Kinetics of the Gas-Phase Reactions of Chlorine Atoms with CH$_2$F$_2$, CH$_3$CCl$_3$, and CF$_3$CFH$_2$ 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 N$_2$ 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. CH$_2$F$_2$ (HFC-32) and CF$_3$CFH$_2$ (HFC-134a) are used as refrigerants and have atmospheric lifetimes of approximately 4.9 and 14 years, respectively [1]. CF$_3$CFH$_2$ is used widely in vehicle air conditioning systems and is the most abundant HFC in the atmosphere [1]. CH$_3$CCl$_3$ or 1,1,1-trichloroethane was widely used as an industrial solvent until it was banned under the Montreal protocol. CH$_3$CCl$_3$ has an atmospheric lifetime of approximately 5 years [1]. The global budget of CH$_3$CCl$_3$ 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
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 Tahhaoui 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 CH\(_2\)F\(_2\)/CH\(_3\)/Cl\(_2\), CH\(_3\)CCl\(_3\)/CH\(_2\)F\(_2\)/Cl\(_2\), and CF\(_3\)CFH\(_2\)/CH\(_3\)CCl\(_3\)/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 nonlinear least-squares fitting procedure [15]. Reference spectra of CH\(_4\), HCl, and H\(_2\)O were taken from the HITRAN database [16]. Reference spectra of CH\(_2\)F\(_2\), CH\(_3\)CCl\(_3\), and CF\(_3\)CFH\(_2\) 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\(_2\)F\(_2\) and CH\(_4\) were analyzed in the region 2800–3200 cm\(^{-1}\). HCl is a reaction product, and H\(_2\)O is always observable as a background contaminant in FTIR smog chamber experiments. HCl and H\(_2\)O spectral features were subtracted in the analysis. CH\(_3\)CCl\(_3\) and CF\(_3\)CFH\(_2\) were analyzed in the region 1400–1480 cm\(^{-1}\); here H\(_2\)O 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).

\[
\begin{align*}
\text{Cl} + \text{CH}_2\text{F}_2 & \rightarrow \text{HCl} + \text{CHF}_2 & (1) \\
\text{Cl} + \text{CH}_3\text{CCl}_3 & \rightarrow \text{HCl} + \text{CH}_2\text{CCl}_3 & (2) \\
\text{Cl} + \text{CF}_3\text{CFH}_2 & \rightarrow \text{HCl} + \text{CF}_3\text{CFH} & (3) \\
\text{Cl} + \text{CH}_4 & \rightarrow \text{HCl} + \text{CH}_3 & (4)
\end{align*}
\]

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 \( k_3/k_2, k_3/k_1, \) and \( k_4/k_1 \) 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, \( k_3/k_4 \) 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

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Reference</th>
<th>$\frac{k_{\text{react}}}{k_{\text{reference}}}$</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$F$_2$</td>
<td>CH$_4$</td>
<td>0.277 ± 0.004</td>
<td>253</td>
</tr>
<tr>
<td>CH$_2$F$_2$</td>
<td>CH$_4$</td>
<td>0.283 ± 0.008</td>
<td>273</td>
</tr>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>CH$_4$</td>
<td>0.334 ± 0.016</td>
<td>298</td>
</tr>
<tr>
<td>CH$_2$F$_2$</td>
<td>CH$_4$</td>
<td>0.339 ± 0.010</td>
<td>318</td>
</tr>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>CH$_3$CCl$_3$</td>
<td>0.288 ± 0.006</td>
<td>253</td>
</tr>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>CH$_3$CCl$_3$</td>
<td>0.291 ± 0.005</td>
<td>273</td>
</tr>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>CH$_2$F$_2$</td>
<td>0.294 ± 0.017</td>
<td>298</td>
</tr>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>CH$_2$F$_2$</td>
<td>0.290 ± 0.011</td>
<td>313</td>
</tr>
<tr>
<td>CF$_3$CFH$_2$</td>
<td>CH$_3$CCl$_3$</td>
<td>0.105 ± 0.003</td>
<td>253</td>
</tr>
<tr>
<td>CF$_3$CFH$_2$</td>
<td>CH$_3$CCl$_3$</td>
<td>0.151 ± 0.007</td>
<td>273</td>
</tr>
<tr>
<td>CF$_3$CFH$_2$</td>
<td>CH$_3$CCl$_3$</td>
<td>0.128 ± 0.008</td>
<td>298</td>
</tr>
<tr>
<td>CF$_3$CFH$_2$</td>
<td>CH$_3$CCl$_3$</td>
<td>0.157 ± 0.015</td>
<td>313</td>
</tr>
</tbody>
</table>

