677	2	400	0.95	0.4	40−90%	4.1	30.7
600	5	370	0.88	0.37	16−95%	3.83	47.2
544	3	330	0.78	0.33	15−85%	3.42	63.1
542	2	360	1.24	0.65	50−80%	17.2	66.0
539	1	760	11.9	1.47	70%	9.93	69.2
539	3	150	2.35	0.29	11−80%	1.96	66.0
486	2	310	0.61	6.2	40−90%	15.6	86.3
485	3	300	0.71	0.3	10−80%	3.1	96.1
450	2	310	1.5	0.56	25−70%	14.8	121
384	1	260	0.62	0.26	95%	2.7	216
297[b]	3	230	0.5	0.23	22−95%	2.3	631
297	3	220	1.06	0.4	15−92%	10.5	652
297	1	220	0.43	4.4	47%	11.1	637
297	1	730	1.43	14.6	37%	36.8	615
297	3	230	1.06	0.4	33−92%	10.5	606
297[c]	3	225	4.3	1.03	15−90%	10.5	621
267[b]	5	210	0.99	0.4	24−98%	10.1	1050
255[b]	4	210	0.99	0.4	21−94%	9.9	1237
252[b]	1	210	0.98	0.4	17−40%	10.2	1351

[a] Range of ethane consumed (% of $[C_2H_6]_0$). [b] These tests were carried out in the jacketed reactor. All other tests were performed in the high-temperature reactor. [c] This test was carried out using N_2 as a diluent. All other tests used He.

3.2. GC Reactor System Measurement of k_1/k_2 at 250−700 K. The experiments in the GC reactor system were carried out using a variety of pressures and reactant compositions to verify that k_1/k_2 is independent of initial conditions with the exception of temperature. At 297 K, experiments were carried out over the pressure range 220−730 Torr. The initial compositions tested at 297 K were Cl_2 (2 000−20 000 ppm), CH_4 (10 000−50 000 ppm), and C_2H_6 (1 000−20 000 ppm). At 540 K, experiments were carried out over the pressure range 150−760 Torr. The initial compositions tested at 540 K were Cl_2 (2 350−16 000 ppm), CH_4 (10 000−50 000 ppm), and C_2H_6 (1000−2000 ppm). No change in k_1/k_2 was observed over these ranges in pressure and initial composition to within experimental error. Table 1 presents details of the mixture compositions and measured rate constant ratios.

Figure 3 presents log−log plots of the consumption of C_2H_6 and CH_4 at four representative temperatures. The ratio of the rate constant for the Cl reaction with C_2H_6 to that with CH_4 (k_1/k_2) can be calculated from the slope of the linear regressions through the data points at each temperature. Note that each plot is forced through the origin and that the regressions fit the data very well. On the basis of the slopes in this figure, the rate constant ratios at each of the four temperatures are 1050 (267 K), 96.1 (485 K), 66 (539 K), and 47.2 (600 K). The estimated uncertainty in these measurements is 10% including data scatter and measurement of reactant consumption. The approximate ranges of C_2H_6 and CH_4 consumption are 20−97% and 0.03−0.36%, respectively, at 267 K and 15−95% and 0.35−6.8%, respectively, at 600 K.

In Figure 4, all rate constant ratios obtained by the GC method at ambient temperature are presented as individual points. The filled circles were obtained using the high-temperature reactor, and the open circles were obtained using the low-temperature reactor. The data from the two reactors agree very well, verifying

