Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

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

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ARTICLE INFO

Article history: Received 20 October 2008 In final form 22 December 2008 Available online 30 December 2008

ABSTRACT

The kinetics of the gas-phase reactions of chlorine atoms with H-chloroform and D-chloroform was studied experimentally. The relative rate method was applied using Cl + CH₃Br as the reference reaction. The rate constants for H-abstraction from CHCl₃ ($k_{\rm H}$) and D-abstraction from CDCl₃ ($k_{\rm D}$) were measured in the temperature range of 297–527 K and at total pressure of 100 Torr. The derived temperature dependencies of the rate constants are given by $k_{\rm H} = (4.8 \pm 0.5) \times 10^{-12} \times \exp(-1160 \pm 30/T)$ and $k_{\rm D} = (6.4 \pm 2.1) \times 10^{-12} \times \exp(-1660 \pm 110/T) \text{ cm}^3$ molecule⁻¹ s⁻¹. The kinetic isotope effect described by the ratio $k_{\rm H}/k_{\rm D}$ was $(0.77 \pm 0.25) \times \exp(500 \pm 95/T)$.

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1. Introduction

Chloroalkanes and products of their atmospheric reactions are considered toxic and biocumulative species. Chloroform is among the most abundant chlorine-containing compounds in the atmosphere. Ninety percent or more of the atmospheric CHCl₃ is emitted from natural sources such as the oceans, soil, and termites. The rest is a result of such industrial activity as paper manufacturing, water treatment, and waste incineration [1–5]. The products of the atmospheric destruction of CHCl₃ may be involved in various catalytic atmospheric reaction cycles responsible for the depletion of the ozone layer. The stratospheric lifetime of CHCl₃ is estimated to be over 3 years [5,6]. The chemical degradation initiated by OH radicals is a major loss pathway for atmospheric chloroform [6,7]. However, in marine areas and polar regions, especially during sunrise events, reactions with Cl atoms can also be of some importance [5]. The reaction of chloroform with chlorine atoms

$$\mathsf{CHCl}_3 + \mathsf{Cl} \to \mathsf{CCl}_3 + \mathsf{HCl} \tag{1}$$

has been the subject of several experimental [8–17] and theoretical studies [18–21]. Results of the experimental investigations show, however, substantial scattering in the values of the measured rate constant $k_{\rm H}$ for reaction (1). Distinct differences occur in values for either the pre-exponential factor or the activation energy. Estimates of the rate constant $k_{\rm H}$ at room temperature cover a range of $(0.4–3.2) \times 10^{-13} \, {\rm cm}^3$ molecule⁻¹ s⁻¹. Despite the discrepancies in the values of kinetic measurements, the most recent IUPAC and NASA evaluations of the kinetic data recommend very similar values of the rate constant, i.e. $k_{\rm H}$ of 1.1×10^{-13} [22] and $1.2 \times 10^{-13} \, {\rm cm}^3$ molecule⁻¹ s⁻¹ [23] at 298 K, respectively.

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In this study, we present measurements of the rate constant for the hydrogen abstraction reaction (1) using the relative rate technique. The experiments were performed in the temperature range of 297–527 K to examine the temperature dependence of $k_{\rm H}$ and the values of the activation energy available in literature. The reaction of deuterated chloroform

$$CDCl_3 + Cl \rightarrow CCl_3 + DCl \tag{2}$$

was also included in our kinetic investigation. The independent measurement of the rate constant $k_{\rm D}$ for reaction (2) enabled us to estimate the kinetic isotope effect (KIE). Values of KIE provide information useful for interpreting the stable isotope composition of the organic compounds in the atmosphere. The experimental data on the kinetics of isotopomers of CHCl₃ are very limited. To the best of our knowledge, only the old study by Clyne and Walker [9] showed measurements of the kinetic isotope rate constant ratio $k_{\rm H}/k_{\rm D}$ in a wide temperature range. The hydrogen abstraction reaction

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

was selected as the reference reaction in our investigations. The rate constant k_3 for reaction (3) and its temperature dependence are well known and have been estimated with satisfactorily accuracy [24].

