

Kinetics of the Gas-Phase Reactions of Chlorine Atoms with CH₂F₂, CH₃CCl₃, and CF₃CFH₂ over the Temperature Range 253–553 K

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ABSTRACT: Relative rate techniques were used to study the title reactions in 930–1200 mbar of N₂ diluent. The reaction rate coefficients measured in the present work are summarized by the expressions $k(\text{Cl} + \text{CH}_2\text{F}_2) = 1.19 \times 10^{-17} T^2 \exp(-1023/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (253–553 K), $k(\text{Cl} + \text{CH}_3\text{CCl}_3) = 2.41 \times 10^{-12} \exp(-1630/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (253–313 K), and $k(\text{Cl} + \text{CF}_3\text{CFH}_2) = 1.27 \times 10^{-12} \exp(-2019/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (253–313 K). Results are discussed with respect to the literature data. © 2009 Wiley Periodicals, Inc. *Int J Chem Kinet* 41: 401–406, 2009

INTRODUCTION

The title compounds are released into the atmosphere as the result of human activities. CH₂F₂ (HFC-32) and CF₃CFH₂ (HFC-134a) are used as refrigerants and have atmospheric lifetimes of approximately 4.9 and 14 years, respectively [1]. CF₃CFH₂ is used widely in

vehicle air conditioning systems and is the most abundant HFC in the atmosphere [1]. CH₃CCl₃ or 1,1,1-trichloroethane was widely used as an industrial solvent until it was banned under the Montreal protocol. CH₃CCl₃ has an atmospheric lifetime of approximately 5 years [1]. The global budget of CH₃CCl₃ has been used to estimate the global average tropospheric OH concentration [2].

Chlorine atoms are often used to initiate the oxidation of organic compounds in smog chamber studies of the atmospheric chemistry of halogenated organic

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compounds. Accurate kinetic data for the reactions of chlorine atoms with halogenated organics are needed for the analysis of such smog chamber data. Unfortunately, there are significant uncertainties in the kinetic data at ambient temperature and very limited information concerning the temperature dependence for such reactions. Measurements of $k(\text{Cl} + \text{CH}_2\text{F}_2)$ at 298 K by Tschuikow-Roux et al. [3] and Nielsen et al. [4] differ by a factor of 2, and the work by Tschuikow-Roux et al. [3] provides the only information concerning the temperature dependence of the reaction. Measurements of $k(\text{Cl} + \text{CH}_3\text{CCl}_3)$ at 280–418 K by Cillien et al. [5], Tschuikow-Roux et al. [6], Platz et al. [7], and Talhaoui et al. [8] span a range of approximately 2. Measurements of $k(\text{Cl} + \text{CF}_3\text{CFH}_2)$ at 298 K by Sawerysyn et al. [9], Wallington and Hurley [10], Tuazon et al. [11], Louis et al. [12], and Kaiser [13] are in excellent agreement; however, only limited data are available at temperatures below ambient. To improve our understanding of the kinetics of the reactions of chlorine atoms with halogenated organic compounds, we have measured $k(\text{Cl} + \text{CH}_2\text{F}_2)$ relative to $k(\text{Cl} + \text{CH}_4)$, $k(\text{Cl} + \text{CH}_3\text{CCl}_3)$ relative to $k(\text{Cl} + \text{CH}_2\text{F}_2)$, and $k(\text{Cl} + \text{CF}_3\text{CFH}_2)$ relative to $k(\text{Cl} + \text{CH}_3\text{CCl}_3)$ over the temperature range 253–553 K in 930–1200 mbar of N_2 diluent.

EXPERIMENTAL

Experiments were performed using the reaction systems at the University of Copenhagen and the University of Michigan–Dearborn. Unless stated otherwise, quoted uncertainties are two standard deviations from least-squares regression analysis.