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 $k_2/k_3$ 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.

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

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 $k_{\text{react}}$ and $k_{\text{ref}}$ 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-cm$^3$ Pyrex cylinder reactor (26 mm ID x ~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 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-cm$^3$ transfer flask outside of the oven. This sample was diluted with N$_2$ 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 CH$_2$F$_2$ was 7%–40%.

The unreacted mixture contained CH$_4$ (~1000 ppm), CH$_2$F$_2$ (~500 ppm), and CF$_3$CFH$_2$ (~500 ppm as an internal calibrant to allow normalization for small variations in the amount of reaction mixture extracted for the GC analysis), Cl$_2$ (1200–2500 ppm), and N$_2$. The CF$_3$CFH$_2$ internal calibrant reacts slowly with Cl atoms. The measured CF$_3$CFH$_2$ concentration was corrected for loss using the measured loss of CH$_4$ 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 CF$_3$H$_2$ versus loss of CH$_4$. They are entirely consistent with the data obtained at lower temperature...
Table II  Rate Constant Ratios Measured at the University of Michigan–Dearborn

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( k_{\text{CH}_2\text{F}<em>2}/k</em>{\text{CH}_4} )</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.324</td>
<td>297</td>
<td>0.429</td>
</tr>
<tr>
<td>0.308</td>
<td>297</td>
<td>0.422</td>
</tr>
<tr>
<td>0.317</td>
<td>297</td>
<td>0.389</td>
</tr>
<tr>
<td>0.341</td>
<td>297</td>
<td>0.481</td>
</tr>
<tr>
<td>0.323</td>
<td>297</td>
<td>0.437</td>
</tr>
<tr>
<td>0.339</td>
<td>344</td>
<td>0.439</td>
</tr>
<tr>
<td>0.357</td>
<td>345</td>
<td>0.422</td>
</tr>
<tr>
<td>0.379</td>
<td>398</td>
<td>0.490</td>
</tr>
<tr>
<td>0.394</td>
<td>400</td>
<td>0.444</td>
</tr>
<tr>
<td>0.417</td>
<td>402</td>
<td></td>
</tr>
</tbody>
</table>

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\(_2\)F\(_2\) 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 \( \ln([\text{CH}_2\text{F}_2]_0/[\text{CH}_2\text{F}_2]_t) \) versus \( \ln([\text{CH}_4]_0/[\text{CH}_4]_t) \) 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 \( k_4 = 5.69 \times 10^{-19} T^{2.49} \exp(-609/T) \) cm\(^3\) molecule\(^{-1}\) 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 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\(_2\)Cl and CH\(_3\)Cl following UV irradiation of CH\(_2\)F\(_2\)/CH\(_4\)/Cl\(_2\) mixtures. The formation of CHF\(_2\)Cl and CH\(_3\)Cl was measured by GC-FID and used to infer the loss of CH\(_2\)F\(_2\) 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\(_2\)Cl. 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 \( k_1 = 1.19 \times 10^{-17} T^2 \exp(-1023/T) \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). As seen from Fig. 2, this expression fits the data to within ±15% across the entire temperature range.
Table III Rate Constant Ratios Measured at Copenhagen, Scaled to $k(\text{Cl} + \text{CH}_4)$