2. Experimental

The experiments were carried out in a greaseless static system using a cylindrical Pyrex reactor of ca. 250 cm^3 (dead volume: $\sim 2\%$) placed in an aluminium heating block. The gas-phase reactions of chlorine atoms with chloroform and D-chloroform were investigated using the reaction with bromomethane as the reference at six temperatures in the temperature range of 297–527 K. The temperature was maintained by a power regulator connected to a tem-



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perature regulator equipped with a Pt-100 resistance sensor placed inside the chamber of the heating block. A chrome–nickel thermocouple located in the middle of the side wall of the reactor was used to measure the temperature. The temperature of the reaction cell was constant to within 0.5° during the experiment. The reactants were introduced into the cell by expansion, starting from CHCl₃ or CDCl₃ followed by CH₃Br and a mixture of Cl₂ in N₂, and finally filled up with N₂ to a total pressure of 100 Torr.

All the experiments were carried out at a total pressure of 100 Torr with the partial pressure of Cl₂ varying from 7 to 10 Torr. The partial pressure of CHCl₃/CDCl₃ and CH₃Br was in the range of 0.5-4 Torr. The mixtures of Cl₂ in N₂ were prepared (at least 48 h before the first use) from pure Cl₂ (>99.5%) and N₂ (>99.99%) and stored in a 4L blackened Pyrex bulb. The reactants CHCl₃, CDCl₃, and CH₃Br were degassing using the freeze-pump-thaw method and stored under vacuum in light-tight containers. The pressure was measured by a Model 127 A MKS Baratron capacitance manometer equipped with two gauges (0-100 and 0-1000 Torr). A Xe arc lamp (Osram XBO 150W/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 with a band variability of 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, was reflected back by the mirror placed above the upper window of the reactor. The reaction cell, feed lines, and 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 analyses. Chlorine atoms were generated in their ground state $(Cl(^{2}P_{3/2}) > 99\%, Cl(^{2}P_{1/2}) > 1\%$, at 298 K) [25] by the photolysis of Cl₂ at 420 nm. The irradiation time (2–20 min) and the slit width (2-20 nm) varied depending on the reaction temperature in order to obtain appropriate conversion of reactants.

The loss of reactants was monitored by thermal conductivity gas chromatography (HP, Model 5890 Series II) using a 25 m \times 0.53 mm ParaPlot Q Chrompack capillary column with temperature–time programming between 70 and 200 °C with helium as the carrier gas. Before and after the experiments, calibration of the reactive peak area vs. the pressure for each reactant at any temperature was determined by GC analysis. The reactants used in this study and their minimal purity were bromomethane (99.7%), H-chloroform (99.7%), and D-chloroform (99.7%) and were from Aldrich. The reaction products were purified three times using the freeze-pump-thaw method.

3. Results and discussion

Expressions describing the kinetics of the competitive reactions of two reactants with the same reactive species are the basis of the relative rate method used. Let us consider the H-abstraction reaction from two reactants, AH and BH, by chlorine atoms

 $AH + Cl \rightarrow A + HCl$ (k_A) $BH + Cl \rightarrow B + HCl$ (k_B)

where k_A and k_B denote the rate constants describing the rate of formation of the channel reaction products. Assuming that reactants AH and BH are only consumed in reaction with chlorine atoms, their concentrations change during the reactions according to the relation:

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

where $[AH]_0$ and $[BH]_0$ are the starting concentrations of the reactants AH and BH and $[AH]_t$ and $[BH]_t$ are the concentrations at a given time *t*. The plot of $\ln([AH]_0/[AH]_t)$ vs. $\ln([BH]_0/[BH]_t)$ should be linear, which enables an estimation of the rate constant ratio k_A/k_B as the slope. Consequently, the rate constant k_A can easily be derived if k_B is known with sufficient accuracy.

The results of measurements of the concentrations of the reactant AH (CHCl₃ or CDCl₃) and the reference reactant BH (CH₃Br) at the same time are analyzed according to Eq. (4). The CCl_3 and CH₂Br radicals formed in competing reaction channels may interfere with each other or initiate different subsequent reactions. Eq. (4) is exact assuming an absence of fast radical processes in the reaction system resulting in changes in the concentrations of CHCl₃, CDCl₃, and CH₃Br. The reaction rate depends on either the magnitude of the rate constant or the concentrations of reactants. The reverse reactions $CCl_3 + HCl/DCl (-1, -2)$ and $CH_2Br + HCl$ (-3), which reproduce the parent compounds CHCl₃/CDCl₃ and CH₃Br, are very slow [22,23] and are hence considered unimportant processes even at a higher degree of conversion of the reactants. The major fate of the CCl₃ and CH₂Br radicals formed is reaction with molecular chlorine, Cl₂, because of the large excess of Cl₂ in the reaction system. The influence of the secondary radical reactions on the kinetics of the primary H-abstraction reactions (1-3) is negligible under the reaction conditions applied in our investigations.

