Temperature Dependence of Rate Coefficients for the Reactions of Chlorine Atoms with Halomethanes of Type CHCl3-xFx (x) 0, 1, and 2)

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Temperature Dependence of Rate Coefficients for the Reactions of Chlorine Atoms with Halomethanes of Type CHCl$_{3-x}$F$_x$ ($x = 0$, 1, and 2)

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The rate coefficients for the hydrogen abstraction reactions from CHCl$_3$ (k_1), CHCl$_2$F (k_2), and CHClF$_2$ (k_3) by chlorine atoms in the gas phase have been measured over the temperature range 298−430 K using the discharge flow/mass spectrometry technique (DF/MS) under pseudo-first-order conditions with Cl atoms in large excess with respect to the halomethane. The temperature dependence of the rate coefficients is expressed in the Arrhenius form: $k_1 = (8.0^{+1.8}_{-1.7}) \times 10^{-12}$ exp[$-(1390 \pm 80)/T$], $k_2 = (5.2^{+0.9}_{-0.8}) \times 10^{-12}$ exp[$-(1675 \pm 60)/T$], $k_3 = (5.3^{+1.5}_{-1.3}) \times 10^{-12}$ exp[$-(2430 \pm 90)/T$]. The units of the rate constants are cm^3 molecule^{-1} s^{-1} and the quoted uncertainties are 2σ. Wall loss and recombination of atomic chlorine (Cl + Cl + M) rate coefficients, k_w and k_r respectively, were measured and utilized in calculation of the rate coefficients. Inclusion of the Cl atom losses is shown to be important for the slower reactions requiring longer reaction times. Arrhenius expressions are in good agreement with available literature data and in very good agreement with recently reported theoretical (ab initio) calculations.
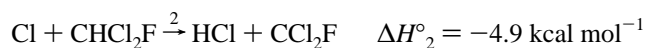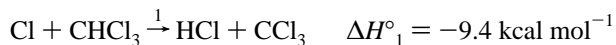
Introduction

Over the past several years, a number of recent kinetic studies have been reported on hydrogen abstraction reactions from halogen substituted hydrocarbons by chlorine atoms in the gas phase. These investigations have been stimulated by several motivations: (i) the important role of these reactions in the processes of industrial chlorination or in the incineration of hazardous halogenated wastes;[1] (ii) the use of the above reactions as sources of haloalkyl radicals and other subsequent radical species for laboratory kinetic studies involving the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) proposed for replacing the chlorofluorocarbons (CFCs) phased out by the end of 1995; (iii) the assessment of the contribution of the removal processes of HCFCs and HFCs by Cl attack to the mean tropospheric lifetimes of these species.

As the mean Cl concentration in the troposphere was predicted[2] to be in the order of 10^3 atoms cm^{-3}, i.e, about 10^3 times smaller than OH concentration, which is estimated[3] to be in the order of 10^6 radicals cm^{-3}, the removal of HCFCs and HFCs by Cl atoms in the troposphere and lower stratosphere was considered negligible compared to removal processes by OH radicals. However, new heterogeneous reactions in the polluted marine surface air have been postulated[4−7] as potential sources of photolytic precursors of Cl atoms (i.e., Cl$_2$, HOCl, NOCl, ClNO$_2$, ...). The concentration of atomic chlorine in the marine boundary layer has been recently evaluated by a photochemical model[8] as between 10^4 and 10^5 atoms cm^{-3}, much higher than the 10^3 atoms cm^{-3} previously predicted[2] by assuming the reaction OH + HCl as the only source of Cl atoms. Despite this concentration of Cl, it is assumed[9] that the volume of this boundary layer remains largely negligible compared to the volume of the troposphere. Consequently, Cl reactions with HCFCs and HFCs cannot compete with OH reactions in lowering the lifetimes of these species in the troposphere.

A number of recent rate coefficient measurements on the reactions of Cl atoms with HCFCs and HFCs have been performed at room temperature using various methods.[10−13]

These researchers have shown that, for most of HCFCs and HFCs, the rate coefficients of reactions with Cl measured at room temperature were in the same order of magnitude as the rate coefficients measured with OH (ranged from 10^{-13} to 10^{-16} cm^3 molecule^{-1} s^{-1} at 298 K).[14,15]

Limited experimental data has been published on the temperature dependence of the rate coefficients for Cl reactions with HCFCs and HFCs. In this paper, we report the first measurements of absolute rate coefficients as a function of temperature for the reactions of CHCl$_2$F (HCFC-21) and CHClF$_2$ (HCFC-22) with chlorine atoms. In order to gain insight into the reactivity trends in the series of halomethanes of type CHCl$_{3-x}$F$_x$, we have also investigated the reaction Cl + CHCl$_3$ for which several sets of Arrhenius parameters have been reported. The kinetic data reported in the present work for the reactions

$$\text{Cl} + \text{CHCl}_3 \xrightarrow{1} \text{HCl} + \text{CCl}_3 \quad \Delta H°_1 = -9.4 \text{ kcal mol}^{-1}$$

$$\text{Cl} + \text{CHCl}_2\text{F} \xrightarrow{2} \text{HCl} + \text{CCl}_2\text{F} \quad \Delta H°_2 = -4.9 \text{ kcal mol}^{-1}$$

$$\text{Cl} + \text{CHClF}_2 \xrightarrow{3} \text{HCl} + \text{CClF}_2 \quad \Delta H°_3 = -2.4 \text{ kcal mol}^{-1}$$

have been used to validate the predictions (Arrhenius parameters, reactivity trends) performed by ab initio calculations[16] on these reactions. The above reaction enthalpies have been calculated at 298 K using the experimental formation enthalpies[15] for different species of interest.