Measurement of k_1 at the University of Copenhagen

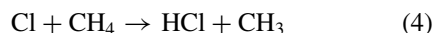
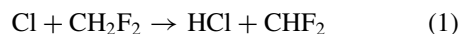
The reaction chamber at the University of Copenhagen consists of a 100-L cylindrical quartz reaction chamber in a temperature-controlled housing described in detail elsewhere [14]. Experiments were performed using $\text{CH}_2\text{F}_2/\text{CH}_4/\text{Cl}_2$, $\text{CH}_3\text{CCl}_3/\text{CH}_2\text{F}_2/\text{Cl}_2$, and $\text{CF}_3\text{CFH}_2/\text{CH}_3\text{CCl}_3/\text{Cl}_2$ mixtures in 930 mbar of N_2 diluent at 253, 273, 298, and 313 or 318 K. A Bruker IFS 66v/s FTIR spectrometer was used to monitor the loss of the organic compounds following successive UV irradiation of the reaction mixtures. FTIR spectra were analyzed using an iterative non-linear least-squares fitting procedure [15]. Reference spectra of CH_4 , HCl , and H_2O were taken from the HITRAN database [16]. Reference spectra of CH_2F_2 , CH_3CCl_3 , and CF_3CFH_2 were recorded under the

same conditions as photolysis experiments (resolution 0.125 cm^{-1} , pressure 930 mbar N_2), three spectra were taken for each compound and averaged to give the reference spectra used in the analysis.

The reference spectra were recorded at a temperature of 298 K and used for the analysis at all temperatures. Spectra of reaction mixtures of CH_2F_2 and CH_4 were analyzed in the region 2800–3200 cm^{-1} . HCl is a reaction product, and H_2O is always observable as a background contaminant in FTIR smog chamber experiments. HCl and H_2O spectral features were subtracted in the analysis. CH_3CCl_3 and CF_3CFH_2 were analyzed in the region 1400–1480 cm^{-1} ; here H_2O was also included in the analysis.

The partial pressures of the organic compounds were in the range 0.01–0.06 mbar. The partial pressure of Cl_2 was 1–3 mbar. Chlorine atoms were produced by the photolysis of molecular chlorine using UVA lamps with an emission maximum at about 368 nm. Typically, four to six irradiations were performed for each reaction mixture. The mixture was allowed to stabilize for 2 min after each photolysis step. The pressure in the cell was monitored to quantify potential temperature changes induced by the lamps. There was no discernable change ($<0.2\%$) in the pressure of the gas mixtures in the chamber, indicating that there was less than 1 K change in gas temperature during an experiment. Control experiments were performed to check for possible loss of reactants and reference compounds in the chamber in the absence of UV irradiation. There was no ($<1\%$) loss of reactants and/or reference compounds when reaction mixtures were left to stand in the dark for 60 min.

The relative rate method is a well-established technique for measuring the reactivity of Cl atoms with organic compounds [17]. Kinetic data are derived by monitoring the loss of the reactant and the reference compound. In the present work, we have measured the kinetics of reactions ((1)–(3)) relative to the well-established kinetics of reaction (4).



The rates of reactions (3) and (4) differ by approximately a factor of 100, precluding a direct measurement of k_3/k_4 . Values of k_3/k_4 were derived by measuring k_3/k_2 , k_2/k_1 , and k_1/k_4 and using the equality $k_3/k_4 = k_3/k_2 \times k_2/k_1 \times k_1/k_4$. In a similar fashion, k_2/k_4 was obtained from $k_2/k_1 \times k_1/k_4$. As indicated in

Table I Rate Constant Ratios Measured at the University of Copenhagen

Reactant	Reference	$k_{\text{reactant}}/k_{\text{reference}}$	Temperature (K)
CH ₂ F ₂	CH ₄	0.277 ± 0.004	253
CH ₂ F ₂	CH ₄	0.283 ± 0.008	273
CH ₂ F ₂	CH ₄	0.334 ± 0.016	298
CH ₂ F ₂	CH ₄	0.339 ± 0.010	318
CH ₃ CCl ₃	CH ₂ F ₂	0.288 ± 0.006	253
CH ₃ CCl ₃	CH ₂ F ₂	0.291 ± 0.005	273
CH ₃ CCl ₃	CH ₂ F ₂	0.294 ± 0.017	298
CH ₃ CCl ₃	CH ₂ F ₂	0.290 ± 0.011	313
CF ₃ CFH ₂	CH ₃ CCl ₃	0.105 ± 0.003	253
CF ₃ CFH ₂	CH ₃ CCl ₃	0.151 ± 0.007	273
CF ₃ CFH ₂	CH ₃ CCl ₃	0.128 ± 0.008	298
CF ₃ CFH ₂	CH ₃ CCl ₃	0.157 ± 0.015	313