The preliminary tests showed that ca. 10 min of mixing time was sufficient to reach ambient temperature by the reactants in



Fig. 1. Relative rate data obtained at 527 K and a pressure of 100 Torr for the reactions of Cl with CHCl₃ (\bullet) and CDCl₃ (\blacksquare) using CH₃Br as the reference compound.

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 derived values of the kinetic isotope effect $k_{\rm H}/k_{\rm D}$.

T (K)	$k_{\rm H}/k_3$	$10^{13} \times k_{\rm H}$ (cm ³ molecule ⁻¹ s ⁻¹)	$k_{\rm D}/k_3$	$10^{14} \times k_{\rm D}$ (cm ³ molecule ⁻¹ s ⁻¹)	$k_{\rm H}/k_{\rm H}$
297.3	0.240	1.04 (0.4–3.2) ^a	0.0512	2.21	4.7
326.9	0.247	1.47	0.0772	4.59	3.2
337.0	0.226	1.49	0.0704	4.62	3.2
383.3	0.238	2.33	0.0817	8.00	2.9
448.6	0.244	3.77	0.117	18.1	2.1
526.9	0.235	5.56	0.106	25.1	2.2

^a The range of estimated values of $k_{\rm H}$ at room temperature from Refs. [8–17].

the cell and confirmed that dark reactions were never observed. Possible photolysis or thermal decomposition of the organic reactants were taken into account. The mixtures of organics were irradiated in the absence of Cl_2 at the highest temperature for more than 60 min. Neither photolysis nor thermal dissociation reactions of $CHCl_3/CDCl_3$ and CH_3Br were observed. Any kinetic experiment at a temperature above 295 K was preceded by tests for dark reactions. The mixtures of organic species and molecular chlorine were prepared and placed in the dark for at least 60 min. At temperatures below 448 K, the reaction of the organic species with molecular chlorine was negligible in the absence of photolytic light. No destruction of the reactants was observed. At the highest temperature of this study (527 K), thermal dissociation of Cl_2 as an additional source of chlorine atoms. A blind test with the radical pre-



Fig. 2. Arrhenius plot for the reactions of Cl atoms with $CHCl_3(\bullet)$ and $CDCl_3(\blacksquare)$ in the temperature range from 297 to 527 K.

cursor ensured us that chloroform is chemically and photochemically stable in the reaction chamber. It is not produced by the oxidation of impurities and is not adsorbed on the cell walls.

The values of the rate constants for reactions (1) and (2) were determined at six temperatures between 297 and 527 K at a nearly constant total pressure of 100 Torr. In Fig. 1 are shown sample kinetic data obtained from the experiments plotted according to Eq. (4) for the reaction of Cl with CHCl₃ and CDCl₃ measured with respect to CH₃Br at 527 K. The kinetic expression obtained by Piety et al. [24] describing the temperature dependence of the rate constant for the reaction CH₃Br + Cl \rightarrow CH₂Br + HCl of k₃/cm³ molecule⁻¹ s⁻¹ = 3.32 × 10⁻¹² × (*T*/298)^{1.42} × exp(-605/*T*) was utilized in our experiments. The results of the measurements were analyzed using a weighted least squares procedure which included uncertainties in 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 six temperatures (297, 326, 337, 383, 448, and 527 K) are gathered in Table 1.

Fig. 2 shows the Arrhenius plot of $k_{\rm H}$ and $k_{\rm D}$. There is little scattering of experimental points around the regression lines, which indicates a satisfactory repeatability of the experiments. The temperature dependence of the rate constant $k_{\rm H}$ can be expressed in the temperature range of 297–527 K as:

$$k_{\rm H} = (4.8 \pm 0.5) \times 10^{-12} \times \exp(-1160 \pm 30/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$$
(5)

with the 2σ error limits. The value of $(1.0 \pm 0.2) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ of $k_{\rm H}$ derived from the above expression at room temperature is in good agreement with available kinetic data. Our value of $k_{\rm H}$ is only slightly lower than those of 1.1×10^{-13} , 1.2×10^{-13} , and



Fig. 3. Arrhenius plot for the CHCl₃ + Cl reaction comparing available results of kinetic measurements. The solid line corresponds to the plot of Eq. (5).