Experimental Section

Method. The experiments were performed using the conventional discharge flow/mass spectrometry technique (DF/MS). Details concerning the modulated molecular beam sampling technique and the mass spectrometer have been previously reported.[17]

The reaction vessel is a 2.4 cm i.d Pyrex tube inserted into a circulating fluid cooling/heating jacket housing a 40 cm long reaction zone where temperature is constant at ±1 K. The temperature along the reaction zone was monitored with an

alumel−chromel thermocouple inserted through a coaxial injector. Heating of the flow tube was achieved by a circulation of externally heated silicone oil.

The target halomethane, highly diluted in helium, was introduced in the flow tube through the 0.6 cm o.d movable Pyrex injector tube terminated by a multihole tip (radially directed flow).

Chlorine atoms were generated by a microwave discharge in a mixture of Cl_2/He through a fixed side arm located in the upstream part of the flow tube. In order to minimize the loss of Cl atoms on Pyrex surfaces, all internal surfaces of the flow tube were coated with pure orthophosphoric acid. Initial concentrations of chlorine atoms were determinated by mass spectrometric measurement on the extent of Cl_2 to Cl conversion and occasionally by titration with C_2H_3Br as proposed by Park et al.,[18] both methods leading to results in good agreement.

Flow rates of different gases were regulated by calibrated mass flow controllers. Average flow velocities were over the range $3-18$ m s^{-1}. The pressure in the flow tube (range $1-5$ Torr) was measured upstream and downstream by a capacitance manometer.

Monitoring of the Reactions. All experiments were carried out under pseudo-first-order conditions with chlorine atoms in large excess with respect to the initial concentration of the studied halomethane. Kinetic measurements were performed by monitoring the temporal decay of the intensity $I(CHCl_{2-x}F_x^+)$ of the base peak corresponding to each halomethane. $CHCl_3$ was detected at the mass/charge ratio $m/e = 83$ corresponding to the fragment ion $CH^{35}Cl_2^+$, $CHCl_2F$ at $m/e = 67$ ($CH^{35}ClF^+$) and $CHClF_2$ at $m/e = 51$ (CHF_2^+). These fragment ions (detected at 40 eV) are specific to the respective halomethane.

Compared to the alternative pseudo-first-order conditions where the halomethane is in large excess with respect to chlorine atoms, the present approach offers a more advantageous operation of the mass spectrometer/kinetic apparatus, both in specificity and sensitivity. Use of chlorine atoms as minor reactant requires measuring the temporal decay of the signal of $^{35}Cl^+$, the intensity of which can be contaminated by contributions from the fragmentation of all chlorinated species present in the reaction medium. Inteferences result from $CHCl_{3-x}F_x$ in large excess, undissociated Cl_2, HCl, $CCl_{3-x}F_x$ radicals as reaction products, plus other secondary species. These additional contributions to the peak $m/e = 35$ assigned to the chlorine atom can be avoided to some extent; but it is necessary to operate at low electron energy (<20 eV) leading to a significant lowering of the sensitivity of the mass spectrometer.

Purities. The purities of HCFCs supplied by ELF-Atochem were $>99.9\%$ for HCFC-21 and $>99.5\%$ for HCFC-22. $CHCl_3$ ($>99.8\%$) was obtained from Aldrich. These three halomethanes were used without further purification. The source of Cl_2 was a commercial mixture (Alphagaz) constituted of 2% of Cl_2 ($>99.99\%$) in helium ($>99.9995\%$). As an additional diluent, helium (Air Liquide, purity $>99.995\%$) was purified by circulating through a liquid nitrogen trap.

Treatment of Kinetic Data

For the bimolecular reaction

$$Cl + CHCl_{3-x}F_x \rightarrow HCl + CCl_{3-x}F_x$$
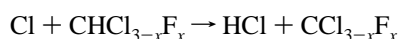
the consumption rate equation of the halomethane is defined as

$$-d[CHCl_{3-x}F_x]/dt = k[CHCl_{3-x}F_x][Cl] \qquad (1)$$

with k the bimolecular rate constant.

Under the pseudo-first-order conditions where $[CHCl_{3-x}F_x]_0 \ll [Cl]_0$, the consumption of chlorine atoms due to the reaction with the halomethane can be neglected and, in a first step, the temporal Cl concentration can be assumed constant and equal to $[Cl]_0$ along the flow tube. $[CHCl_{3-x}F_x]_0$ and $[Cl]_0$ are respectively the initial concentrations of $CHCl_{3-x}F_x$ and Cl. The rate equation (1) is usually simplified as follows

$$-d[CHCl_{3-x}F_x]/dt = k[CHCl_{3-x}F_x][Cl]_0 \approx$$
$$k_{obs}[CHCl_{3-x}F_x] \qquad (2)$$

with $k_{obs} = k[Cl]_0$, the pseudo-first-order rate constant.

