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Kinetic study of the reaction of chlorine atoms with chloromethane in the gas phase

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ABSTRACT

The kinetics of the gas phase reactions of chlorine atoms with chloromethane and D-chloromethane CD₃Cl was studied experimentally. The relative rate method was applied using Cl + CH₃Br as the reference reaction. The rate constants for H-abstraction from CH₃Cl ($k_{\rm H}$) and D-abstraction from CD₃Cl ($k_{\rm D}$) were measured in the temperature range of 298–527 K and at a total pressure of 100 Torr. The derived temperature dependencies of the rate constants are given by $k_{\rm H} = (1.7 \pm 0.1) \times 10^{-11} \times \exp(-1040 \pm 10/T)$ and $k_{\rm D} = (1.3 \pm 0.2) \times 10^{-11} \times \exp(-1470 \pm 10/T) \text{ cm}^3$ molecule⁻¹ s⁻¹. The kinetic isotope effect, described by the ratio $k_{\rm H}/k_{\rm D}$, was $(1.35 \pm 0.05) \times \exp(420 \pm 10/T)$.

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1. Introduction

Chloromethane (CH₃Cl) is the most abundant naturally produced chlorine-containing organic compound in the atmosphere [1]. The annual global flux of CH₃Cl into the atmosphere is estimated to be at least 4 million t [1,2], with an atmospheric lifetime of 17 months [1,3]. Chloromethane has a significant impact on chlorine chemistry in the atmosphere and is involved in various catalytic cycles responsible for the depletion of the stratospheric ozone layer. Despite its importance, the understanding of the atmospheric budget of CH₃Cl is still unsatisfactory [4,5]. The recognized sources of CH₃Cl can only account for approximately 50% of the emission required to balance the known sinks. The reaction of CH₃Cl with OH is the dominant loss pathway for atmospheric CH₃Cl, but in the marine boundary layer and polar regions, reaction with Cl atoms can also become of some importance [4]. The reaction of chloromethane with chlorine atoms

$$CH_3Cl + Cl \rightarrow CH_2Cl + HCl$$
 (1)

has been the subject of several experimental [6–16] and theoretical studies [17–20]. It is worth noting that the reported room temperature values of the rate constant, $k_{\rm H}$, for reaction (1) estimated by different experimental techniques are in satisfactory agreement. The most recent IUPAC and NASA evaluations of the kinetic data therefore recommend very similar values for $k_{\rm H}$ of $(4.8 \pm 0.5) \times 10^{-13}$ [21] and $(4.9 \pm 0.5) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ [22], respectively, at 298 K. The temperature dependencies of $k_{\rm H}$ expressed in the Arrhenius form show some differences in the reported values of both the A-factor and activation energy. However, only the results of Clyne and Walker [8] differ markedly from the other measurements at high-temperature dependence of

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 $k_{\rm H}$ [17,18] than that found experimentally [6–10,13,14]. Therefore, a credible estimation of the temperature dependence of $k_{\rm H}$ was among the main aims of our kinetic investigations.

In this study we present measurements of the rate constant for the hydrogen abstraction reaction from CH₃Cl by Cl atoms using the relative rate technique. The experiments were performed in the temperature range of 298–527 K to examine the temperature dependence of the rate constant $k_{\rm H}$ and the values of the activation energy reported in literature. The reaction of the entirely deuterated chloromethane

$$CD_3Cl + Cl \rightarrow CD_2Cl + DCl$$
 (2)

was also studied in the same temperature range. The independent measurements of the rate constant k_D for reaction (2) enabled us to estimate the kinetic isotope effect (KIE). Values of KIE can provide useful information for interpreting the stable isotope composition of the organic compounds in the atmosphere. Experimental information on the kinetics of isotopomers of CH₃Cl is limited to only a single estimate of KIE at room temperature obtained by Gola et al. [16]. The hydrogen abstraction from bromomethane by chlorine atoms

$$CH_3Br + Cl \rightarrow CH_2Br + HCl$$
 (3)

was utilized as a reference reaction in our investigations. Reaction (3) has been studied by the flash photolysis-resonance fluorescence technique by Piety et al. [23] over a wide range of temperatures using nitrogen as a buffer gas. The rate constant k_3 for reaction (3) and its temperature dependence are well known and have been determined with sufficiently high accuracy.

