

Kinetic study of the reaction of chlorine atoms with dichloromethane and D-dichloromethane in the gas phase

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ABSTRACT

The kinetics of the gas-phase reactions of chlorine atoms with dichloromethane (CH_2Cl_2) and D-dichloromethane (CD_2Cl_2) was studied using the relative rate method with $\text{Cl} + \text{CH}_3\text{Br}$ as the reference reaction. The rate constants for H-abstraction from CH_2Cl_2 (k_{H}) and D-abstraction from CD_2Cl_2 (k_{D}) were measured in the temperature range of 298–527 K and at a total pressure of 100 Torr using N_2 as a diluent. The temperature dependencies of the rate constants (with the 2σ error limits) are described by the expressions: $k_{\text{H}} = (8.69 \pm 0.82) \times 10^{-12} \times \exp(-955 \pm 20/T)$ and $k_{\text{D}} = (6.98 \pm 0.91) \times 10^{-12} \times \exp(-1285 \pm 25/T)$ cm^3 molecule $^{-1}$ s $^{-1}$. The kinetic isotope effect, described by the ratio $k_{\text{H}}/k_{\text{D}}$, was found of 3.8 ± 0.2 at room temperature.

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1. Introduction

Chlorine atoms are important stratospheric species, and they participate extensively in ozone destruction cycles. The reactions of the hydrogen abstraction from hydrocarbons and halogenated hydrocarbons by chlorine atoms have received considerable attention related with the search for possible sinks for photochemically produced chlorine atoms in the atmosphere [1]. Chloroalkanes and products of their atmospheric reactions are considered as toxic and biocumulative species. Dichloromethane (CH_2Cl_2) is amongst the most abundant chlorine-containing compounds in the atmosphere [1–3]. It is primarily released from industrial processes associated with such industrial activity as the production of polycarbonate resins and urethane foam, plastic fabrication, the paint industry and the food industry as an extraction solvent for spices, caffeine and hops.

The atmospheric lifetime of dichloromethane estimated to be of 5–6 months is long enough to enable a part of CH_2Cl_2 to survive transport through the lower atmosphere and reach the stratosphere [4]. The fate of atmospheric CH_2Cl_2 is primarily determined by degradation processes in the troposphere, especially by its reaction with OH radicals. However, the reaction CH_2Cl_2 with OH is relatively slow with the rate constant of 1.0×10^{-13} cm^3 molecule $^{-1}$ s $^{-1}$ at 298 K [5,6]. In the marine boundary layer and polar regions where the concentration of chlorine atoms is significant, the Cl-initiated degradation of dichloromethane becomes of some importance in the competition with the reaction of hydroxyl

radicals [7]. The hydrogen abstraction reaction from dichloromethane by chlorine atoms



has been the subject of several experimental [8–15] and theoretical [16–19] studies. The reported room-temperature values of the rate constant, k_{H} , for reaction (1) estimated by different experimental techniques agree very well. The most recent IUPAC and NASA evaluations of the kinetic data recommend very similar values for k_{H} at 298 K of $(3.4 \pm 0.3) \times 10^{-13}$ [5] and $(3.5 \pm 0.3) \times 10^{-13}$ cm^3 molecule $^{-1}$ s $^{-1}$ [6], respectively. Less consistent are the results of the temperature dependence of k_{H} . The kinetic investigations performed in the widest range of temperature by Clyne and Walker (298–621 K) [9], Tschuikow-Roux et al. (273–368 K) [11] and Bryukov et al. (296–790 K) [15] predict distinctly different dependence on temperature of the rate constant. Therefore, a credible estimation of the temperature dependence of k_{H} was among the main aims of our investigations.

In this letter, we present the results of kinetic measurements of the rate constant for reaction (1) in the relatively wide temperature range of 298–527 K in order to examine the temperature dependence of k_{H} and values of the activation energy available in literature. To the best of our knowledge there is no information on the kinetics of the deuterated dichloromethane with atomic chlorine. The reaction of entirely deuterated dichloromethane (CD_2Cl_2) with Cl atoms



was also included in our kinetic investigation. The independent measurements of the rate constants k_{H} and k_{D} for the H/D-abstraction from $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$ performed in the same temperature range

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enabled us to determine the kinetic isotope effect (KIE), and its dependence on temperature. The derived values of KIE can provide useful information for interpreting the stable isotope composition of the organic compounds in the atmosphere.