 1.4×10^{-13} cm³ molecule⁻¹ s⁻¹ obtained by Catoire et al. [15], Beichert et al. [12] and Brahan et al. [13], and Orlando [16], respectively. It is also very close to the values of 1.1×10^{-13} [22] and 1.2×10^{-13} cm³ molecule⁻¹ s⁻¹ [23] recommended by recent kinetic data evaluations. However, these evaluations probably do not take into account results of the newest study by Bryukov et al. [17], who obtained a value of 9.5×10^{-14} cm³ molecule⁻¹ s⁻¹ at room temperature. This value is also very close to that found in our study. Only the results of the oldest and probably least credible experiments [8,9] deviate distinctly from our estimates. The values of 4.1×10^{-14} cm³ molecule⁻¹ s⁻¹ obtained by Knox et al. [8] and 3.2×10^{-13} cm³ molecule⁻¹ s⁻¹ by Clyde and Walker [9] mark out the lower and upper limits of the reported experimental measurements.

The magnitude of the exponential parameter in Eq. (5) indicates a low value of the activation energy for the reaction studied. This implies a weak dependence of $k_{\rm H}$ on temperature. However, there are only a few measurements of $k_{\rm H}$ at temperatures considerably higher than ambient, so the temperature dependence of $k_{\rm H}$ is less recognized. Results of former kinetic measurements are compared in Fig. 3. The most credible investigations were performed by Bryukov et al. [17], who did a thorough study of the reaction kinetics in the range of 297–854 K. Our value of 2.6×10^{-13} cm³ molecule⁻¹ s⁻¹ derived from Eq. (5) at 400 K is in good agreement with the values of 2.4×10^{-13} of Bryukov et al. [17] and 2.5×10^{-13} cm³ molecule⁻¹ s⁻¹ of Talhaoui et al. [14]. At a temperature of 500 K our $k_{\rm H}$ reached a value of 4.7×10^{-13} cm³ molecule⁻¹ s⁻¹. This is also in line with the estimate of



Fig. 4. Comparison of the derived values of the kinetic isotope effect $k_{\rm H}/k_{\rm D}$ (\bullet – experimental points). The full line represents the plot of Eq. (7)) with results obtained by Clyne and Walker [9].

 $4.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by Bryukov et al. [17] and confirms the reliability of the rate constant $k_{\rm H}$ and its dependence on temperature derived in this study.

The kinetic analysis of the experiments performed for the reaction of deuterated chloroform with chlorine leads to the expression

$$K_{\rm D} = (6.4 \pm 2.1) \times 10^{-12} \times \exp(-1660 \pm 110/T) \,\mathrm{cm^3 \, molecule^{-1} \, s^{-1}}$$
(6)

which is also valid in the temperature range of 297-527 K. The abstraction of deuterium from CDCl₃ proceeds distinctly more slowly than the abstraction of a hydrogen atom from unsubstituted chloroform. The value of k_D of $(2.6 \pm 0.9) \times 10^{-14} \text{ cm}^3$ molecule⁻¹ s⁻¹ at room temperature is one fourth of that of $k_{\rm H}$ at 298 K. The significance of the kinetic isotope effect declines with rising temperature. At 500 K the value of KIE only slightly exceeds 2. The temperature dependence of KIE, described by the ratio $k_{\rm H}/k_{\rm D}$, can be expressed in the form

$$k_{\rm H}/k_{\rm D} = (0.77 \pm 0.25) \times \exp(500 \pm 95/T)$$
 (7)

The derived values of KIE are in line with the results of Clyne and Walker [9]. As can be seen in Fig. 4, the agreement is good, especially at higher temperatures. The largest difference in the values of KIE occurs at the lowest temperatures of both studies, i.e. at room temperature. However, even in this case the difference does not exceed 20% of the KIE value. This supports the reliability of the derived temperature dependence of KIE.

4. Conclusion

The rate constants and their temperature dependence for the reactions of chlorine atoms with CHCl₃ and CDCl₃ were estimated using the relative rate method. Isotopic substitution distinctly changes the reaction rate. The rate constant for the reaction of Dchloroform is consequently several times lower than that of Habstraction from CHCl₃. The kinetic isotope effect distinctly depends on temperature. The results of our investigations are in very good accordance with the recently reported measurements and values recommended by kinetic data evaluations. The analytical kinetic expressions derived in this study allow a successful description of the reaction kinetics and KIE in a wide range of temperature, which has significant importance for modelling of the kinetics of complex reaction systems in the gas phase.

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