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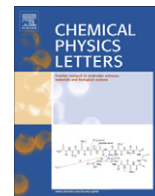
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Kinetics of the reaction of Cl atoms with CHCl₃ over the temperature range 253–313 K

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ABSTRACT

The reaction $CHCl_3 + Cl \rightarrow CCl_3 + HCl$ was studied in the atmospherically relevant temperature range from 253 to 313 K and in 930 mbar of N_2 diluent using the relative rate method. A temperature dependent reaction rate constant, valid in the temperature range 220–330 K, was determined by a fit to the result of the present study and that of Orlando (1999); $k = (3.77 \pm 0.32) \times 10^{-12} \exp((-1011 \pm 24)/T)$ cm^3 molecule^{-1} s^{-1}.

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1. Introduction

Chloroform is present in the atmosphere with an average global atmospheric concentration of about 18.5 pptv, with seasonal, altitudinal, and latitudinal variability [1]. Due to its reaction with hydroxyl radicals chloroform has a relatively short lifetime in the atmosphere, and thus high variability in concentration. Global atmospheric chloroform budgets have been presented by several groups [1–3]. The inventories of McCulloch and of Khalil and Rasmussen estimate the total emission of chloroform to be 660 ± 220 Gg yr^{-1} and 350–600 Gg yr^{-1}, respectively.

Sources of chloroform to the atmosphere are both natural and anthropogenic. The pulp and paper industry, and drinking and wastewater treatment are significant anthropogenic sources, while a smaller contribution comes from the pharmaceutical industry [1,2,4–6]. The dominant natural source is an as yet unidentified, probably biological, process in the oceans, while soil processes constitute the second most important contribution [2]. The uncertainties in the natural sources are large.

While chloroform is not classified as a greenhouse gas or considered to be a threat to the ozone layer, its reactivity is important to our understanding of the behavior of the halogenated methane derivatives. Reaction with Cl atoms is an often used method in investigations of the oxidation of atmospherically relevant halogenated hydrocarbons in smog chambers. For the analysis of such experiments well determined rate coefficients are needed. A number of absolute and relative rate studies have been reported for the $CHCl_3 + Cl$ reaction at room temperature [7–11], unfortunately the results from different studies show significant scatter. The value for the rate coefficient at 298 K currently recommended by JPL is 1.2×10^{-13} cm^3 molecule^{-1} s^{-1}. The latest JPL data evaluation [12] recommend a temperature dependent rate coefficient following the Arrhenius expression: $k = 3.31 \times 10^{-12} \exp(-990/T)$ cm^3 molecule^{-1} s^{-1}. A slightly different temperature dependence is currently recommended by IUPAC [13]: $k(220–500 \text{ K}) = 2.4 \times 10^{-12} \exp(-920/T)$ cm^3 molecule^{-1} s^{-1}. The recommendations build on the studies by Orlando in the range 222–298 K [14] and Bryukov et al. in the range 297–854 K [15]. Sparse data and discrepancies in the literature call for a new determination of the temperature dependent rate coefficients of the title reaction. Recently Gola et al. published a study where they used the relative rate method to investigate the temperature dependence of the reaction in the range 297–527 K [16]. In the present study we have studied the reaction in the atmospherically relevant range of 253–313 K.

2. Experimental method

In relative rate studies the rate of a reaction is determined relative to the rate of a well known reference reaction. The method relies on the assumption that no reactions other than the investigated one consume the reactants to a significant degree. If this is true the following expression is valid

$$\ln \frac{[A]_0}{[A]_t} = \frac{k_A}{k_B} \ln \frac{[B]_0}{[B]_t} \tag{1}$$

where, $[A]_0$, $[A]_t$, $[B]_0$ and $[B]_t$, are the concentrations of the compounds at times 0 and t. In a plot of $\ln([A]_0/[A]_t)$ versus $\ln([B]_0/[B]_t)$ the slope will equal the relative rate of the reaction.