2. Experimental

The experiments were conducted in a greaseless static system in a cylindrical Pyrex reactor of ca. 250 cm^3 (dead volume $\sim 2\%$) placed in an aluminium heating block. Reactions of chlorine atoms



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with chloromethane and D-chloromethane were investigated with bromomethane used as the reference at five temperatures over the temperature range of 298–527 K. Temperature was maintained by a power regulator connected to a temperature regulator equipped with a Pt-100 resistance sensor placed inside the chamber of the electrically heated block. A chrome–nickel thermocouple, used for temperature measurements, was fixed at half length of the side wall of the reactor. The temperature of the reactor was constant to within 0.5° during the experiments. The reactants were introduced into the reaction cell by expansion, starting from CH₃Cl or CD₃Cl followed by CH₃Br and the mixture Cl₂/N₂. At the end, N₂ was introduced to reach a total pressure of 100 Torr.

All experiments were conducted at a total pressure of about 100 Torr, while the partial pressure was varied from 9 to 10 Torr for Cl_2 and from 3 to 5 Torr for CH_3Cl/CD_3Cl and CH_3Br . The Cl_2 mixtures in N_2 were prepared (at least 24 h prior to their first use) from pure Cl_2 (>99.5%) and N_2 (>99.995%) and stored in 4L blackened Pyrex bulbs. The reactants CH_3Cl, CD_3Cl , and CH_3Br were expanded under vacuum from the producers' containers into light-tight Pyrex bulbs for storage. Pressure measurements were carried out with a 127A MKS Baratron capacity manometer equipped with two gauges (0–100 and 0–1000 Torr).

A Xe arc lamp (Osram XBO 150 W/1 OFR) served as the light source. The optical train consisted of a manually operated shutter, a condensing lens, a variable-width slit, and a monochromator with the Czerny-Turner optical system (dispersing element: a 1200 line/mm grating and aperture F/4, range: 200–900 nm, band variability: 2-20 nm) of a Hitachi MPF-4 fluorescence spectrophotometer. The light from the monochromator was introduced into the cylindrical reactor through its bottom window and, after passing through the reactor, reflected back by a mirror placed above the upper window of the reactor. The reaction cell, feed lines, and the optical assembly were housed in a light-tight enclosure to prevent photolysis initiated by room or stray light. The absence of such reactions was confirmed by repeated blank analysis. Chlorine atoms were generated in their ground state $(Cl(^{2}P_{3/2}) > 99\%)$, $Cl(^{2}P_{1/2}) < 1\%$ at 298 K) [24] by the photolysis of Cl_{2} at 420 nm or by thermolysis at 527 K. The irradiation time (0.25-45 min) was varied depending on the reaction temperature in order to obtain appropriate conversion of the reactants.

Quantitative analysis of the products was performed by a gas chromatograph (HP, Model 5890 Series II) equipped with a thermal conductivity detector. All separations were done with a 25 m long \times 0.53 mm PoraPlot Q Chrompack capillary column using temperature programming. Helium was used as the carrier gas and a 2 ml thermostated stainless steel gas loop as the sampling unit. Before and after every experiment, calibration of the reactant's peak area vs. its partial pressure in the reactor was conducted by GC analysis. The reactants used in this study had the following stated minimum purities CH₃Br (>99.5%), cH₃Cl (>99.5%), and Cl₂ (>99.5%) from Aldrich, CD₃Cl (>99.5%) from Isotec Inc., and N₂ (99.999%) from BOC. All reactants were used directly from the producers' containers.