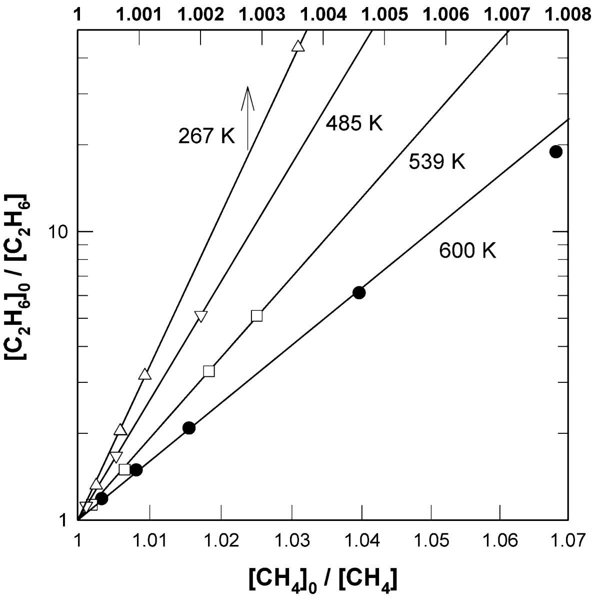

Figure 3. Log−log plot of $[C_2H_6]_0/[C_2H_6]$ vs $[CH_4]_0/[CH_4]$ at four temperatures using the high-temperature reactor with GC analysis. For the 267 K data, the top *x*-axis is used. For all other data, the bottom *x*-axis is used. On the basis of the slopes of the linear regressions, k_1/k_2 at each temperature is 267 K (1050), 485 K (96.1), 539 K (66), and 600 K (47.2).

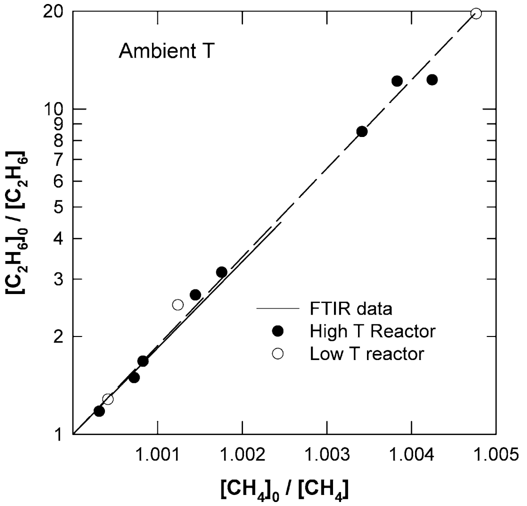

Figure 4. Log−log plot of $[C_2H_6]_0/[C_2H_6]$ vs $[CH_4]_0/[CH_4]$ at ambient temperature in the high-temperature GC reactor (●), the low-temperature GC reactor (○), and in the FTIR smog chamber (— regression from Figure 2). The linear regression to all of the GC data is shown as a dashed line (- - -).

that the GC measurement is independent of the reactor used. Fitting these GC data with a linear regression (dashed line) gives a rate constant ratio $k_1/k_2 = 628 \pm 60$. Also shown is a solid line representing the fit to the FTIR data in Figure 2 over the range of reactant consumption studied. The value of k_1/k_2 at ambient temperature determined by the GC method (628) agrees within 3% with that determined by the FTIR method (609). This agreement is well within the combined (and also individual) estimated error limits, demonstrating again that the measured ratio is independent of reactor, initial mixture, and analytical technique. In addition, it verifies that k_1/k_2 in He is identical to that in N_2, because the GC experiments used He (with the exception of one test in N_2; see Table 1) and FTIR used N_2 as the diluent.

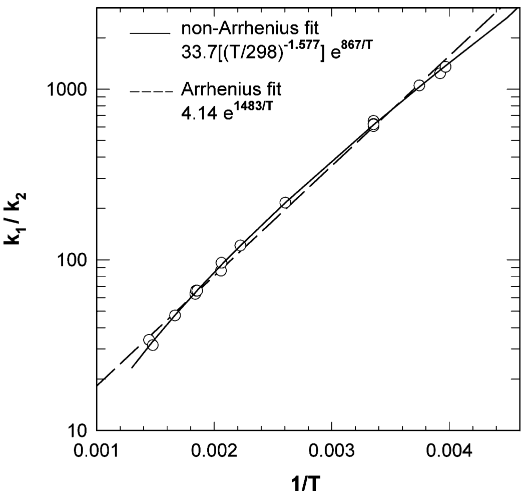

Figure 5. Log $[k_1/k_2]$ plotted as a function of $1/T$ for data obtained using the GC method. Arrhenius [$=4.14 \exp(1483/T)$] and non-Arrhenius [$=33.7(T/298)^{-1.577} \exp(867/T)$] fits to the data are shown.