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Reference</th>
<th>$k_{\text{Reactant}}/k_{\text{CH}_4}$</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>CH$_2$F$_2$</td>
<td>0.0796 ± 0.0021</td>
<td>253</td>
</tr>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>CH$_2$F$_2$</td>
<td>0.0825 ± 0.0026</td>
<td>273</td>
</tr>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>CH$_2$F$_2$</td>
<td>0.0982 ± 0.0074</td>
<td>298</td>
</tr>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>CH$_2$F$_2$</td>
<td>0.0981 ± 0.0048</td>
<td>313</td>
</tr>
<tr>
<td>CF$_2$CFH$_2$</td>
<td>CH$_2$F$_2$</td>
<td>0.00838 ± 0.00032</td>
<td>253</td>
</tr>
<tr>
<td>CF$_2$CFH$_2$</td>
<td>CH$_2$F$_2$</td>
<td>0.0125 ± 0.0007</td>
<td>273</td>
</tr>
<tr>
<td>CF$_3$CFH$_2$</td>
<td>CH$_2$F$_2$</td>
<td>0.0126 ± 0.0012</td>
<td>298</td>
</tr>
<tr>
<td>CF$_3$CFH$_2$</td>
<td>CH$_2$F$_2$</td>
<td>0.0154 ± 0.0017</td>
<td>313</td>
</tr>
</tbody>
</table>

$k(\text{Cl} + \text{CH}_2\text{CCl}_3)$

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 $k_4 = 5.69 \times 10^{-10} T^{-2.49} \exp(-609/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [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. [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 $k(\text{Cl} + \text{CH}_2\text{CCl}_3) = 2.41 \times 10^{-12} \exp(-1630/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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

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 $k_4 = 5.69 \times 10^{-10} T^{-2.49} \exp(-609/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [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 $k_3/k(CF_3CFCH)$ using the temperature dependent expression for $k(CF_3CFCH)$ 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 3 Arrhenius plot for $k(\text{Cl} + \text{CH}_2\text{CCl}_3)$. The solid line is a fit to the data from the present work: $k_2 = 2.41 \times 10^{-12} \exp(-1630/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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 $k_3 = 1.27 \times 10^{-12} \exp(-2019/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The solid line is a fit to the combined data set from all studies, which gives $k_3 = 2.13 \times 10^{-12} \exp(-2165/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

**DISCUSSION**

We report a substantial and self-consistent set of kinetic data for the reactions of chlorine atoms with CH$_2$F$_2$, CH$_3$CCl$_3$, and CF$_3$CFH$_2$. The kinetic data for the reaction of chlorine atoms with CH$_2$F$_2$ 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$_3$CFH$_2$ 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 $k_3 = 2.13 \times 10^{-12} \exp(-2165/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

As shown in Fig. 3, there is substantial scatter in the kinetic data for the reaction of chlorine atoms with CH$_3$CCl$_3$. 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$_3$CFH$_2$ 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$_3$CCl$_3$ was measured indirectly by observing the formation of the chlorinated product CH$_2$ClCCl$_3$. A correction factor of 2.35 was applied to account for the reduced sensitivity of the flame ionization detector toward CH$_2$ClCCl$_3$. In the same study, Tschuikow-Roux et al. [6] report $k(\text{Cl} + \text{C}_2\text{H}_4)/k(\text{Cl} + \text{CH}_4) = 7.33 \exp(1298/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ [20] gives a value of $k(\text{Cl} + \text{C}_2\text{H}_4) = 3.98 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K, which is significantly different from the well-established value of $k(\text{Cl} + \text{C}_2\text{H}_4) = 5.9 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ 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$_3$CCl$_3$ inferred from CH$_2$ClCCl$_3$ formation measured by GC) and reported similar results (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.

**BIBLIOGRAPHY**