2. Experimental

The gas-phase reactions of chlorine atoms with dichloromethane and D-dichloromethane were investigated using reaction with bromomethane as the reference in the temperature range of 298–527 K. The experiments were carried out in a greaseless static system using a cylindrical Pyrex reactor of ca. 150 cm³ (dead volume ~2%) placed in an aluminum heating block. The 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 heating block. A chromo-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 °C during the experiment. The reactants were introduced into the cell by expansion, starting from the mixture of CH₂Cl₂ in CH₃Br or CD₂Cl₂ in CH₃Br followed by the mixture of Cl₂ in N₂ to a total pressure of 100 Torr. The mixture of CH₂Cl₂ in CH₃Br or CD₂Cl₂ in CH₃Br were prepared before every set of measurements in one temperature and was kept for 12 h before the first use. The ratio of concentration of CH₂Cl₂ or CD₂Cl₂ to CH₃Br was around 1:1.

All experiments were carried out at a total pressure of 100 Torr with the partial pressure of Cl₂ varying from 9.3 to 9.8 Torr. At the temperature of 298 K, the set of the experiments for the reaction of CH₂Cl₂ + Cl and CD₂Cl₂ + Cl has been repeated at the total pressure of 750 Torr. At the temperature of 528 K the set of the analogous experiments has been repeated at total pressure 50, 200 and 750 Torr for the reaction CH₂Cl₂ + Cl and at total pressure of 750 Torr for the reaction CD₂Cl₂ + Cl. The partial pressure of CH₂Cl₂, CD₂Cl₂ and CH₃Br were in the range of 4.4–5.6 Torr. The mixture of Cl₂ in N₂ were prepared (at least 24 h before the first use) from pure Cl₂ (>99.5%) and N₂ (>99.999%) and stored in a 4 L blackened Pyrex bulb. The reactants CH₂Cl₂, CD₂Cl₂ and CH₃Br were degassed using the freeze–pump–thaw method before the mixtures CH₂Cl₂/CH₃Br and CD₂Cl₂/CH₃Br were prepared. The mixtures were stored under vacuum in light-tight containers. The pressure was measured by a Model 127A 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 a Czerny-Turner optical system (dispersing element: 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 the reactor, was reflected back by a 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. In order to obtain the highest possible Cl atoms concentration, the photolysis of Cl₂ at 330 nm was used as a Cl atoms source. At this wavelength the molar extinction coefficient for Cl₂ is the highest [20]. The irradiation time (0.25–60 min) and band width (5, 10, 15 or 20 nm) varied depending on the reaction temperature in order to obtain appropriate conversion of the reactants.

The loss of the reactants and products formation were monitored by chromatograph (HP, Model 5890 Series II) with thermal conductivity detector using 30 m long × 0.53 mm Restek Rt-Q-PLOT capillary column with temperature–time programming

between 100 and 200 °C with helium as the carrier gas. Before and after the experiments calibrations of the peak area of CH₂Cl₂ or CD₂Cl₂ and CH₃Br vs. its partial pressures were determined by GC analysis. The reactants used in this letter and their minimal stated purity were CH₂Cl₂ (99.8%) from Sigma–Aldrich, CD₂Cl₂ (99.9%), CH₃Br (99.5%), Cl₂ (99.5%) from Aldrich, N₂ (99.999%) from BOC. The reaction reagents were purified three times using the freeze–pump–thaw method.

3. Results and discussion

The kinetics of the reactions under investigation was analyzed using the relative rate method. This experimental approach is based on the competition between two reactants reacting with the same reactive species. The H-abstraction from bromomethane by chlorine atoms



was selected as the reference reaction. If two reactants CH₂Cl₂ (or CD₂Cl₂) and CH₃Br react with chlorine atoms, and assuming that reaction with Cl atoms is the only significant loss for both reactants, it can be shown that

$$\ln \frac{[\text{CX}_2\text{Cl}_2]_0}{[\text{CX}_2\text{Cl}_2]_t} = \frac{k_X}{k_3} \cdot \ln \frac{[\text{CH}_3\text{Br}]_0}{[\text{CH}_3\text{Br}]_t} \quad (4)$$

where k_3 denotes the rate constant for the reaction (3), X = H or D, and the subscripts 0 or t indicate the concentrations of the reactants at the beginning of the experiment and at a given time t , respectively. The plot of $\ln([\text{CX}_2\text{Cl}_2]_0/[\text{CX}_2\text{Cl}_2]_t)$ vs. $\ln([\text{CH}_3\text{Br}]_0/[\text{CH}_3\text{Br}]_t)$ should be linear, which enables a determination of the rate constant ratio k_X/k_3 as the slope and, finally, k_H or k_D using values of k_3 from the equation