Table I, values of k_3/k_2 , k_2/k_1 , and k_1/k_4 were measured at 253, 273, and 298 K and calculation of k_3/k_4 and k_2/k_4 at these temperatures is straightforward. While values of k_3/k_2 and k_2/k_1 were measured at 313 K, k_1/k_4 was determined at 318 K. An Arrhenius fit to the measured values of k_1/k_4 was used to provide a value of k_1/k_4 at 313 K (the uncertainty was assumed to be the same as that for the measured ratio at 318 K), which enabled calculation of k_3/k_4 and k_2/k_4 at 313 K.

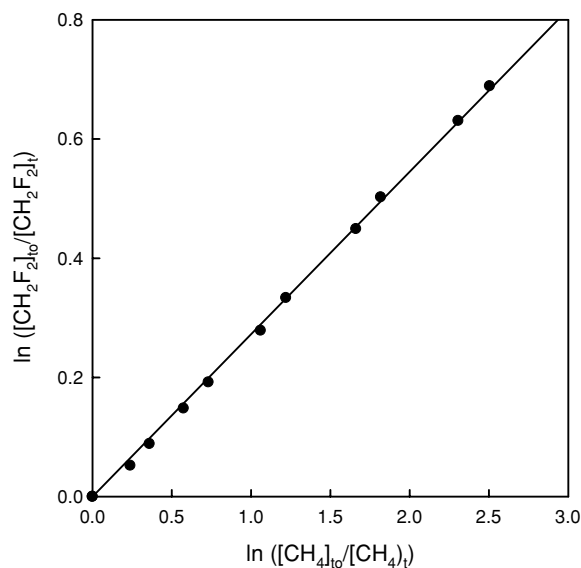
$\ln([\text{reactant}]_{t_0}/[\text{reactant}]_t)$ versus $\ln([\text{reference}]_{t_0}/[\text{reference}]_t)$ was plotted using the expression

$$\ln\left(\frac{[\text{reactant}]_{t_0}}{[\text{reactant}]_t}\right) = \frac{k_{\text{react}}}{k_{\text{ref}}} \ln\left(\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right)$$

where $[\text{reactant}]_{t_0}$, $[\text{reactant}]_t$, $[\text{reference}]_{t_0}$, and $[\text{reference}]_t$ are the concentrations of reactant and reference at times “to” and t (see Fig. 1), and k_{react} and k_{ref} are the rate constants for reactions of Cl atoms with the reactant and reference. Plots of $\ln([\text{reactant}]_{t_0}/[\text{reactant}]_t)$ versus $\ln([\text{reference}]_{t_0}/[\text{reference}]_t)$ should be linear, pass through the origin and have a slope of $k_{\text{react}}/k_{\text{ref}}$.

Measurement of k_1 at the University of Michigan

Experiments were performed over the temperature range 297–553 K using a 40-cm³ Pyrex cylinder reactor (26 mm ID × ~7 cm length) with a thermocouple well down the center and a stopcock attached to a Pyrex capillary tube on the other end. The reactor was placed inside a tube oven whose lid was open approximately 6 mm to allow radiation from a UVA fluorescent lamp to enter. The calibration of the Chromel–Alumel thermocouple was checked in ice and boiling water. The temperature along the axis of the reactor was uniform

**Figure 1** Loss of CH₂F₂ versus CH₄ following exposure to chlorine atoms at 253 K.

to ~2 K from the mean. During a reaction, a portion of the unreacted mixture was placed into the reactor at pressures varying from 930 to 1200 mbar depending on the depletion in the reactant storage flask. The mixture was then irradiated for a chosen time, and the contents were withdrawn into a 100-cm³ transfer flask outside of the oven. This sample was diluted with N₂ and then injected into the GC using a gas-tight syringe. Only one irradiation was possible per sample placed into the reactor. The consumption of CH₂F₂ was 7%–40%.