The integration of eq 2 gives

$$\ln[CHCl_{3-x}F_x] = -k_{obs}t + \text{constant} \qquad (3)$$

If plots of $\ln[I(CHCl_{2-x}F_x^+)]$ versus reaction time for different initial concentrations of chlorine atoms, at constant temperature, are well fitted to straight lines, the concentration of chlorine atoms can be considered fairly constant along the reaction distance. The conventional treatment of kinetic data obtained under pseudo-first-order conditions can be then applied. The slopes obtained using the least-squares treatment from the plots $\ln[I(CHCl_{2-x}F_x^+)]$ versus reaction time yield values of the pseudo-first-order rate constant k_{obs} for the respective values of $[Cl]_0$. Errors in measured k_{obs} due to the radial and/or axial diffusion of the minor reactant (herein $CHCl_{3-x}F_x$ chosen for monitoring the reaction) can be corrected if necessary by using the treatment proposed by Taylor[19] and Kaufman.[20] These results are then evaluated by plotting corrected k_{obs} versus $[Cl]_0$ and fitting the results to a line the slope of which is taken as k.

Inspection of the plots $\ln[I(CHCl_{2-x}F_x^+)]$ versus reaction time can reveal some deviations of experimental values, with respect to the mean straight line, for long reaction times and/or for high initial concentrations of chlorine. This behavior suggests the occurrence of secondary reactions modifying the concentration of chlorine atoms along the reaction distance. As the consumption of chlorine atoms due to the primary reaction can be neglected under pseudo-first-order conditions, the variation of Cl concentration is generally attributed to homogeneous and heterogeneous recombinations of chlorine atoms in large excess:

$$Cl + Cl + He \xrightarrow{k_r} Cl_2 + He \qquad (a)$$

$$Cl \xrightarrow{k_w} 1/2\ Cl_2 \qquad (b)$$
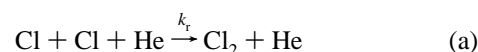
where k_r is the three-body gas phase recombination rate constant and k_w the wall decay rate constant.

If these recombination reactions are the only processes responsible for the decrease of chlorine atoms along the reaction zone, the equation of the $[Cl]_0$ decay rate is given by

$$-d[Cl]_{0,t}/dt = 2k_r[Cl]_{0,t}^2[He] + k_w[Cl]_{0,t} \qquad (4)$$

Integrating, we have

$$[Cl]_{0,t} = \frac{k_w[Cl]_{o,o}\exp(k_w t)}{2k_r[He][Cl]_{o,o}[1 - \exp(k_w t)] + k_w} \qquad (5)$$

The absolute concentration of chlorine atoms observed downstream at the outlet of the flow tube, defined by $[Cl]_{o,o}$, can be evaluated by measuring the intensity of the signal

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assigned to $^{35}Cl_2^+$ ($m/e = 70$) with and without microwave discharge:

$$[Cl]_{o,o} = 2([Cl_2]_{0,i} - [Cl_2]_{o,o}) \tag{6}$$

$[Cl_2]_{0,i}$ represents the initial concentration of Cl_2 (discharge switched off) and $[Cl_2]_{o,o}$ the concentration of Cl_2 measured at the outlet of the flow tube with the discharge switched on.

By replacing $[Cl]_0$ by $[Cl]_{0,t}$ in eq 2 and integrating, we obtain the following relationship

$$\ln[CHCl_{3-x}F_x] = P \ln Q(t) + R \tag{7}$$

with

$$P = k/2k_r[He]$$

$$Q(t) = 2k_r[He][Cl]_{o,o}(1 - \exp(k_w t)) + k_w$$

$$R = \text{integration constant}$$

Plots of $\ln[CHCl_{3-x}F_x]$ vs $\dfrac{\ln Q(t)}{2k_r[He]}$ are straight lines and the slopes yield corrected values of the bimolecular rate constant k, then denoted as k_c.

This treatment of kinetic data takes into account the temporal variation of the Cl concentration along the reaction zone due to their homogeneous and heterogeneous recombinations. However, it requires the knowledge of the rate constants k_r and k_w governing these processes. For this reason, we have performed a preliminary determination of k_r and k_w under our experimental conditions.

Results and Discussion

Rate Coefficients of Heterogeneous Recombination of Cl Atoms (k_w). In order to determine the heterogeneous rate constant k_w of chlorine atoms on surfaces coated with ortho-phosphoric acid, we have changed the experimental protocol by introducing the Cl atoms through the central injector and using concentrations (10^{13} atoms cm^{-3}) low enough to make their recombination negligible in the gas phase. k_w is obtained from the plots $\ln[Cl] = -k_w t + C^{st}$. Cl atoms were detected at 20 eV and the contribution to the signal measured at $m/e = 35$ from Cl_2 substracted. Table 1 gives the mean values of k_w measured at 298, 317, and 351 K and the corresponding values of recombination efficiency γ assuming the plug flow approximation.

The values of k_w and γ measured for chlorine atoms on surfaces coated with orthophosphoric acid are relatively low as shown in Table 1. Our values are in good agreement with values previously reported by Clyne and Stedman[21] for chlorine on the same coating.

TABLE 1: Mean Values of the Heterogeneous Rate Coefficient k_w of Cl Atoms and the Corresponding Recombination Efficiency γ Measured on Surfaces Coated with Pure Orthophosphoric Acid

T (K)	expts	k_w (s^{-1})	$\gamma \times 10^5$
298	8	0.7 ± 0.4	4 ± 2
317	6	0.5 ± 0.5	3 ± 3
351	6	$0.1 - 0.5$	$0.5 - 3$

Rate Coefficients of Homogeneous Recombination of Cl Atoms (k_r). The same experimental procedure has been used for measuring the rate coefficients of homogeneous recombination of Cl atoms, but with the level of Cl in the range of 10^{15}

atoms cm^{-3}. Experiments were carried out only at 298 K over the pressure range 3−6 Torr with the flow velocities from 100 to 340 cm s^{-1}. Our purpose was not to achieve a systematic study of the pressure dependence of the rate coefficient for the reaction $Cl + Cl + He \rightarrow Cl_2 + He$ but only to determine a mean value of this rate coefficient over the limited pressure range used in this work.[22] It is well-known that atom recombination is in the low pressure limit under the used pressure conditions.