3. Results and discussion

The relative rate method was employed in these kinetic investigations. This experimental approach is based on the competition between two reactants reacting with the same reactive species. The concentrations at any given time of two reactants, AH and BH, reacting simultaneously with chlorine atoms are described by the relation:

$$\ln\frac{[AH]_0}{[AH]_t} = \frac{k_A}{k_B} \cdot \ln\frac{[BH]_0}{[BH]_t}$$
(4)

where k_A and k_B are the rate constants for the competing reaction channels, $[AH]_0$ and $[BH]_0$ the starting concentrations of AH and BH, and $[AH]_t$ and $[BH]_t$ the concentrations of the reactants at a given time *t*. Eq. (4) is valid only when both reactants, AH and BH, are consumed only in the reaction with chlorine atoms. The plot of $\ln([AH]_0/[AH]_t)$ vs. $\ln([BH]_0/[BH]_t)$ should therefore be linear, which enables a determination of the rate constant ratio k_A/k_B as the slope and, finally, k_A if the absolute value of k_B is known with sufficient accuracy at the given temperature.

The results of these measurements were analyzed on the basis of Eq. (4) with the reactant AH (CH₃Cl or CD₃Cl), the reference reactant BH (CH₃Br), and the rate constants $k_A (k_H \text{ or } k_D)$ and $k_B = k_3$. All experiments were conducted at a high concentration of molecular chlorine Cl₂. A large excess of Cl₂ causes the reactions of $Cl_2 + CH_2Cl/CD_2Cl/CH_2Br$ producing chlorine atoms to be the fastest secondary processes in the reaction system. Other radical processes, such as radical-radical recombinations and reactions of radicals with the reactants CH₃Cl, CD₃Cl, and CH₃Br proceed considerably more slowly. The reverse reactions CH₂Cl/CD₂Cl + HCl/ DCl (-1,-2) and CH₂Br + HCl (-3), which reproduce the parent compounds CH₃Cl/CD₃Cl and CH₃Br, are very slow [21,22] and hence are considered unimportant processes even at a higher degree of conversion of the reactants. The influence of secondary radical reactions on the kinetics of the primary H-abstraction reactions (1-3) is therefore negligible under the reaction conditions applied in our investigation.

Preliminary tests showed that a ca. 10 min mixing time was sufficient for the reactants in the cell to reach ambient temperature. In order to test possible photolysis or thermal decomposition of the organic reactants, mixtures of the organics were irradiated in the absence of Cl₂ at the highest temperature used for more than 60 min. No photolysis or thermal reaction of CH₃Cl, CD₃Cl, and CH₃Br was observed. Prior to each set of experiments at temperatures above 298 K, tests for a dark reaction were performed. A mixture of the organic species and molecular chlorine was allowed to stand in the dark for at least 60 min. At temperatures of 448 K and lower, the reaction of the organic species with molecular chlorine was negligible in the absence of photolytic light. No products of the thermal reaction were detected. At the highest temperature of this study (527 K), thermolysis of Cl₂ occurred. This allowed us to utilize the thermolysis of Cl₂ as an additional source of Cl atoms at this temperature. Photolysis of only Cl₂ in the reactor ensured that CH₃Cl or CD₃Cl were not produced by the reaction of impurities on the wall of the reactor.

The values of the rate constants for the studied reactions were determined at five temperatures in the temperature range of 298 to 527 K at a nearly constant total pressure of 100 Torr. Fig. 1 shows sample kinetic data obtained from the experiments at 381 K plotted according to Eq. (4) for the reaction of Cl with CH₃Cl and CD₃Cl measured with respect to CH₃Br. The linearity of the plots shown in Fig. 1 supports the assumption that the organic reactants are consumed only in reaction with chlorine atoms. The kinetic expression derived by Piety et al. [23] describing the temperature dependence of the rate constant k_3 for the reaction $CH_3Br + Cl \rightarrow CH_2Br + HCl$ as $k_3 = 3.32 \times 10^{-12} \times (T/298)^{1.42} \times 10^{-12}$ $\exp(-605/T)$ cm³ molecule⁻¹ s⁻¹ was utilized in our experiments. The results of the measurements were analyzed using a weighted least squares procedure which included uncertainties in the reactant concentrations and allowed a zero-point offset. Values of the ratios $k_{\rm H}/k_3$ and $k_{\rm D}/k_3$ as well as the absolute values of $k_{\rm H}$ and $k_{\rm D}$ at five temperatures (298, 325, 381, 448, and 527 K) are gathered in Table 1.