The unreacted mixture contained CH₄ (~1000 ppm), CH₂F₂ (~500 ppm), and CF₃CFH₂ (~500 ppm as an internal calibrant to allow normalization for small variations in the amount of reaction mixture extracted for the GC analysis), Cl₂ (1200–2500 ppm), and N₂. The CF₃CFH₂ internal calibrant reacts slowly with Cl atoms. The measured CF₃CFH₂ concentration was corrected for loss using the measured loss of CH₄ and the value of k_3/k_4 discussed herein. This correction never exceeded 3%. For selected samples, two analyses were performed to assess sample stability, which showed that the samples were always stable over 10–15 min. In addition, unirradiated mixtures were also placed in the reactor to determine the degree of thermal reaction that may occur as the temperature is increased. Significant thermal reaction was only observed at the highest temperature (~550 K). The two highest temperature data points in shown in Fig. 2, for which a thermal reaction was observed, were derived from the loss of CF₂H₂ versus loss of CH₄. They are entirely consistent with the data obtained at lower temperature

Table II Rate Constant Ratios Measured at the University of Michigan–Dearborn

$k_{\text{CH}_2\text{F}_2}/k_{\text{CH}_4}$	Temperature (K)	$k_{\text{CH}_2\text{F}_2}/k_{\text{CH}_4}$	Temperature (K)
0.324	297	0.429	449
0.308	297	0.422	457
0.317	297	0.389	457
0.341	297	0.481	508
0.323	297	0.437	510
0.339	344	0.439	511
0.357	345	0.422	511
0.379	398	0.490	548
0.394	400	0.444	553
0.417	402		

where no thermal reaction occurs. Thus, the reactivity of chlorine atoms is not impacted by the method by which chlorine atoms are formed in the system (photolysis of Cl_2 or thermal decomposition of Cl_2 followed by chain chlorination chemistry).

At ambient temperature, experiments were performed in both the high-temperature reactor described above and in a 0.5-L spherical Pyrex flask. The rate constant ratios were indistinguishable in these two reactors (see Table II—first three entries at 297 K are in the high-temperature reactor; remaining two are in the 0.5-L flask), verifying that surface reactions play no significant role in these measurements.

RESULTS

$k(\text{Cl} + \text{CH}_2\text{F}_2)$

Figure 1 shows plots of the observed decay of CH_2F_2 versus CH_4 for experiments performed in Copenhagen. Consistent with expectations, as discussed in the section “Measurement of k_1 at the University of Copenhagen,” plots of $\ln([\text{CH}_2\text{F}_2]_{t_0}/[\text{CH}_2\text{F}_2]_t)$ versus $\ln([\text{CH}_4]_{t_0}/[\text{CH}_4]_t)$ were linear and passed through the origin. The lines through the data in Fig. 1 are linear least-squares fits that give the values of k_1/k_4 listed in Table I. To place these rate constant ratios on an absolute basis, we chose to use $k_4 = 5.69 \times 10^{-19} T^{2.49} \exp(-609/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ derived from a fit by Bryukov et al. [18] to the available literature data over the temperature range 200–1000 K. The resulting values of k_1 are shown in the Arrhenius plot in Fig. 2. Rate constant ratios k_1/k_4 measured in Dearborn are listed in Table II and are also plotted as rate constants in Fig. 2.