Equation 5 expresses the temporal profile of [Cl] along the reaction zone when both homogeneous and heterogeneous recombinations of Cl atoms are taken into account. In this equation $[Cl]_{i,0}$ is substituted for $[Cl]_{o,o}$ to represent the concentration of chlorine atoms exiting from the injector tip, the location of which defines the initial time for recombination reactions. Equation 5 can also be written as

$$\frac{1}{[Cl]} = K \exp(k_w t) - \frac{2k_r[He]}{k_w} \tag{8}$$

with

$$K = \frac{2k_r[He][Cl]_{i,0} + k_w}{k_w[Cl]_{i,0}} = \text{constant}$$

The plots $1/[Cl]$ vs $\exp(k_w t)$ correspond to straight lines. The Y_{axis} intercept, determined by least-squares linear regression, plus knowledge of k_w enable us to estimate k_r. Using our experimental value of $k_w = 0.7 \pm 0.4$ s^{-1} determined at 298 K and eight values of k_r measured at 298 K over the pressure range 3−6 Torr, we obtain a mean value for k_r equal to $(4.3 \pm 2.6) \times 10^{-33}$ cm^6 molecule^{-2} s^{-1}. Within the range of uncertainties, our determination is in good agreement with the values of 6.3×10^{-33} and 3.86×10^{-33} cm^6 molecule^{-2} s^{-1}, respectively measured by Widman and DeGraff[23] and Hippler and Troe.[24]

$Cl + CHCl_3 \rightarrow HCl + CCl_3$ (k_1). Plots of $\ln[I(CHCl_2^+)]$ as a function of time at 298 K for several concentrations of chlorine atoms are shown in Figure 1. The values of $[Cl]_0$ reported in the caption of this figure correspond to the concentration of chlorine atoms $[Cl]_{o,o}$ measured at the outlet of the flow tube using the mass spectrometric measurement of Cl_2 to Cl conversion. In the framework of the usual treatment used for pseudo-first-order conditions, Cl concentrations are assumed constant along the reaction zone; i.e., recombination reactions of Cl atoms are considered negligible. It is worth pointing out that the correlation coefficients (r^2) for these straight lines range between 0.9952 and 0.9994, suggesting that the conventional pseudo-first-order treatment is acceptable here. Least-squares analysis yields values of the pseudo-first-order rate constant, k_{obs}, and plot of k_{obs} vs $[Cl]_0$ gives the value of
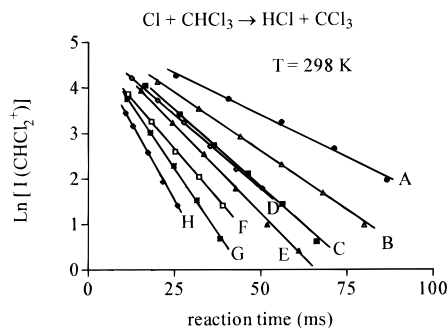

Figure 1. Plots of $\ln[I(CHCl_2^+)]$ vs reaction time at 298 K. $[Cl]_0$ (10^{14} atoms cm^{-3}): A = 5.16; B = 6.64; C = 8.34; D = 8.61; E = 9.83; F = 10.20; G = 13.20; H = 17.60.
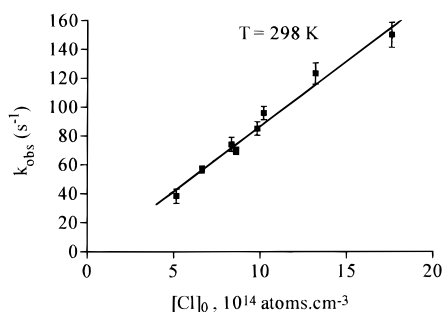
Figure 2. Pseudo-first-order rate constants k_{obs} plotted vs $[Cl]_0$ for the reaction Cl + CHCl$_3$ at 298 K (without correction of Cl loss).

the bimolecular rate constant k_1. Corrections due to the radial and axial diffusions of CHCl$_3$ have been applied to the values of k_{obs} reported in Figure 2. The following value is obtained for k_1

$$k_1(298 \text{ K}) = (9.1 \pm 1.1) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

within statistical errors of 2σ. Compared to the previous measurements (Table 2), this value is about 11% higher than the value measured by Knox[25] using a relative method but is 38% lower than the value obtained by Clyne and Walker[26] using a similar experimental method. The value of k_1 obtained by using the conventional treatment in this study is also 12% higher than the values recommended by Atkinson et al.[14] and DeMore et al.[15] which are based on the relative rate study of Knox[25] normalized to the values of the rate constant for the two reference reactions (Cl + CH$_4$ and Cl + CH$_3$Cl) recommended in their evaluation.

A careful inspection of Figure 1 shows some deviations from linearity for experimental points corresponding to long residence times, suggesting homogeneous and heterogeneous recombination reactions of Cl atoms might be responsible for a significant decay of these atoms along the reaction zone.
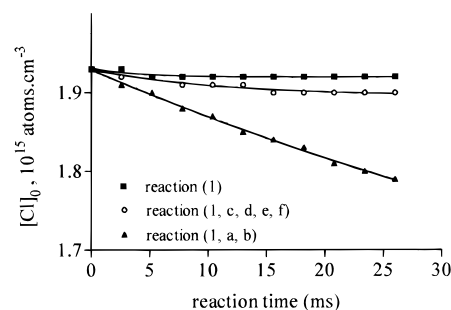

Figure 3. Changes in the temporal profiles of [Cl] at 298 K resulting from calculations using three different sets of reactions (see Table 3) $[Cl]_{o,o} = 17.60 \times 10^{14}$ atoms cm^{-3}. Note amplified scale.