Fig. 2 shows the Arrhenius plots for the reactions studied. The experimental points are only slightly scattered around the regression lines, which indicates the validity of the experimental meth-



Fig. 1. Relative rate data obtained at 527 K and a pressure of 100 Torr for the reactions of Cl with CH_3Cl (\bullet) and CD_3Cl (\blacksquare) using CH_3Br as the reference compound.

odology used. The temperature dependence of the rate constant $k_{\rm H}$ can be expressed in the temperature range 298–527 K as:

$$k_{\rm H} = (1.7 \pm 0.1) \times 10^{-11} \times \exp(-1040 \pm 10/T)$$

cm³ molecule⁻¹ s⁻¹ (5)

where the error limits include either the 2σ error of the derived ratio $k_{\rm H}/k_3$ and the 2σ error of the rate constant k_3 for the reference reaction CH₃Br + Cl reported by Piety et al. [23] (details in Table room temperature The value of 1). kн of $(5.2 \pm 0.4) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ derived from Eq. (5) is in line with the absolute rate determinations of $(5.4 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ of Manning and Kurylo [9] and $(5.1 \pm 1.3) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ obtained by Pritchard et al. [6] using the standard relative rate technique. A similar value of $(5.1 \pm 0.7) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 298 K can be derived from the expression describing the temperature dependence of the rate constant found by Tschuikow-Roux et al. [10]. Our $k_{\rm H}$ value is also in excellent agreement with the recent estimate of $(5.2 \pm 0.3) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ of Bryukov et al. [14]. Only the result of $(4.4 \pm 0.6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K obtained in the relative rate study of Beichert et al. [12] differs more distinctly from our $k_{\rm H}$ value. However, their finding was based on a value of 9.4×10^{-14} cm³ molecule⁻¹ s⁻¹ for the rate constant of



Fig. 2. Arrhenius plot for the reactions of Cl atoms with $CH_3Cl(\bullet)$ and $CD_3Cl(\blacksquare)$ in the temperature range of 298 to 527 K (error limits represent 2σ).

the reference reaction CH₄ + Cl. Using the value for k(CH₄ + Cl) of 1.0×10^{-13} cm³ molecule⁻¹ s⁻¹ presently recommended by IUPAC and NASA kinetic data evaluations [21,22] results in an increase in the estimate of Beichert et al. [12] to 4.7×10^{-13} cm³ molecule⁻¹ s⁻¹ at 298 K. Values for the rate constant $k_{\rm H}$ were determined by Orlando [13] relative to two reference reactions: $CH_4 + Cl$ and $CH_3Br + Cl$. The room temperature value for $k(CH_3Br + Cl)$ of 4.3×10^{-13} cm³ molecule⁻¹ s⁻¹ of Gierczak et al. [25] used by Orlando [13] is very close to that of 4.4×10^{-13} cm³ molecule⁻¹ s⁻¹ of Piety et al. [23] utilized in our study. The ratios of $k_{\rm H}$ / $k(CH_4 + CI) = 4.7 \pm 0.6$ and $k_H/k(CH_3Br + CI) = 1.1 \pm 0.1$ at 298 K derived by Orlando [13] combined with the values of the rate constant for reference reactions [21,22,25] yield a mean value for $k_{\rm H}$ of $(4.7 \pm 0.6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value, similarly to that of $(4.8 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Wallington et al. [11], are a little lower than the $(5.2 \pm 0.4) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ found in this study. The values of $(4.8 \pm 0.5) \times 10^{-13}$ [21] and $(4.9 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [22] recommended by the kinetic data evaluations at 298 K are also less than our estimate. This is certainly caused by the favoring of the results of the relative rate studies of Tschuikow-Roux et al. [10], Wallington et al. [11], and Beichert et al. [12] in the IUPAC and NASA kinetic analysis [21,22]. The results of our investigations predict a slightly higher value of $k_{\rm H}$ at room temperature. The insert of Fig. 3 shows a comparison of the experimental results obtained near room temperature. A large portion of the results is located above the bottom