As seen from Fig. 2, where comparison is possible at temperatures near ambient the data obtained

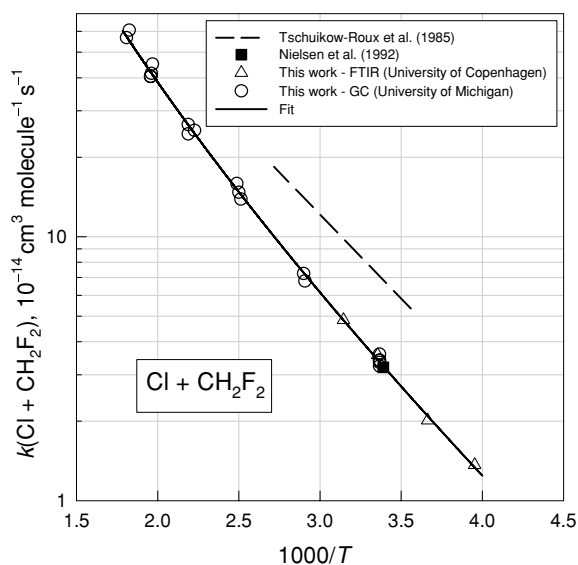


Figure 2 Arrhenius plot for $k(\text{Cl} + \text{CH}_2\text{F}_2)$. The data obtained at the University of Copenhagen are represented by triangles, and the data obtained at the University of Michigan are represented by circles. The solid line is a fit to the data of Nielsen et al. [4] and the present work: $k_1 = 1.19 \times 10^{-17} T^2 \exp(-1023/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

in Copenhagen and Dearborn are in excellent agreement. Also, both sets of data are in good agreement with the previous measurement by Nielsen et al. [4], which was obtained 16 years ago in the FTIR-smog chamber system at the Ford Motor Company laboratory in Dearborn. The results obtained in the present work and by Nielsen et al. [4] are approximately a factor of 2 lower than in the study by Tschuikow-Roux et al. [3].

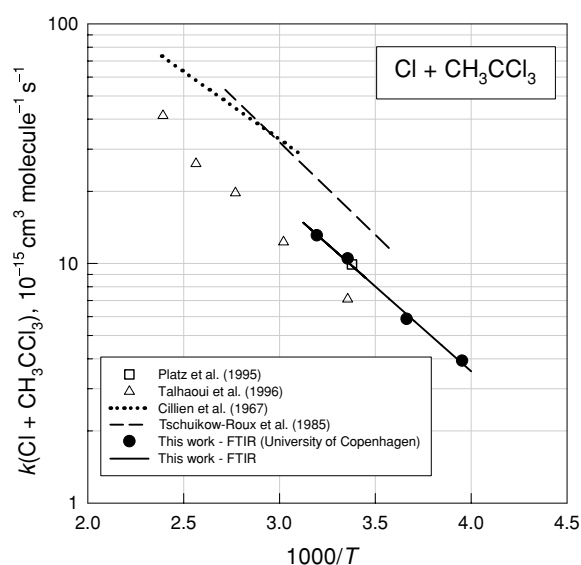
In the relative rate study by Tschuikow-Roux et al. [3], rate constant ratios k_1/k_4 were measured by monitoring the formation of CHF_2Cl and CH_3Cl following UV irradiation of $\text{CH}_2\text{F}_2/\text{CH}_4/\text{Cl}_2$ mixtures. The formation of CHF_2Cl and CH_3Cl was measured by GC-FID and used to infer the loss of CH_2F_2 and CH_4 . Tschuikow-Roux et al. [3] found it necessary to apply an “unexpectedly large” correction factor of 5.838 to account for the response of the GC-FID to CHF_2Cl . The use of a smaller correction factor would lead to better agreement with results from the present work and from Nielsen et al. [4]. It seems clear that k_1 was overestimated by Tschuikow-Roux et al. [3]. The curve through the data in Fig. 2 is a least-squares fit of the expression $k = CT^2 \exp(-D/T)$ to the combined data set from the present work, which gives $k_1 = 1.19 \times 10^{-17} T^2 \exp(-1023/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As seen from Fig. 2, this expression fits the data to within $\pm 15\%$ across the entire temperature range.