In order to evaluate the impact of possible secondary reactions on the concentration profile of Cl atoms along the reactor, we have computed using a modeling program the [Cl] profiles due to the inclusion of reaction 1: reactions 1c−f; and reactions 1a,b (Table 3, Figure 3). This modeling shows that only homogeneous and heterogeneous recombination reactions (a) and (b) have a significant impact on the temporal evolution of Cl. Consumption of 5.6−10.6% of Cl atoms at 298 K is predicted at the end of the flow tube depending on the experimental conditions. This variation of Cl introduces a systematic error when the treatment of kinetic data without Cl loss is used. Accounting for the variation of Cl concentration, the plots obtained using the mean values of k_r and k_w are displayed in Figure 4 and the corrected rate coefficient $k_{1,c}$ is

$$k_{1,c}(298 \text{ K}) = (7.6 \pm 1.3) \, 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

As expected, inclusions of Cl recombination reactions leads to a corrected value, $k_{1,c}$, lower than the value of k_1 obtained using the conventional treatment of data. The corrected value $k_{1,c}$ at 298 K is in excellent agreement with the recommended values in recent reviews,[14,15] as shown in Table 2.

TABLE 2: Comparison of Our Kinetic Results with the Previous Literature Data

reaction	technique[a]	$k(298 \pm 2 \text{ K}) \times 10^{14}$ [b,c]	T range (K)	$A \times 10^{12}$ [b,c]	E/R^c (K)	ref
Cl + CHCl$_3$	RR	8.2	240−593	8.6	1385	Knox[25]
	DF/MS	14.7 ± 3.5	297−652	14.5	1379 ± 44	Clyne et al.[26]
	evaluation	7.6^d	240−330	4.9	1240 ± 400	IUPAC, 1992[14]
	evaluation	7.6^e		4.9	1240 ± 500	NASA, 1994[15]
	DF/MS	7.6 ± 1.3	298−435	8.0$^{+1.8}_{-1.7}$	1390 ± 80	this work
Cl + CHCl$_2$F	DF/MS	3.1 ± 0.5				Jourdain et al.[31]
	RR	2.1 ± 0.4				Tuazon et al.[11]
	evaluation	2.1^e				NASA, 1994[15]
	DF/MS	1.9 ± 0.3	298−433	5.2$^{+0.9}_{-0.8}$	1675 ± 60	this work
Cl + CHClF$_2$	DF/MS	0.14 ± 0.02				Jourdain et al.[31]
	RR	0.20 ± 0.04				Tuazon et al.[11]
	DF/MS	0.17 ± 0.02				Sawerysyn et al.[12]
	evaluation	0.19^e				NASA, 1994[15]
	DF/MS	0.14 ± 0.03	296−411	5.3$^{+1.5}_{-1.3}$	2430 ± 90	this work

^{a} RR = relative rate; DF/MS = discharge flow/mass spectrometry. ^{b} Units are cm^3 molecule^{-1} s^{-1}. ^{c} Uncertainties are 2σ. ^{d} The accuracy quoted as the term $\Delta \log k$ is ± 0.3 at 298 K. ^{e} The uncertainty factors of k at 298 K are estimated to be equal to 3.0, 2.0, and 1.4 for the reactions Cl + CHCl$_3$, Cl + CHCl$_2$F, and Cl + CHClF$_2$, respectively.

TABLE 3: Secondary Reaction Considered for Modeling the Temporal Profiles of Cl Atoms along the Reaction Distance for the System Cl + CHCl$_3$

reactions	k (298 K)	ref
(a) Cl + Cl + He → Cl$_2$ + He	4.3×10^{-33} cm^6 molecule^{-2} s^{-1}	this work
(b) Cl → 0.5 Cl$_2$	0.7 s^{-1}	this work
(c) Cl$_2$ + CCl$_3$ → Cl + CCl$_4$	1.8×10^{-16} cm^3 molecule^{-1} s^{-1}	ref 28
(d) CCl$_3$ + CCl$_3$ + M → C$_2$Cl$_6$ + M	6×10^{-12} cm^3 molecule^{-1} s^{-1} (760 Torr; M = SF$_6$)	ref 29
(e) CCl$_3$ + HCl → CHCl$_3$ + Cl	8×10^{-11} cm^3 molecule^{-1} s^{-1}	ref 30
(f) Cl + CCl$_3$ + M → CCl$_4$ + M	6×10^{-11} cm^3 molecule^{-1} s^{-1} (760 Torr; M = SF$_6$)^a	ref 29