Figure 5 presents the temperature-dependent data obtained for k_1/k_2 over the temperature range 250−700 K. Two fits to these data are shown: an Arrhenius expression and a non-Arrhenius expression. Of these two expressions, the non-Arrhenius fit is slightly better over the temperature range covered in these experiments, because the data do show slight curvature, although the Arrhenius expression also fits the data nearly within the observed scatter. To explore the statistical significance of the apparent curvature in the data presented in Figure 5, the data points for $T \leq 298$ K and $T \geq 485$ K were each fit by a linear least-squares expression. The temperature dependence for $T \leq 298$ K is $E/R = 1240 \pm 68$, and for $T \geq 485$ K, it is 1720 ± 180, in which the error limits represent 2σ. On the basis of these results, there is a statistically significant curvature to the temperature-dependent GC relative rate data in Figure 5.

4. Discussion

The experiments presented here provide measurements of k_1/k_2 over the temperature range 250−700 K. Experiments were performed using a range of initial reactant concentrations and two completely different reactors and detection techniques at ambient temperature. Results obtained with the two techniques are indistinguishable within the experimental uncertainties. The present work is the most comprehensive relative rate study of k_1/k_2 available to date.

4.1. Comparison with Previous Relative Rate Data. The values of k_1/k_2 obtained in the present work are compared to all previous relative rate measurements[5−9] in Figure 6. As shown in Figure 6, with the exception of the results from Lee and Rowland,[7] the data from all relative rate studies are in excellent agreement. The solid line is an Arrhenius fit to the combined data set (except data from Lee and Rowland[7]) which gives $k_1/k_2 = 4.62 \exp(1423/T)$. This expression describes the majority of the data points from 5 previous studies[5−9] and the present work to within 10%. The consistency of the relative rate data acquired over the past 50 years is quite remarkable. From the agreement evident in Figure 6, it seems reasonable to conclude that the rate constant ratio k_1/k_2 is well established (within 10%) over the temperature range 200−700 K. The dotted and dashed lines in Figure 6 show the ratio of the individual rate constants for k_1 and k_2 given by the NASA JPL[10] and IUPAC[2] data evaluation panels. It is clear from Figure 6 that the data from both evaluation panels provide a reasonable description of k_1/k_2 over most of the temperature range (200−300 K) for which values of k_2 are recommended. At higher temperatures (500−700 K),