$$k_3 = (1.43 \pm 0.22) \times 10^{-11} \times \exp(-1040 \pm 30/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

derived earlier in our laboratory [21]. The reference reaction CH₃Br + Cl was the subject of many experimental investigations [11,21–26]. The room-temperature values of the rate constant k_3 obtained by the different experimental techniques are very similar. However, at higher temperatures the results of the kinetic measurements show some dispersion. The temperature dependence of k_3 recommended by NASA [6] is derived from experiments conducted at temperatures of 298 K and below. Results of the study of Piety et al. [25] performed in the widest temperature range of 161–697 K indicate a distinct non-Arrhenius behavior of the reaction kinetics at high temperatures. However, the other experimental investigations which were carried out at lower temperatures do not show curvature of the Arrhenius plot [11,21–24]. The results of our earlier measurements obtained in the same temperature range of 298–527 K [21] show only very little dispersion around the Arrhenius' line. This lends support to using Eq. (5) in the description of kinetics of the reference reaction.

In order to test for possible photolysis or thermal decomposition of the organic reactants, mixtures of the organics were irradiated for more than 60 min in the absence of Cl₂ at every temperature used. No photolysis or thermal decomposition of CH₂Cl₂, CD₂Cl₂ and CH₃Br were observed. Prior to each set of experiments at temperatures above 298 K, tests for dark reactions were performed. Prepared mixtures of organic species and molecular chlorine were allowed to stand in the dark for at least 60 min. At temperatures of 450 K and lower, the reaction of the organic species with molecular chlorine was negligible in the absence of photolytic light. No products of a 'dark' reaction were detected. At the highest temperature (527 K) the thermal decomposition of Cl₂ was observed. In this case we used the thermal decomposition of Cl₂ as

the Cl atoms source for experiments with low organics conversion. In the experiments with the highest conversion of the organics, the UV lamp was on in order to obtain the highest possible Cl atoms concentration which shortens the reaction time.

The rate constants of the studied reactions were determined at five temperatures in the temperature range of 298–527 K at a nearly constant total pressure of 100 Torr. At a temperature of 298 K, the experiments for the reaction $\text{CH}_2\text{Cl}_2 + \text{Cl}$ and $\text{CD}_2\text{Cl}_2 + \text{Cl}$ were also repeated at a total pressure of 750 Torr in order to check the pressure dependence of the rate constants. For the same reason, at a temperature of 527 K the measurements were repeated at a total pressure of 750 Torr for the reaction $\text{CD}_2\text{Cl}_2 + \text{Cl}$, and at total pressures of 50, 200 and 750 Torr for the reaction of $\text{CH}_2\text{Cl}_2 + \text{Cl}$.

Figure 1 shows sample kinetic data obtained from the experiments at 450 K plotted according to Eq. (4) for the reaction of Cl atoms with CH_2Cl_2 and CD_2Cl_2 measured with respect to CH_3Br . The results of the measurements were analyzed using a weighted least squares procedure, which allowed a zero point offset. The values of the offset were always negative with the absolute value lower than 0.03 in every experiment. The values of the ratios k_{H}/k_3 and

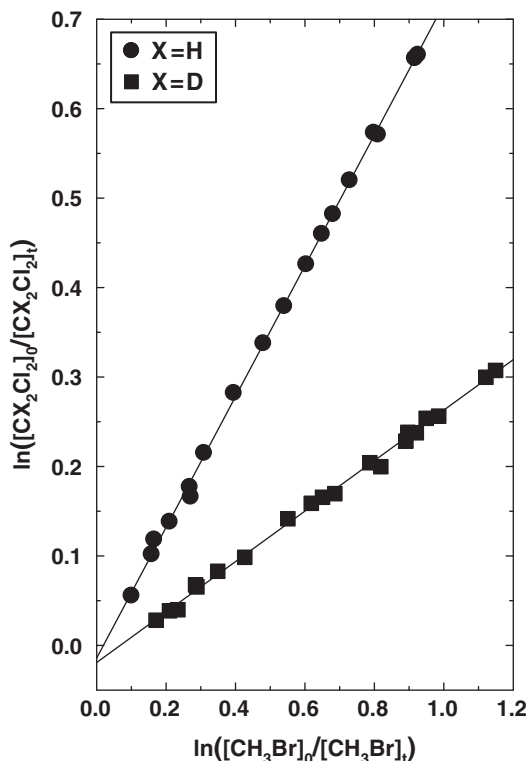


Figure 1. Relative rate data obtained at 450 K and a pressure of 100 Torr for the reactions of Cl with CH_2Cl_2 (●) and CD_2Cl_2 (■) using CH_3Br as the reference compound.