^{a} Upper limit for k_f. Actual k will be lower due to substitution of He for SF$_6$. Reaction is shown to be unimportant. Thus further analysis of k is not undertaken.
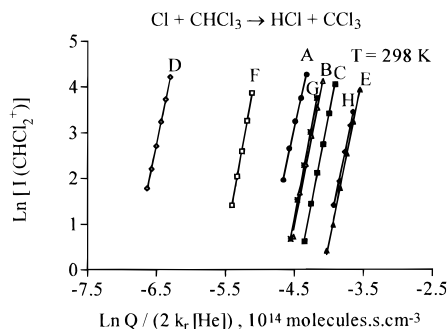
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Figure 4. Plots of $\ln[I(CHCl_2^+)]$ vs $(\ln Q)/2k_r[He]$, eq 5 to obtain $k_{1,c}$ incorporating heterogeneous loss, k_w, and homogeneous recombination, k_r, of Cl atoms. For the correction, the mean values of k_r and k_w (4.3×10^{-33} cm^{-6} molecule^{-2} s^{-1} and 0.7 s^{-1}, respectively) were used.
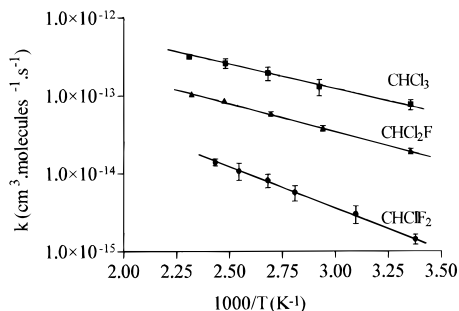

Figure 5. Arrhenius plots for the reactions of Cl atoms with CHCl$_3$ (squares), CHCl$_2$F (triangles), and CHClF$_2$ (dots). Rate coefficients for each reaction were determined at various temperatures as described in the caption of Figure 4.

The results obtained as a function of temperature are listed in Table 4. Rate constants for each temperature, results from the temporal variation of $[Cl]_{0,t}$, and mean values of k_r and k_w determined in this work have been used for the corrections. Least-squares treatment of $\ln k_{1,c}$ vs $1/T$ (Figure 5) yields the following Arrhenius expression:

$$k_{1,c}(298-435 \text{ K}) = (8.0^{+1.8}_{-1.7}) \times 10^{-12} \times$$
$$\exp[-(1390 \pm 80)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This expression is in very good agreement with the expressions proposed by Knox,[25] Atkinson et al.,[14] and DeMore et al.[15] (Table 2). The reported uncertainties in $k_{1,c}$ are 2σ. Our experimental value of the activation energy (2.8 kcal mol^{-1}) supports the value of 2.1 kcal mol^{-1} predicted by ab initio calculation by Rayez et al.[16]

Cl + CHCl$_2$F → HCl + CCl$_2$F (k_2). The plot of the pseudo-first-order rate constant k_{obs} as a function of $[Cl]_0$ (assumed constant) along the reaction zone is displayed in Figure 6. Under the operating conditions used, corrections of measured k_{obs} due the to radial and axial diffusions of CHCl$_2$F are negligible (<1%). Least-squares linear regression gives the following value for k_2 (uncorrected $[Cl]_0$) within statistical
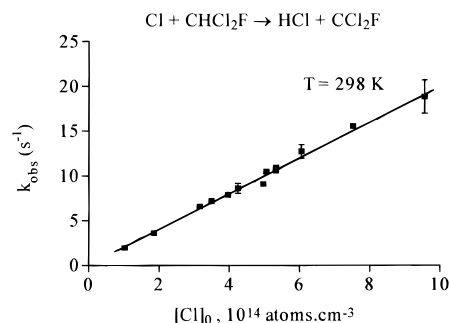

Figure 6. Pseudo-first-order rate constants k_{obs} plotted vs $[Cl]_0$ for the reaction Cl + CHCl$_2$F at 298 K (without correction of Cl loss).

uncertainties of 2σ:

$$k_2(298 \text{ K}) = (2.0 \pm 0.2) \, 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This value is lower than the value determined by Jourdain et al.[29] using a technique similar to ours (Table 2), but our value is in very good agreement with the one obtained by Tuazon et al.[11] using a relative rate method. In their review of 1994, DeMore et al.[15] prefer the recent value of the rate constant determined at 298 K for k_2 by Tuazon et al.[11] over the earlier value of Glavas and Heicklen.[27] As above, we estimate the systematic error due to the homogeneous and heterogeneous recombinations of Cl under our experimental conditions. Consumption of Cl at the end of the flow tube between 3.7 and 14.1% can be predicted at 298 K by modeling at the end of the flow tube. The kinetic data accounting for the Cl recombination reactions leads to a corrected value $k_{2,c}$ for k_2 very close to the uncorrected value:

$$k_{2,c}(298 \text{ K}) = (1.9 \pm 0.3) \times 10^{-14} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$$

Table 5 gives the results obtained for this reaction at various temperatures and relevant experimental conditions. By a least-squares treatment of the plot $\ln k_{2,c}$ vs $1/T$, (Figure 5), we obtain the following Arrhenius expression:

$$k_{2,c}(298-433 \text{ K}) = (5.2^{+0.9}_{-0.8}) \times 10^{-12} \times$$
$$\exp[(-1675 \pm 60)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

To our best knowledge, this is the first Arrhenius expression determined for Cl + CHCl$_2$F. Our experimental determination of the activation energy validates the theoretical value of 3.3 kcal mol^{-1} predicted at 300 K by Rayez et al.[16]

Cl + CHClF$_2$ → HCl + CClF$_2$ (k_3). Conventional treatment of kinetic data without correction for [Cl] loss leads to the plot k_{obs} vs $[Cl]_0$ shown in Figure 7. As in the previous study, corrections on k_{obs} due to the diffusion of CHClF$_2$ are negligible. This new study confirms the value of the bimolecular rate

TABLE 4: Summary of Relevant Experimental Conditions and Rate Coefficients k_1 (uncorrected) and $k_{1,c}$ (with Correction Incorporating the Wall Loss and Homogeneous Recombination Reactions of Cl Atoms) at Various Temperatures for the Reaction Cl + CHCl$_3$