The rate of the title reaction, Eq. (R1), was determined relative to reactions Eqs. (R2) and (R3).

$$CHCl_3 + Cl \rightarrow CCl_3 + HCl \tag{R1}$$
$$CH_2F_2 + Cl \rightarrow CHF_2 + HCl \tag{R2}$$
$$CH_4 + Cl \rightarrow CH_3 + HCl \tag{R3}$$

Cl atoms were produced by the photolysis of Cl_2 using broadband UV-A lamps from OSRAM, $\lambda_{max} \sim 350$ nm, leading to the production of ground state chlorine atoms

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$$Cl_2 + h\nu \rightarrow 2Cl \qquad\qquad (R4)$$

Partial pressures of chloroform and the reference compounds were in the range of 10–90 μbar, and partial pressures of Cl_2 were 10–20 times higher than the total pressure of chloroform and reference compound in each experiment. Details on the experiments are presented in Table 1. In Ref. [17] the photolysis capacity of the experimental system is calculated to be 0.005 s^{-1} per lamp at room temperature. Up to eight lamps were used in the present study which result in Cl concentrations in the range 1×10^{13} to 5×10^{14} cm^{-3} at 298 K. At colder temperatures the lamps are less efficient, at 268 K it is estimated to be about 1/3 of the capacity at 298 K.

To check for possible photolytic removal of chloroform and methane, experiments were performed where no Cl_2 was present in the chamber. A reaction mixture of $CHCl_3$ and CH_4 in nitrogen bath gas was irradiated for several minutes and no decrease in the reactants was detected. Experiments where also performed where the reaction mixture was left in the dark, to check for possible reactions with Cl_2. Small amounts of HCl were seen, but no change in concentration of the reactants, $CHCl_3$, CH_2F_2 or CH_4. HCl was probably the result of reaction of Cl_2 with some impurities in the system, possibly on the walls.

The relative rate experiments were carried out in a photochemical reactor at the University of Copenhagen. The reaction chamber is a quartz tube with stainless steel end flanges; it is 2 m long and has a volume of 101.4 l. The chamber is confined in a temperature controlled housing enabling experiments in the temperature range 240–330 K. The experimental setup is described in detail by Nilsson et al. [17]. The spectra were recorded using a Bruker IFS 66v/S infrared spectrometer with a liquid nitrogen cooled MCT detector. For the experiments with Eq. (R3) as reference reaction a resolution of 0.125 cm^{-1} was used to capture the fine structure of the methane spectra, while for experiments with Eq. (R2) as the reference reaction a resolution of 0.5 cm^{-1} was sufficient. Reactant and reference compounds were monitored using absorption over the following wavenumber ranges (cm^{-1}): $CHCl_3$, 2390–2500; CH_4, 3000–3200; CH_2F_2, 1380–1480. For each spectrum 32 scans were co-added to give an acceptable signal to noise ratio, and the interferograms were Fourier transformed using boxcar apodization. During each experiment the reaction mixture was photolyzed 4–15 times, using up to eight lamps. Each photolysis step was followed by a stabilization time, typically 2 min, before the FTIR spectrum was recorded. The experiments were terminated when around 30–70% of the reactant species were consumed. Experiments were performed at temperatures of 303, 283, 298 and 268 K with Eq. (R2) as the reference, and at 313, 273 and 253 K with Eq. (R3) as reference. Nitrogen was used as the bath gas and experiments were done at a total pressure of 930 mbar. Chemicals were purified by three freeze–pump–thaw cycles. FTIR spectra were analyzed using a non-linear least squares fitting procedure developed by Griffith [18]. The errors in the spectral fit were used to determine the error in the relative rate according to the method of York [19]. Reference spectra of CH_4 and HCl were taken from the HITRAN database [20], while for $CHCl_3$ and CH_2F_2 reference spectra were recorded using the same conditions as employed in the kinetics experiments.

3. Results and discussion

Fig. 1 shows a relative rate plot of chloroform versus CH_2F_2; data from two experiments at 313 K are included. This type of plot is constructed for all experiments to yield the relative reaction rates at the different temperatures. Table 2 lists the relative reaction rates obtained at each temperature, as well as the absolute rates calculated using the known reaction rates of the reference compounds. The result at each temperature is based on two experiments. The errors given for the rate constants in last column of Table 2 include uncertainties due to uncertainties in the rate constants of the reference reactions. The uncertainty in reference reactions is the largest source of error. Rate coefficients used for the reference reactions are $k(CH_2F_2 + Cl) = 1.19 \times 10^{-17}$ T^2 exp $(-1023/T)$ cm^3 molecule^{-1} s^{-1} [21] and $k(CH_4 + Cl) = 5.69 \times 10^{-19}$ T$^{2.49}$ exp $(-609/T)$ cm^3 molecule^{-1} s^{-1} [15].