Table 1

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

T (K)	$k_{\text{H}}/k_3^{\text{a}}$	$10^{13} \times k_{\text{H}}^{\text{b}}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	$k_{\text{D}}/k_3^{\text{a}}$	$10^{13} \times k_{\text{D}}^{\text{b}}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	$k_{\text{H}}/k_{\text{D}}^{\text{a}}$
298	0.809 ± 0.009	3.53 ± 0.22	0.215 ± 0.010	0.936 ± 0.095	3.77 ± 0.21
325	0.798 ± 0.008	4.65 ± 0.34	0.221 ± 0.015	1.29 ± 0.13	3.61 ± 0.29
385	0.773 ± 0.013	7.39 ± 0.69	0.261 ± 0.013	2.49 ± 0.32	2.96 ± 0.20
450	0.731 ± 0.011	10.4 ± 1.1	0.282 ± 0.007	3.99 ± 0.45	2.59 ± 0.10
527	0.711 ± 0.012	14.2 ± 1.6	0.307 ± 0.016	6.14 ± 0.91	2.31 ± 0.16

^a With 2σ error limits.

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

k_{D}/k_3 as well as the derived absolute values of the k_{H} and k_{D} are presented in Table 1. The results of measurements conducted at different temperatures show no pressure dependence of kinetics of the investigated reactions. The differences in values of the ratios k_{X}/k_3 obtained at total pressures between 50 and 750 Torr do not exceed 3% of the values of k_{H}/k_3 and k_{D}/k_3 at 298 and 527 K. This level of discrepancy is lower or comparable with value of the experimental error.

The Arrhenius plot for the reaction studied is shown in Figure 2. The temperature dependence of the overall rate constant k_{H} for $\text{CH}_2\text{Cl}_2 + \text{Cl}$ reaction can be expressed in the temperature range of 298–527 K as:

$$k_{\text{H}} = (8.69 \pm 0.82) \times 10^{-12} \times \exp(-955 \pm 20/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

with the 2σ error limits. Our room temperature value of k_{H} of $(3.5 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is in excellent agreement with value of the absolute rate determinations of $(3.5 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ of Bryukov et al. [15] and $(3.2 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Beichert et al. [12] but it is distinctly lower compared to the older estimates of $(5.5 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ of Davis et al. [8] and $(7.5 \pm 1.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ derived by Clyne and Walker [9].

The quality of results obtained by the relative rate method is determined by the reliability of the reference kinetic parameters. However, the obtained results can easily be corrected in the case of the appearance of new, more credible and recommended kinetic data related to the reference reaction. Using the reaction $\text{CH}_3\text{Cl} + \text{Cl}$ as reference, Niki et al. [10] have obtained the value of k_{H} at 298 K of $(3.8 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. That value can be corrected to $(3.6_5 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ when the ratio of the rate constants $k_{\text{H}}/k(\text{CH}_3\text{Cl} + \text{Cl})$ measured by Niki et al. [10] is multiplied by the current value of $k(\text{CH}_3\text{Cl} + \text{Cl})$ of $4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ recommended by IUPAC [5].

The reaction $\text{CH}_4 + \text{Cl}$ has frequently been used as the reference in kinetic experiments. The kinetics of $\text{CH}_4 + \text{Cl}$ was the subject of many experimental investigations conducted in a wide temperature range using different experimental techniques. The agreement among most of these studies is very good. The recent IUPAC [5] and NASA [6] evaluations of the kinetic data recommend the same value of the rate constant for $\text{CH}_4 + \text{Cl}$ of $1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Using the recommended value of $k_{298}(\text{CH}_4 + \text{Cl})$ leads to only small changes of the original results of the relative rate measurements. The value of $(3.2 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Tschuikow-Roux et al. [11] can be corrected in this way to $(3.3 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and that of $(3.2 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ derived by Beichert et al. [12] modified to $(3.4_5 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The results of $(3.5 \pm 0.1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Catoire et al. [13] and that of $(3.2 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ of Orlando [14] were obtained on basis of the current value of the rate constant for the reference reaction $\text{CH}_4 + \text{Cl}$.