Table III Rate Constant Ratios Measured at Copenhagen, Scaled to $k(\text{Cl} + \text{CH}_4)$

Reactant	Reference	$k_{\text{Reactant}}/k_{\text{CH}_4}$	Temperature (K)
CH ₃ CCl ₃	CH ₂ F ₂	0.0796 ± 0.0021	253
CH ₃ CCl ₃	CH ₂ F ₂	0.0825 ± 0.0026	273
CH ₃ CCl ₃	CH ₂ F ₂	0.0982 ± 0.0074	298
CH ₃ CCl ₃	CH ₂ F ₂	0.0981 ± 0.0048	313
CF ₃ CFH ₂	CH ₃ CCl ₃	0.00838 ± 0.00032	253
CF ₃ CFH ₂	CH ₃ CCl ₃	0.0125 ± 0.0007	273
CF ₃ CFH ₂	CH ₃ CCl ₃	0.0126 ± 0.0012	298
CF ₃ CFH ₂	CH ₃ CCl ₃	0.0154 ± 0.0017	313

$k(\text{Cl} + \text{CH}_3\text{CCl}_3)$

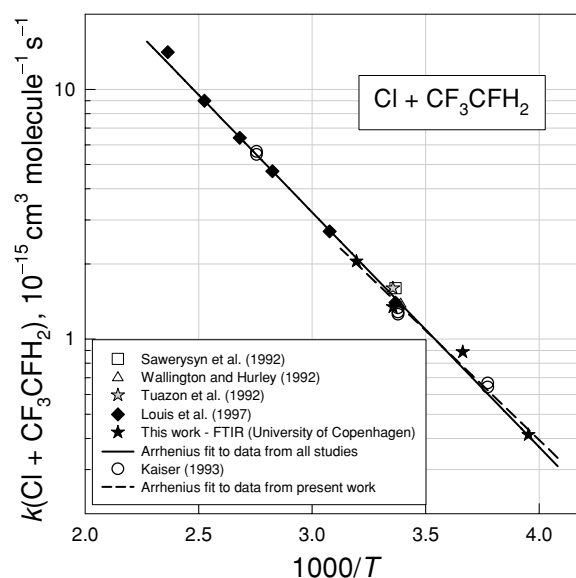
Rate constant ratios k_2/k_1 measured in Copenhagen are given in Table I. Multiplication by the appropriate values of k_1/k_4 (in Table I, see the section “Measurement of k_1 at the University of Copenhagen” regarding k_1/k_4 data point at 318 K) gives the values of k_2/k_4 listed in Table III. Uncertainties in Table III were computed using standard error propagation. The values of k_2/k_4 in Table III can be placed on an absolute basis using $k_4 = 5.69 \times 10^{-19} T^{2.49} \exp(-609/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [18] and are shown in the Arrhenius plot in Fig. 3. As seen from Fig. 3, the results from the present work are in good agreement with the previous relative rate measurement by Platz et al. [7] using the FTIR-smog chamber system at Ford. However, the results from the discharge flow absolute rate study by Talhaoui et al.

**Figure 3** Arrhenius plot for $k(\text{Cl} + \text{CH}_3\text{CCl}_3)$. The solid line is a fit to the data from the present work: $k_2 = 2.41 \times 10^{-12} \exp(-1630/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

[8] lie about 25% below the present work, whereas those from the relative rate study by Tschuikow-Roux et al. [6] are about 60% above those from the present work. A linear least-squares regression analysis to the data from the present work gives $k(\text{Cl} + \text{CH}_3\text{CCl}_3) = 2.41 \times 10^{-12} \exp(-1630/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

$k(\text{Cl} + \text{CF}_3\text{CFH}_2)$

Rate constant ratios k_3/k_2 measured in Copenhagen are given in Table I. Multiplication by the appropriate values of k_1/k_4 and k_2/k_1 (in Table I; see the section “Measurement of k_1 at the University of Copenhagen” regarding k_1/k_4 data point at 318 K) gives the values of k_3/k_4 listed in Table III. Uncertainties in Table III were computed using standard error propagation. The values of k_3/k_4 in Table III can be placed on an absolute basis using $k_4 = 5.69 \times 10^{-19} T^{2.49} \exp(-609/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [18] and are shown in the Arrhenius plot in Fig. 4. As seen from Fig. 4, there is excellent agreement between the values of k_3 at ambient temperature reported by Sawerysyn et al. [9], Wallington and Hurley [10], Tuazon et al. [11], Kaiser [13] (calculated from measured values of $k_3/k(\text{CF}_3\text{CFClH})$ using the temperature dependent expression for $k(\text{CF}_3\text{CFClH})$ determined by Warren and Ravishankara [19]), Louis et al. [12], and the present work. Inspection of Fig. 4 also reveals that the temperature dependence of k_3