Table 1

The measured rate constant ratios $k_{\rm H}/k_3$ and $k_{\rm D}/k_3$, the absolute values of $k_{\rm H}$ and $k_{\rm D}$, and the derived values of the kinetic isotope effect $k_{\rm H}/k_{\rm D}$.

Т (К)	$k_{\rm H}/k_3^{\rm a}$	$10^{13} \times k_{\rm H}^{\rm b}$ (cm ³ molecule ⁻¹ s ⁻¹)	$k_{\rm D}/k_{\rm 3}{}^{\rm a}$	$10^{14} \times k_{\rm D}^{\rm b}$ (cm ³ molecule ⁻¹ s ⁻¹)	$k_{ m H}/k_{ m D}{}^{ m a}$
298	1.189 ± 0.026	5.2 ± 0.4	0.220 ± 0.012	9.7 ± 1.1	5.4 ± 0.3
325	1.183 ± 0.038	6.9 ± 0.6	0.226 ± 0.024	13.2 ± 2.1	5.2 ± 0.5
381	1.141 ± 0.024	11.0 ± 0.9	0.271 ± 0.006	26.1 ± 2.1	4.2 ± 0.2
448	1.053 ± 0.016	16.2 ± 1.0	0.310 ± 0.008	47.7 ± 3.4	3.4 ± 0.2
527	0.999 ± 0.022	23.7 ± 1.8	0.343 ± 0.012	81.3 ± 7.3	2.9 ± 0.2

^a With 2σ error limits.

^b With errors derived as the sum of the 2σ errors of $k_{\rm H(D)}/k_3$ and of the reference rate constant k_3 .



Fig. 3. Arrhenius plot for the $CH_3CI + CI$ reaction comparing the available results of kinetic measurements. The solid line corresponds to the plot of Eq. (5). The insert shows experimental results obtained in the temperature range of 295–308 K.

limit of our estimate at 298 K. However, our $k_{\rm H}$ is within the error limits of the recommended IUPAC and NASA values [21,22].

The temperature dependence of the rate constant $k_{\rm H}$ is determined by the value of the activation energy which, as calculated from Eq. (5), is small (8.6 kJ mol⁻¹). This implies a weak dependence of $k_{\rm H}$ on temperature. A comparison of the former measurements of the temperature dependence of $k_{\rm H}$ is shown in Fig. 3. The results reported by Clyne and Walker [8] are characterized by a significantly higher value of the activation energy and a strong temperature dependence of $k_{\rm H}$. However, their high-temperature results are rather overestimated because they distinctly exceed the results of measurements of the other researchers. The temperature dependence of $k_{\rm H}$ derived in this study is in good agreement with the results of previous experimental investigations [7-10,13,14] and can be considered the best compromise for all experimental points below 500 K. At the high-temperature range, i.e. above 500 K, only the results of Bryukov et al. [14] are greater than those obtained from Eq. (5). The temperature dependence of the rate constant $k_{\rm H}$ derived by Bryukov et al. [14] is steeper in this temperature range and shows a non-Arrhenius behavior. Unfortunately, there are no other credible measurements which can verify the results of the high-temperature experiments of Bryukov et al. [14].