A part of experiments of Orlando [14] has been conducted with $\text{CH}_3\text{Br} + \text{Cl}$ used as the reference reaction. The value of k_{H} of $(3.4 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K was derived in his investigations using the still valid value of $k_{298}(\text{CH}_3\text{Br} + \text{Cl})$. The insert of Figure 2 shows a comparison of the experimental results obtained near room temperature. With the exception of the oldest and probably least credible measurements of Davis et al. [8] and Clyne and Walker [9] the results of the other experiments are very similar to the experimental points focused on a very narrow area of the plot despite the large scale of the insert. Our k_{H} -value of $(3.5 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 is in excellent agreement with those of $(3.4 \pm 0.3) \times 10^{-13}$ [5] and $(3.5 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [6] recommended by the IUPAC and NASA evaluations, respectively.

The comparison of the rate constants for the reaction of chlorine atoms with methane and chloromethanes is very interesting. The first chlorine atom substituted to methane distinctly increases the rate of the H-abstraction process, which is reflected in the values of the rate constant. The value of the rate constant of $(1.0 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [5,6] at 298 K recommended for reaction $\text{CH}_4 + \text{Cl}$ is over five times lower than that of $(5.2 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [27] obtained for $\text{CH}_3\text{Cl} + \text{Cl}$. However, a substitution of the subsequent chlorine atoms decreases reactivity of the chlorinated methanes towards atomic chlorine. This is confirmed by our estimate of k_{H} of $(3.5 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $\text{CH}_2\text{Cl}_2 + \text{Cl}$ and the still lower value of $(1.0 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [28] derived for the reaction $\text{CHCl}_3 + \text{Cl}$, which is equal to the value of the rate constant for reaction $\text{CH}_4 + \text{Cl}$.

The rate of reactions of the halogenated methanes with chlorine atoms depends also on the kind of halogen atoms substituted to the methane molecule. The values of the rate constants for reactions of the bi-substituted halogenated methanes CH_2X_2 (X = F, Cl

and Br) available in literature show a substantial dispersion. Despite the existing divergences, the reported k_{H} -values derived at 298 K for reactions $\text{CH}_2\text{F}_2 + \text{Cl}$, $\text{CH}_2\text{Cl}_2 + \text{Cl}$ and $\text{CH}_2\text{Br}_2 + \text{Cl}$ are in ascending order as: $(3.2\text{--}5.0) \times 10^{-14}$ [5,6], $(3.5 \pm 0.2) \times 10^{-13}$ (this letter) and $(4.3 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [6], respectively. This comparison made for the reactions of Cl atoms with substituted methanes CH_2X_2 (X = F, Cl and Br) shows a rise in k_{H} -values with the increasing dimension of the halogen atom X.

The reported room-temperature values of the rate constant, k_{H} , obtained by different experimental techniques are very similar. Considerably less consistent are the results of the temperature dependence of k_{H} , which expressed in the Arrhenius form show distinct differences in the values of both the pre-exponential factor and the activation energy. The reported values of the activation energy cover a range of 6.4–12.1 kJ mol^{-1} [9,11,14,15]. The results of the most recent experiments of Bryukov et al. [15] predict non-Arrhenius behavior of the reaction kinetics at the high-temperature range, i.e. above 500 K. The kinetic data evaluations recommend using an activation energy of 7.1 kJ mol^{-1} [5] and 7.6 kJ mol^{-1} [6] for the description of the temperature dependence of k_{H} at a temperature below 400 K.

Figure 2 shows a comparison of the former measurements of k_{H} in a wide temperature range. The temperature dependence of k_{H} described by Eq. (6) is related to the activation energy of 7.9 kJ mol^{-1} . It implies a slightly stronger temperature dependence of the rate constant than predicted by the IUPAC and NASA kinetic data evaluations [5,6]. The Arrhenius plot based on the experimental data published since 1980 is denoted in Figure 2 by the dotted line. The slope of the line, which describes the average temperature dependence of the rate constants k_{H} over the temperature range 222–790 K, corresponds to the activation energy of 8.6 kJ mol^{-1} . This value is only by 0.7 kJ mol^{-1} higher than the one derived from our measurements.