In Fig. 2 the results are plotted together with the results of previous studies in the temperature range 220–330 K. The result of the present work is in agreement with the temperature dependence study by Orlando [14], when Orlando's results have been put on an absolute scale using the same rate constant for the reference reaction $CH_4 + Cl$, as used in the present work [15]. In addition to $CH_4 + Cl$, it is interesting to note that Orlando also used $CH_3Br + Cl$ as a reference reaction and when the data or Orlando were recalculated the agreement between the result obtained using the two reference reactions improved. In this case the JPL value was taken for the $CH_3Br + Cl$ rate [12]. Gola et al. used $CH_3Br + Cl$ as the reference reaction, but their relative rate data are not in agreement with Orlando at 298 K, the only temperature where the two studies overlap [14,16].

The room temperature relative rate studies, by Beichert et al. [7], Brahan et al. [8] and Catoire et al. [9], all used Eq. (R3) as the reference reaction, and the rate coefficients shown in Fig. 2 are recalculated using the rate of the Eq. (R3) determined by Bryukov et al. [15]. The rate constant determined using absolute methods at

Table 1
Experimental details; reactant concentrations and photolysis time. The photolysis time is normalized to one lamp.

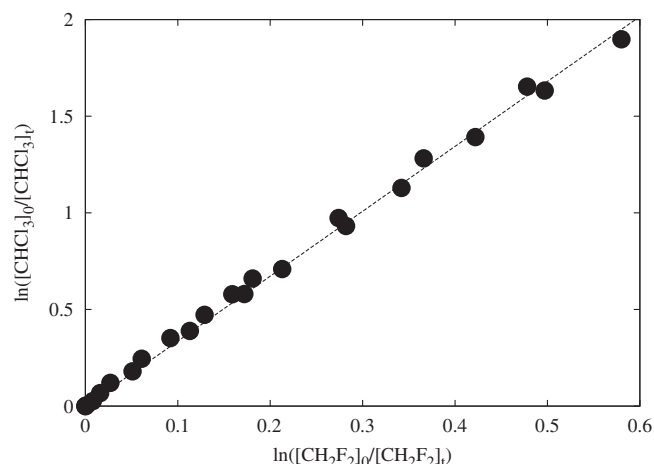| T (K)	[CHCl$_3$] (μbar)	[Ref.] (μbar)	Ref. compound	$t_{photolysis}$ (s)
253	22	13	CH$_4$	870
253	21	13	CH$_4$	900
268	30	50	CH$_2$F$_2$	500
268	40	10	CH$_2$F$_2$	360
273	14	60	CH$_4$	390
273	15	80	CH$_4$	480
283	10	40	CH$_2$F$_2$	170
283	30	90	CH$_2$F$_2$	240
298	50	50	CH$_2$F$_2$	540
298	10	50	CH$_2$F$_2$	180
308	20	13	CH$_2$F$_2$	180
308	21	17	CH$_2$F$_2$	240
313	20	40	CH$_4$	120
313	60	55	CH$_4$	180

Fig. 1. Loss of CHCl$_3$ versus loss of the reference compound CH$_2$F$_2$ following reaction with Cl atoms, at 313 K. Error bars of spectral fits are within symbols.

Table 2

Rate constant ratios for the title reaction relative to the two reference compounds, and the value of the rate coefficients based on an average of two determinations. Errors for the relative rates are based on the error on the slope of the relative rate plot, while in the error bar in the rate constants in last column also includes uncertainties due to uncertainties in the reference reaction rate constants.

T (K)	$k_{CHCl_3+Cl}/$ k_{REF+Cl}	Ref. compound	k_{CHCl_3+Cl} (10^{-13} cm^3 molecules^{-1} s^{-1})
253	1.39 ± 0.01	CH$_4$	0.688 ± 0.079
268	4.64 ± 0.07	CH$_2$F$_2$	0.873 ± 0.131
273	1.23 ± 0.10	CH$_4$	0.877 ± 0.133
283	4.33 ± 0.06	CH$_2$F$_2$	1.11 ± 0.17
298	3.65 ± 0.04	CH$_2$F$_2$	1.25 ± 0.19
308	1.14 ± 0.10	CH$_4$	1.41 ± 0.21
313	3.36 ± 0.02	CH$_2$F$_2$	1.49 ± 0.22