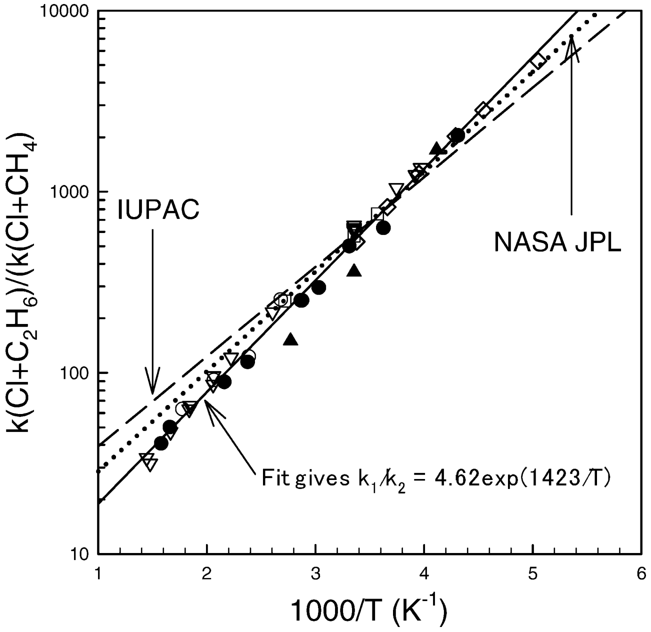

Figure 6. Rate constants measured in the present work (▽), Knox[6] (●), Pritchard et al.[5] (○), Lin et al.,[8] (◇), Lee and Rowland,[7] (▲), and Tschuikow et al.[9] (□). The solid line (—) is a fit to the combined data (except Lee and Rowland). The dotted line (···) was obtained using values of $k_1 = 7.7 \times 10^{-11}$ exp($-90/T$) and $k_2 = 9.6 \times 10^{-12}$ exp($-1360/T$) cm^3 molecule^{-1} s^{-1} from the NASA JPL panel.[10] The dashed line (- - -) was obtained using values of $k_1 = 8.3 \times 10^{-11}$ exp($-100/T$) and $k_2 = 6.6 \times 10^{-12}$ exp($-1240/T$) cm^3 molecule^{-1} s^{-1} from the IUPAC panel.[2]

it is clear that extrapolation of the recommended kinetic data lead to values of k_1/k_2 that are substantially larger than the experimental data with the discrepancy being greatest for the ratio derived from the IUPAC data.

Finally, it is important to note that the data in Figure 5 show non-Arrhenius temperature dependence in a relative rate measurement of k_1/k_2, consistent with the absolute measurements. Combining all previous relative rate measurements into one plot as in Figure 6 shows the consistency of all relative rate measurements, but washes out any evidence of curvature because of the data scatter in each measurement.

4.2. Comparison with Previous Absolute Rate Data. Hickson and Keyser[1] deduced a value of k_1/k_2 from their measurement of k_1 and data for k_2 recommended by the IUPAC panel.[2] On the basis of this comparison, they concluded that the discrepancy between their data and the relative rate data "now lies in the relative rate measurements themselves." While it is reasonable to deduce a value of k_1/k_2 by combining the measurements of k_1 with the values of k_2 recommended by the IUPAC panel, the limited temperature range (200−300 K) over which the recommendation is valid should be noted. Errors can arise when extrapolating to temperatures that are significantly outside the recommended range. For example, extrapolation of the expression recommended by the IUPAC panel, $k_2 = 6.6 \times 10^{-12}$ exp($-1240/T$), gives $k_2 = 8.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 600 K. This result is lower than the measured values of k_2 at 600 K by approximately a factor of 2.[12,13] Use of the IUPAC Arrhenius expression for k_2 at temperatures around 600 K will lead to an overestimation of k_1/k_2 by a factor of approximately 2. This fact explains the discrepancy between the dashed and solid lines in Figure 6 at high temperatures. In contrast to the finding of Hickson and Keyser,[1] we conclude that the discrepancy between their k_1/k_2 values and the relative rate literature data lies in the inappropriate values of k_2 used by Hickson and Keyser.[1]

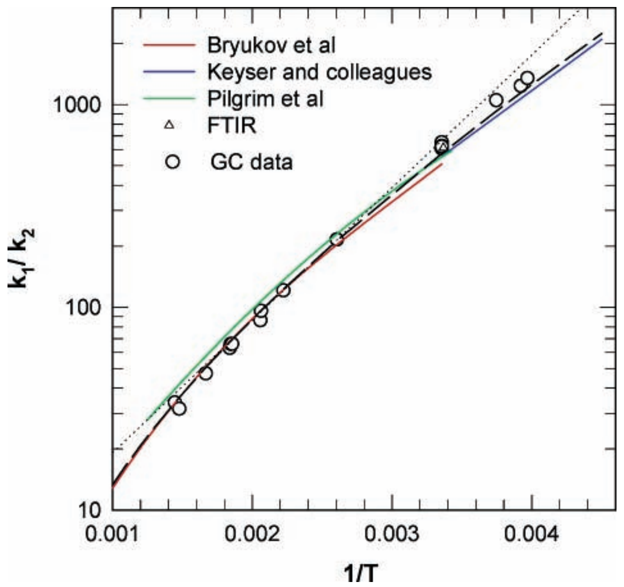

Figure 7. Log [k_1/k_2] plotted as a function of 1/T for the current measurements (○, △), Pilgrim et al.[13] data (green line), Bryukov et al. data[11,12] (red line), Hickson and Keyser[1] and Wang and Keyser[14] (blue line). k_1/k_2 = [4.62 exp(1423/T) (···); k_1/k_2 = [41(T/298)$^{-1.58}$ exp(786/T)] (- - -).