With the exception of the results of Clyne and Walker [9], which systematically overestimate k_{H} , the other values of the rate

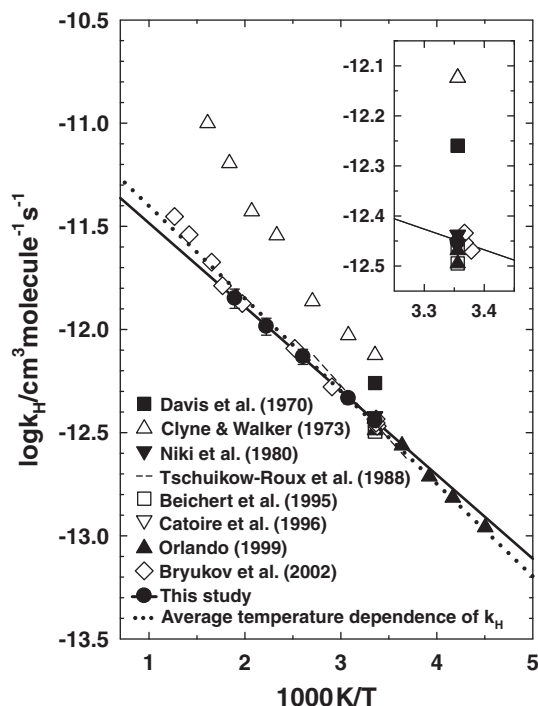


Figure 2. Arrhenius plot for the $\text{CH}_2\text{Cl}_2 + \text{Cl}$ reaction comparing the available results of kinetic measurements. The solid line corresponds to the plot of Eq. (6). The dotted line denotes the Arrhenius plot based on the experimental data published since 1980. The insert shows experimental results obtained near room temperature. Results of the relative rate measurements shown in the insert have been recalculated using the current values of the rate constants of the reference reactions $\text{CH}_3\text{Cl} + \text{Cl}$, $\text{CH}_4 + \text{Cl}$ and $\text{CH}_3\text{Br} + \text{Cl}$ (see the text).

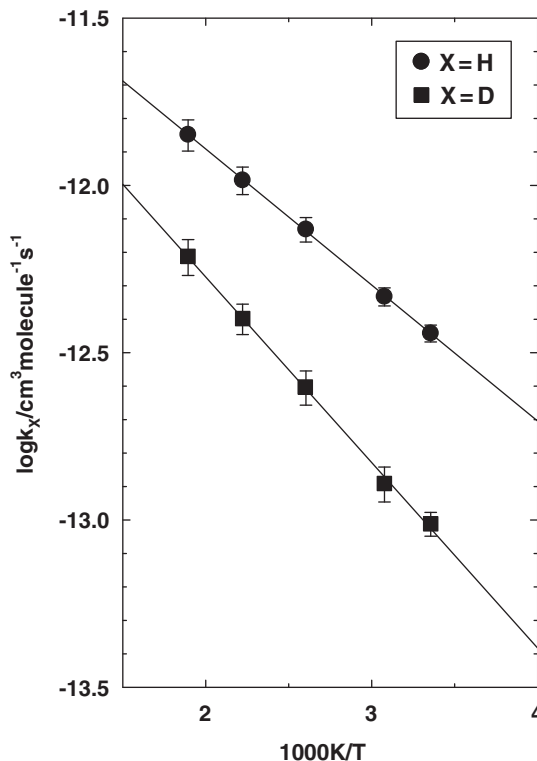


Figure 3. Arrhenius plot for the reactions of CH_2Cl_2 (●) and CD_2Cl_2 (■) with Cl atoms in the temperature range from 298 to 527 K.

constant obtained at temperatures below 550 K, are located around the trend line derived in this letter, with little dispersion. At the high temperature range, i.e. above 550 K, the results of Bryukov et al. [15] are greater than those obtained from Eq. (6). The temperature dependence of the rate constant k_H derived by Bryukov et al. [15] is steeper in this temperature range and shows non-Arrhenius behavior. Unfortunately, there are no other credible measurements which can verify the results of their high temperature experiments. However, the other investigations which were carried out at lower temperatures do not show curvature of the Arrhenius plot [11,14]. Only a little scattering of the experimental points around the regression line described by Eq. (6) confirms the reliability of the values of our rate constant k_H and its dependence on temperature. The Arrhenius parameters derived in this letter provide a successful description of the reaction kinetics in a wide temperature range.

The Arrhenius plot for the reaction $CD_2Cl_2 + Cl$ is shown in Figure 3. The temperature dependence for the reaction of deuterated dichloromethane with chlorine atoms was determined in this letter for the first time. The kinetic analysis of the experimental results in the temperature range of 298–527 K leads to the following temperature dependence of the rate constant k_D :

$$k_D = (6.98 \pm 0.91) \times 10^{-12} \times \exp(-1285 \pm 25/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (7)$$

where the error limits represent 2σ statistical uncertainties. The abstraction of deuterium from CD_2Cl_2 by Cl atom proceeds distinctly more slowly than H atom abstraction from CH_2Cl_2 .