T (K)	P (Torr)	expts	$[CHCl_3]_o{}^a \times 10^{-13}$	$[Cl]_{o,o}{}^a \times 10^{-14}$	$(k_1 \pm 2\sigma)^b \times 10^{14}$	$(k_{1,c} \pm 2\sigma)^b \times 10^{14}$
298	1.5–3.7	8	1.3–1.5	5.16–17.60	9.1 ± 1.1	7.6 ± 1.3
342	0.8–3.3	6	0.6–1.2	2.80–18.60	13.5 ± 1.8	13.2 ± 3.7
373	0.8–2.8	6	0.5–0.9	3.54–14.06	19.9 ± 2.2	19.5 ± 4.0
403	0.6–2.2	6	0.4–0.8	2.57–9.90	27.6 ± 1.2	26.2 ± 4.0
433	0.7–2.1	6	0.4–0.7	2.50–8.86	34.0 ± 1.0	31.6 ± 2.0

a Concentrations are expressed in molecules cm^{-3}. *b* Units are cm^3 molecule^{-1} s^{-1}.

TABLE 5: Summary of Relevant Experimental Conditions and Rate Coefficients k_2 (Uncorrected) and $k_{2,c}$ (with Correction Incorporating the Wall Loss and Homogeneous Recombination Reactions of Cl Atoms) at Various Temperatures for the Reaction Cl + CHCl$_2$F

T (K)	P (Torr)	expts	[CHCl$_2$F]$_o{}^a$ $\times 10^{-12}$	[Cl]$_{o,o}{}^a$ $\times 10^{-14}$	$(k_2 \pm 2\,\sigma),^b \times 10^{14}$	$(k_{2,c} \pm 2\,\sigma),^b \times 10^{14}$
298	2.0–4.2	12	6.7–13.7	1.03–9.55	2.0 ± 0.2	1.9 ± 0.3
340	2.7–3.1	11	7.6–8.8	1.45–8.82	4.1 ± 0.5	3.8 ± 0.4
371	2.1–3.2	10	5.2–8.2	1.93–9.09	6.0 ± 0.5	5.8 ± 0.4
404	1.5–3.0	10	3.5–4.9	1.28–5.09	9.0 ± 0.8	8.6 ± 0.6
433	2.0–2.5	10	4.6–5.6	1.66–6.15	10.8 ± 1.2	10.5 ± 0.8

^{a} Concentrations are expressed in molecules cm^{-3}. ^{b} Units are cm^3 molecule^{-1} s^{-1}.

TABLE 6: Summary of Relevant Experimental Conditions and Rate Coefficients k_3 (uncorrected) and $k_{3,c}$ (with Correction Incorporating the Wall Loss and Homogeneous Recombination Reactions of Cl Atoms) at Various Temperatures for the Reaction Cl + CHClF$_2$
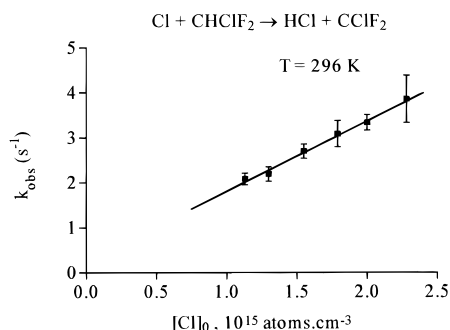
T (K)	P (Torr)	expts	[CHClF$_2$]$_o{}^a$ $\times 10^{-12}$	[Cl]$_{o,o}{}^a$ $\times 10^{-14}$	$(k_3 \pm 2\,\sigma),^b \times 10^{15}$	$(k_{3,c} \pm 2\,\sigma)^b \times 10^{15}$
296	3.0–5.7	6	15.3–22	11.25–22.83	1.7 ± 0.2	1.4 ± 0.3
323	2.3–3.4	4	6.1–22.2	6.57–11.07	3.5 ± 1.6	3.0 ± 0.8
356	1.6–3.5	6	4.5–9.9	2.76–8.66	6.5 ± 1.6	5.7 ± 1.3
373	1.4–3.8	6	5.1–14.9	2.56–8.01	8.4 ± 1.9	8.2 ± 1.6
393	1.3–3.8	7	6.0–18.0	3.22–7.14	11.5 ± 2.0	10.9 ± 2.8
411	1.2–3.6	5	6.5–11.0	3.36–8.29	14.9 ± 2.0	14.0 ± 1.4

^{a} Concentrations are expressed in molecules cm^{-3}. ^{b} Units are cm^3 molecule^{-1} s^{-1}.

Figure 7. Pseudo-first-order rate constants k_{obs} plotted vs [Cl]$_0$ for the reaction Cl + CHClF$_2$ at 296 K (without correction of Cl loss).

constant k_3 at 296 K previously published by the same group.[12]

$$k_3(296\ \text{K}) = (1.7 \pm 0.2) \times 10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

Modeling calculations on temporal profiles of Cl show depletion can range between 19.1 and 32% depending upon experimental conditions. This induces a systematic error which should not be neglected. As previously shown, the slopes of the plots ln[I(CHF$_2{}^+$)] vs ln $Q/2k_r$[He] incorporating the corrected [Cl]$_0$ lead to the value of $k_{3,c}$ within statistical uncertainties of 2σ:

$$k_{3,c}(296\ \text{K}) = (1.4 \pm 0.3) \times 10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

Comparisons to the earlier measurements listed in Table 2 show that this value is lower than the value determined by Tuazon et al.[11] by a relative rate method but remains within their uncertainty range. Our corrected value exhibits excellent agreement with the previous value measured by Jourdain et al.[31] using the same experimental method but with no explicit account for variation of Cl concentration along the reaction distance.