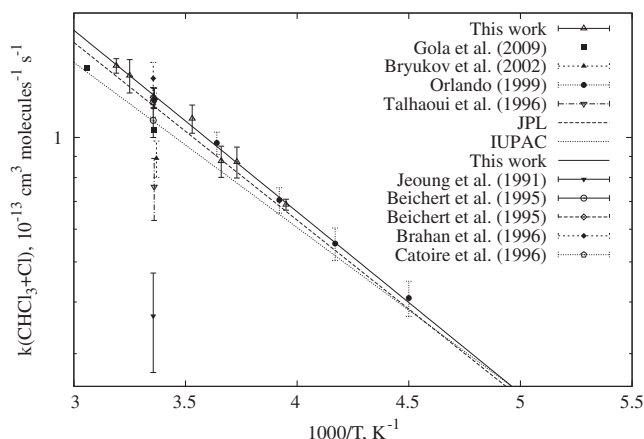**Fig. 2.** Arrhenius plot for k(CHCl$_3$ + Cl) in the range 220–330 K. Results from the present and previous studies plotted with error bars, excluding errors due to uncertainties in reference reactions. The JPL [12] and IUPAC [13] recommendations mentioned in the introduction are plotted as lines. Fulldrawn line is a fit to the data of the present study and the results by Orlando [14] and is expressed by $k = (3.77 ± 0.32) \times 10^{-12}$ exp $(-(1011 ± 23)/T)$ cm^3 molecule^{-1} s^{-1}. The results of the relative rate study by Orlando [14] have been recalculated using the same rate constant expression for the reference reaction, CH$_4$ + Cl, as used in the present study.

298 K have lower values and show a large spread. The current recommendations by JPL [12] and IUPAC [13] are plotted as dashed and dotted lines in Fig. 2. Since both the data set of the present study, and that of Orlando [14] are slightly higher than the recommendations a fit to the two data sets was done. The fit resulted in a temperature dependent rate constant of $k = (3.77 ± 0.32) \times 10^{-12}$ exp $(-(1011 ± 23)/T)$ cm^3 molecule^{-1} s^{-1}, where uncertainties are due to the fit. The expression is represented by the full drawn line in Fig. 2.

Fig. 3 shows the result of the present study plotted together with literature data over a wider temperature range. Again the full drawn line represents a fit to the experimental data from the present study and that of Orlando [14]. The most extensive data set is that of Bryukov et al. [15], reaching from 297 to 854 K, represented by filled triangles and a dashed line.

For temperatures where there is overlap between the present study and that by Gola et al. [16] our results are about 20 % higher. Gola et al. have not provided error bars for the rate constants, and one source of error in their work is the rate constant for their reference reaction CH$_3$Br + Cl. There has only been one study of the reference reaction over the full temperature interval, which makes the reference reaction not better determined than the studied reaction. A strength of the present work is that one of our reference reactions is CH$_4$ + Cl, which is one of the most extensively studied
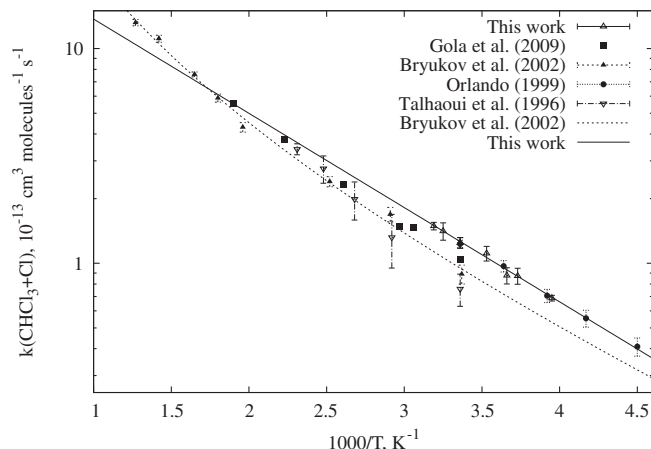

Fig. 3. Arrhenius plot for k(CHCl$_3$ + Cl) in the temperature range 200–1000 K. The results of five different temperature studies, including the present one, are plotted in the figure. The full drawn line is the temperature dependent rate coefficient determined from a fit to the present data set and that of Orlando [14] in the range 220–330 K. The dash-dotted line is the three parameter fit by Bryukov et al. [15], valid at higher temperatures.

hydrocarbon reactions with chlorine. In addition the CH$_2$F$_2$ + Cl reaction has recently been reexamined using FTIR and GCMS analysis in separate reactor systems and the results are in excellent agreement with each other and with an earlier measurement at room temperature [21].

While the temperature dependent rate expression presented in this work is valid in the temperature range 220–330 K, the expression by Bryukov et al. [15] should be used at higher temperatures.

Acknowledgements

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