The Arrhenius plot for the reaction $CD_3Cl + Cl$ is also shown on Fig. 2. The experimental measurements of $k_{\rm H}$ and $k_{\rm D}$ were done at the same temperatures, which also enables us to calculate the values of KIE directly from the results of the measurements. Kinetic analysis of the experimental results obtained in the temperature range 298–527 K leads to the following temperature dependence of $k_{\rm D}$

$$k_{\rm D} = (1.3 \pm 0.2) \times 10^{-11} \times \exp(-1470 \pm 10/T)$$

cm³ molecule⁻¹ s⁻¹ (6)

with a 2σ error limit. The abstraction of deuterium from CD₃Cl proceeds distinctly more slowly and shows a slightly higher dependence on temperature than hydrogen abstraction from CH₃Cl. The room temperature value of the rate constant $k_{\rm D}$ is lower than $k_{\rm H}$



Fig. 4. Comparison of the derived values of the kinetic isotope effect $k_{\rm H}/k_{\rm D}$ (\bullet) with those obtained by Wallington and Hurley [15] at 295 K (\diamond) and Gola et al. [16] at 298 K (\Box). The error limits correspond to 2σ .

by a factor of 5. However, the significance of the kinetic isotope effect declines with rising temperature. At 527 K the value of KIE is slightly lower than 3. The temperature dependence of KIE, described by the ratio $k_{\rm H}/k_{\rm D}$, can be expressed (error limits represent 2σ) in the form

$$k_{\rm H}/k_{\rm D} = (1.35 \pm 0.05) \times \exp(420 \pm 10/T)$$
 (7)

The temperature dependence of KIE was determined for the first time in this study. A single measurement of KIE was performed by Gola et al. [16] at room temperature. Their value of $k_{\rm H}$ $k_{\rm D}$ = 4.91 ± 0.07 is only 10% lower than our estimate of 5.4 ± 0.3. Wallington and Hurley [15] obtained а value of $(8.9 \pm 0.3) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K for the rate constant of the reaction $CD_3Cl + Cl$. Using the k_H value of Wallington et al. [11] leads to a KIE of 5.4 ± 0.4 at 295 K, which is in excellent agreement with our value of 5.4 ± 0.3 at 298 K (see Fig. 4). This agreement supports the reliability of the values for KIE derived in this study. A detailed interpretation of the KIE is difficult without the results of theoretical investigations. Replacing the hydrogen atom by deuterium leads to a change in the molecular properties of the reactants and products. An increase in molecular mass changes the rotational constants only slightly. More distinct changes occur in vibrational frequencies, especially those related to C-H and C-D stretch modes. This decreases the zero-point of the vibrational energy of the D-substituted compound compared with that of the unsubstituted one. D-abstraction is thus related to the higher energy barrier than the H-abstraction process. The changes in the vibrational frequencies of the reactants, the energy barrier, and the tunneling contribution related to deuterium substitution have a dominant share in the KIE at low temperatures. At higher temperatures the value of KIE strongly decreases to unity.

The available kinetic data on KIE related to reactions of chlorine with chloromethanes are very limited. The value derived in this study of a primary KIE of 5.4 ± 0.3 at 298 K is slightly higher than that of 4.7 ± 0.6 we obtained for the reaction system CHCl₃/

CDCl₃ + Cl [26], but considerably lower than the 17.5 ± 2.5 estimated for CH₄/CD₄ + Cl [15,21,22,27]. The value of the KIE of the reactions of chloromethanes with chlorine at room temperature decrease when the number of chlorine atoms in the reactant molecule rises. Explanation of the derived values of KIE needs theoretical calculations, which enable insight into the molecular structure and the properties of the reactants during reaction. Our experimental study provides information on the temperature dependence of KIE for the CH₃Cl/CD₃Cl + Cl reaction system useful for the verification of theoretical results.

4. Conclusion

The rate constants and their temperature dependence for the reactions of chlorine atoms with CH₃Cl and CD₃Cl were estimated using the relative rate method. Isotopic substitution distinctly decreases the reaction rate. The rate constant for the reaction of D-chloromethane is consequently several times lower than that of H-abstraction from CH₃Cl. The kinetic isotope effect shows a distinct dependence on temperature. The temperature dependence of the rate constant $k_{\rm H}$ derived in this study seems to be reliable because our experiments are in very good accordance with the available results of absolute rate studies at temperatures below 500 K.

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