To evaluate k_1/k_2 from absolute rate studies of the individual rate constants, it is desirable to use values of k_1 and k_2 derived in the same laboratory, because any systematic uncertainties are more likely to cancel using such an approach. There have been three recent sets of experiments in which absolute measurements of k_1 and k_2 have been performed by the same authors using the same apparatus in the same laboratory. These experiments were performed by Bryukov, Slagle, and Knyasev (295−1000 K);[11,12] Pilgrim, McIlroy, and Taatjes (298−800 K);[13] and Hickson and Keyser (177−353 K) for ethane[1] and Wang and Keyser (218−298) for methane.[14] The absolute measurements of each rate constant as a function of temperature can be used to deduce a rate constant ratio, which can be compared to the measurements herein. This comparison is presented in Figure 7. The rate constant ratios from absolute measurements were determined from the kinetic expressions derived by the authors for methane and ethane over the temperature range for which both rate constants were determined, because individual rates were not typically measured for methane and ethane at the same temperature. The data in Figure 7 show that the values of k_1/k_2 from Bryukov et al. agree nearly perfectly with the current data, deviating only by 15% at 298 K. The data of Pilgrim et al. deviate from the current data and that of Bryukov by a maximum of 15% at their highest temperature. The data of Keyser and co-workers lie approximately 15% below the current low-temperature data. Thus, the overall agreement of our direct relative rate data with the indirect data deduced from the absolute rate determinations by Bryukov et al., Pilgrim et al., and Keyser and colleagues is excellent. Our relative rate measurements are 15% higher than those deduced from Keyser and colleagues at low temperature, indicating that there may be some discrepancy with these low-temperature absolute measurements. However, the data of Keyser et al. for k_1 and k_2 each have stated error limits of 3%, while we estimate our error limits to be 10%, including data scatter and calibration errors. This suggests that our relative rate experiments are consistent with the absolute data nearly within the estimated combined errors over the temperature range 250−700 K. An Arrhenius expression and a non-Arrhenius expression have been estimated from our relative rate constant ratios and those calculated from the absolute measurements. They are shown as dotted and dashed lines, respectively, in Figure 7.

4.3. Implications for Atmospheric Chemistry. The present work confirms and extends the relative rate kinetic database for reactions of Cl atoms with methane and ethane. As seen from Figure 6, there is excellent agreement between the results of five (including the present work) separate relative rate studies[5,6,8,9] of k_1/k_2 over the temperature range 200−700 K. The expression $k_1/k_2 = 4.62\ \exp(1423/T)$ provides a good description (within 10%) of the reported relative rate data, although the current data indicate the presence of some curvature. As seen from Figure 7, there is excellent agreement between the ratio k_1/k_2 derived from absolute measurements of k_1 and k_2 in three different laboratories. The absolute measurements are consistent with the relative measurements, although including these data suggests that a non-Arrhenius expression $[k_1/k_2 = 41(T/298)^{-1.58}\ \exp(786/T)]$ fits the data somewhat better than the Arrhenius expression presented already. We conclude that the kinetics of reactions 1 and 2 over the temperature range 200−1000 K are reasonably well established, and these reactions can be included in global atmospheric models with relatively little uncertainty. We recommend that the relative rate data shown in Figure 6 be used as one of the fitting constraints in future kinetic data evaluations of k_1 and k_2. Finally, by comparing how the ratio of the concentrations of CH_4 and C_2H_6 in air isolated from fresh emissions (e.g., in the stratosphere) change over time with the rate constant ratio k_1/k_2 discussed herein and $k(OH + C_2H_6)/k(OH + CH_4)$ available elsewhere,[10] the relative importance of the reaction with Cl atoms and OH radicals for the loss of C_2H_6 can be inferred.[15]

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Note Added after ASAP Posting. One of the quantities in the percentage ranges at the end of paragraph 2, Section 3.2. had a misplaced decimal in the version posted ASAP October 26, 2004. The corrected version was posted October 26, 2004.

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