In Figure 4 is shown the temperature dependence of the rate constants k_H and k_D of the reactions of chlorine atoms with a series of chloromethanes (deuterated chloromethanes). The results presented in the figure were derived in our laboratory [27,28] using the same experimental technique. This enables us to make a reliable comparison of the relative reactivity of chloromethanes

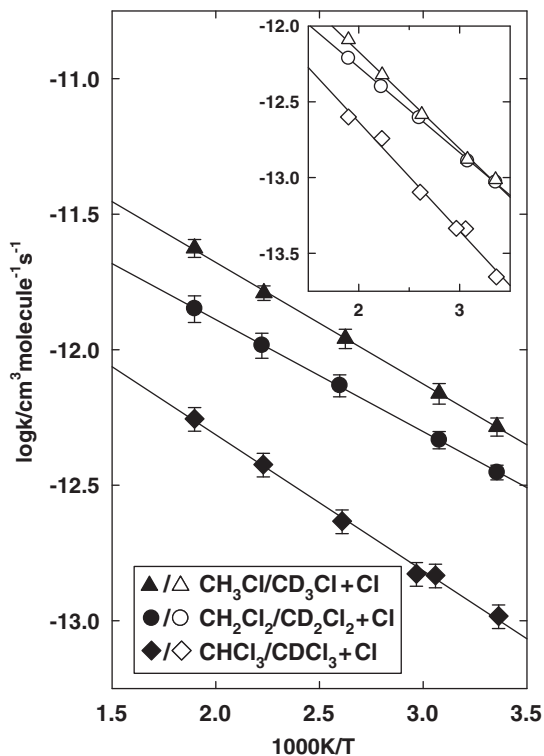


Figure 4. Comparison of the temperature dependence of the rate constants, k_H and k_D (in the insert) obtained for the reactions: $CH_3Cl/CD_3Cl + Cl$ [27], $CH_2Cl_2/CD_2Cl_2 + Cl$ (this letter) and $CHCl_3/CDCl_3 + Cl$ [28].

towards atomic chlorine. The Arrhenius' lines in Figure 4 are almost parallel which implies very similar heights of the energy barrier for all reactions under investigation. The values of the activation energy are relatively small and cover the narrow range of 7.9–9.6 kJ mol⁻¹ [27,28]. This shows that the substitution of the subsequent chlorine atom to chloromethane has only a little influence on the height of the energy barrier for the hydrogen abstraction reaction. The difference in the number of chlorine atoms in the reactant molecule is, however, reflected in values of the rate constants. The substitution of the next electronegative atom to the reactant molecule leads to increase of the electrostatic repulsion between reactants resulting in the descending order of the rate constants, as $k_H(CH_3Cl + Cl) > k_H(CH_2Cl_2 + Cl) > k_H(CHCl_3 + Cl)$. At room temperature the values of k_H are of $(5.2 \pm 0.4) \times 10^{-13}$ [27], $(3.5 \pm 0.2) \times 10^{-13}$ (this letter) and $(1.0 \pm 0.1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [28] for $CH_3Cl + Cl$, $CH_2Cl_2 + Cl$ and $CHCl_3 + Cl$, respectively.

The similar trends in values of the rate constants are also expected for reactions of the other halomethanes with chlorine atoms. This class of reactions has been the subject of many experimental studies [5,6]. The available experimental data show, however, substantial scattering in the values of the rate constants, k_H . The most credible and preferable for the kinetic analysis are then the results of measurements obtained by the same research group and using the same experimental method.

The hydrogen abstraction reactions from bromomethanes $CH_3Br/CH_2Br_2/CHBr_3 + Cl$ were investigated by Kambanis et al. [24] in the temperature range of 273–363 K. The values of k_H derived by Kambanis et al. [24] show the analogous order as in the case of the reactions of chloromethanes, and at 298 K are of 4.6×10^{-13} , 4.0×10^{-13} and $2.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [24] for $CH_3Br + Cl$, $CH_2Br_2 + Cl$ and $CHBr_3 + Cl$, respectively. The reactions of fluoromethanes with atomic chlorine were studied by different research groups using various methodology and experimental techniques [29–33]. Despite the discrepancies in