**Figure 4** Arrhenius plot for $k(\text{Cl} + \text{CF}_3\text{CFH}_2)$. The dashed line is a fit to the data from the present work, which gives $k_3 = 1.27 \times 10^{-12} \exp(-2019/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The solid line is a fit to the combined data set from all studies, which gives $k_3 = 2.13 \times 10^{-12} \exp(-2165/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

observed by Kaiser et al. [13] and Louis et al. [12] is indistinguishable from that observed in the present work. The present work confirms and extends to lower temperatures the subambient data for k_3 . The dashed line is a fit to the data from the present work, which gives $k_3 = 1.27 \times 10^{-12} \exp(-2019/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The solid line is a fit to the combined data set from all studies, which gives $k_3 = 2.13 \times 10^{-12} \exp(-2165/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

DISCUSSION

We report a substantial and self-consistent set of kinetic data for the reactions of chlorine atoms with CH_2F_2 , CH_3CCl_3 , and CF_3CFH_2 . The kinetic data for the reaction of chlorine atoms with CH_2F_2 determined using two independent techniques (FTIR analysis in Copenhagen and GC in Dearborn) are in good agreement. The kinetic data for the reaction of chlorine atoms with CF_3CFH_2 determined in the present work are in good agreement with five previous studies using relative [10,11,13] and absolute [9,12] rate methods. The kinetics of this reaction appear to be very well established, and a fit to the combined data set from six different studies gives $k_3 = 2.13 \times 10^{-12} \exp(-2165/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

As shown in Fig. 3, there is substantial scatter in the kinetic data for the reaction of chlorine atoms with CH_3CCl_3 . As indicated in Table III, we have used $k(\text{Cl} + \text{CH}_3\text{CCl}_3)$ as a "stepping stone" to relate the reactivity of CF_3CFH_2 to CH_4 . The excellent agreement between the values of $k(\text{Cl} + \text{CF}_3\text{CFH}_2)$ measured in the present work and the literature data suggests (but does not prove) that our measurement of $k(\text{Cl} + \text{CH}_3\text{CCl}_3)$ is free from substantial errors. In the relative rate work of Tschuikow-Roux et al. [6], the loss of CH_3CCl_3 was measured indirectly by observing the formation of the chlorinated product $\text{CH}_2\text{ClCCl}_3$. A correction factor of 2.35 was applied to account for the reduced sensitivity of the flame ionization detector toward $\text{CH}_2\text{ClCCl}_3$. In the same study, Tschuikow-Roux et al. [6] report $k(\text{Cl} + \text{C}_2\text{H}_6)/k(\text{Cl} + \text{CH}_4) = 7.33 \exp(1298/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ [20] gives a value of $k(\text{Cl} + \text{C}_2\text{H}_6) = 3.98 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, which is significantly different from the well-established value of $k(\text{Cl} + \text{C}_2\text{H}_6) = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [20]. The study by Tschuikow-Roux et al. [6] appears to have significant systematic errors. The relative rate study by Cillien et al. [5] employed a very similar method to that used by Tschuikow-Roux et al. [6] (loss of CH_3CCl_3 inferred from $\text{CH}_2\text{ClCCl}_3$ formation measured by GC) and reported similar re-

sults (see Fig. 3). It appears that there is a problem with this method.

The data reported herein improve our understanding of the kinetics of reactions (1)–(3) and should facilitate future smog chamber studies of the atmospheric degradation mechanisms of halogenated organics.

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