Kinetic results at various temperatures and relevant experimental conditions are listed in Table 6. Linear least squares regression on data in the ln $k_{3,c}$ vs $1/T$ plot (Figure 5) yields the Arrhenius expression

$$k_{3,c}(296\text{–}411\ \text{K}) = (5.3^{+1.5}_{-1.3}) \times 10^{-12} \times$$
$$\exp[-(2430 \pm 90)/T]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

To the best of our knowledge, this is the first Arrhenius expression reported for this reaction. The experimental value of the activation energy 4.8 kcal mol^{-1} is 17% lower than the value of 5.8 kcal mol^{-1} predicted by ab initio calculations.[16]

Reactivity Trends. A previous ab initio theoretical investigation[16] has calculated the kinetics and thermochemistry of the hydrogen abstraction reactions from nine halogen (F, Cl) substituted methanes by chlorine atom. The conclusions of this theoretical study can be summarized as follows: (i) the values of the preexponential factor for the series of nine halomethanes are all in the same order of magnitude (10^{-12} cm^3 molecule^{-1} s^{-1}); (ii) the difference in reactivity observed on going from CHCl$_3$ to CHClF$_2$ (and CHF$_3$) is mainly controlled by activation energy; (iii) a quadratic correlation (Marcus type[32]) between the activation barriers and the reaction enthalpies calculated by the ab initio methods was shown most suitable for analysis of the reactivity trends in the series of reactions of nine fluoro- and chloro-substituted methanes with chlorine atoms, as opposed to a linear correlation of the Evans–Polanyi type. The experimental data reported herein support the above points i and ii. The experimental values of the preexponential factors for the hydrogen abstraction reactions from the series of halomethanes of type CHCl$_{3-x}$F$_x$ confirm the order of magnitude of 10^{-12} cm^3 molecule^{-1} s^{-1} predicted by our previous ab initio calculations. The small difference observed experimentally (within the uncertainty limits) between them suggests a very small variation of the activation entropies along the studied series. As a matter of fact, the most striking result is the significant increase of the activation energy when Cl atom is replaced by F in the structure of halomethanes of type CHCl$_{3-x}$F$_x$. The measured activation energies vary as 2.8, 3.3, and 4.8 kcal mol^{-1} for the reactions of Cl atoms with CHCl$_3$, CHCl$_2$F, and CHClF$_2$ respectively, in a very good agreement with the values predicted in our previous work (2.1, 3.3, and 5.8 kcal mol^{-1}, respectively). The role of fluorine and chlorine atoms on the structure of organic species has been largely investigated. As halogens, these two elements act as powerful σ acceptors (inductive effect) and somewhat weaker π donors (conjugative effect). As a first-row element, fluorine is both a better σ acceptor and a π donor than chlorine which belongs to the second row. Geminal interaction between two or three fluorine atoms strongly stabilizes the structures of fluoromethanes, whereas the interaction between a fluorine and a

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chlorine atom is weakly stabilizing and chlorine -chlorine interaction is negligible.[33] These different energetic aspects induce some significant variations in the strength values of the broken C−H bond. The strength of this C−H bond, defined as the dissociation enthalpy $D_{298}(H-CX_3)$, can be estimated using the relationship $D_{298}(H-CX_3) = \Delta H(298) + D_{298}(H-Cl)$, where $\Delta H(298)$ represents the reaction enthalpy previously determined for each reaction and $D_{298}(H-Cl)$ the experimental value of the dissociation enthalpy of HCl at 298 K ($D_{298}(H-Cl) = 103.2$ kcal mol^{-1}).[34] It is easy to verify that the C−H bond strength increases when the number of fluorine atoms is increased in the reactant (93.8, 98.3, and 100.8 kcal mol^{-1} for CHCl$_3$, CHCl$_2$F, and CHClF$_2$, respectively). So, as predicted by our theoretical earlier study,[16] a correlation exists between the measured activation energy and the experimental reaction enthalpy (and the broken C−H bond strength) for the investigated reactions. However, the number of reactions of Cl atom with halomethanes experimentally investigated in this study is insufficient to verify if the correlation between the activation barriers and the reaction enthalpies is quadratic or linear. We therefore assembled experimental values in the literature[14,15] for activation energies in this series of reactions, and corresponding reaction enthalpies calculated using the experimental enthalpies of formation.[15] The data indicate that the uncertainty ranges do not allow to validate a quadratic correlation between energy barrier and reaction enthalpy as calculated[16] using values by ab initio methods.

Conclusion

Arrhenius expressions for metathesis reactions of Cl atoms with CHCl$_3$, CHCl$_2$F (HCFC-21), and CHClF$_2$ (HCFC-22) have been determined using the conventional DF/MS technique. Optimized pseudo-first-order conditions resulted in operation under excess Cl atom, as opposed to conventional excess reactant molecule. Wall loss and recombination of atomic chlorine (Cl + Cl + M) rate coefficients, k_w and k_r, respectively, were measured and utilized in calculation of the rate coefficients. Inclusion of Cl atom losses is shown to be important for the slower reactions requiring longer reaction times. Arrhenius expressions are in good agreement with literature data, where available, and in very good agreement with recently reported theoretical (ab initio) calculations.

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