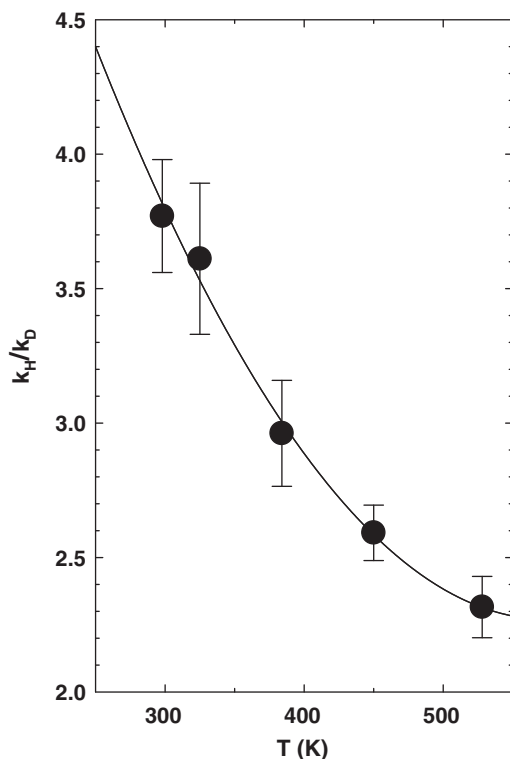


Figure 5. Comparison of the derived values of the kinetic isotope effect k_H/k_D in the temperature range from 298 to 527 K.

experimental results, values of the rate constants, k_H at 298 K of $(3.2\text{--}4.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $\text{CH}_3\text{F} + \text{Cl}$ [29–31], $(3.2\text{--}6.8) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($\text{CH}_2\text{F}_2 + \text{Cl}$) [31,32] and $4.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($\text{CHF}_3 + \text{Cl}$) [33] are in line with the general trend in k_H -values for reactions of the H-abstraction from the other halomethanes by chlorine atoms. The kinetic data for the reactions of iodomethanes with chlorine atoms are still incomplete. However, recent kinetic studies [34,35] show a complex reaction mechanism. The hydrogen abstraction from iodomethanes could either proceed directly in a bimolecular reaction or indirectly via the formation of a weakly bound adduct, which then decomposes via HCl elimination.

The abstraction of deuterium is related with the higher energy barrier comparing to the hydrogen abstraction reaction. The activation energy of 10.7 kJ mol^{-1} derived for $\text{CD}_2\text{Cl}_2 + \text{Cl}$ is 2.8 kJ mol^{-1} higher than that for the reaction $\text{CH}_2\text{Cl}_2 + \text{Cl}$. Consequently, values of the rate constant k_D are lower than k_H , and furthermore, k_D depends on a temperature slightly higher than k_H . Our value of k_D of $(9.7 \pm 1.0) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature is almost four times less than that of k_H at 298 K. The experimental measurements of k_H/k_3 and k_D/k_3 were done at the same temperatures, which allows us to calculate values of the kinetic isotope effect (KIE), described by the ratio k_H/k_D , directly from the results of the relative rate measurements. The room temperature value of KIE is 3.8 ± 0.2 . However, the significance of KIE is distinctly reduced with rising temperature (see Figure 5), and at the highest temperature of this letter (527 K), the derived value of KIE is 2.3 ± 0.2 .

It is interesting to compare the available values of KIE for reactions of atomic chlorine with chloromethanes. The values of KIE of 5.4 ± 0.3 [27] for $\text{CH}_3\text{Cl}/\text{CD}_3\text{Cl} + \text{Cl}$, 3.8 ± 0.2 for $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2 + \text{Cl}$ derived in this letter, and 4.7 ± 0.6 [28] for $\text{CHCl}_3/\text{CDCl}_3 + \text{Cl}$ are considerably lower than the 17.5 ± 2.5 [5,6] estimated for $\text{CH}_4/\text{CD}_4 + \text{Cl}$ at room temperature. An explanation of the reported values of KIE needs theoretical calculations that enable insight into the molecular structure and properties of the reactants during the reaction. The results presented in this letter complete the kinetic data for the reactions of chloromethanes with chlorine atoms: $\text{CH}_3\text{Cl}/\text{CD}_3\text{Cl} + \text{Cl}$, $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2 + \text{Cl}$ and $\text{CHCl}_3/\text{CDCl}_3 + \text{Cl}$ obtained previously in our laboratory using the same experimental technique, the same reference reaction and performed in the same temperature range. These results are valuable reference data, useful in the evaluation of the rate constants using the computational methods of the reaction rate theory.

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