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Temperature dependence of the kinetic isotopic effect of the reaction of Cl atoms with C_2H_5Cl between 298 and 550 K

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ABSTRACT

The kinetics of the gas-phase reactions of chlorine atoms with chloroethane and chloroethane-d₅ was studied experimentally. The relative rate method was applied using Cl + CH₃Cl as the reference reaction. The overall rate constants for H-abstraction from C₂H₅Cl ($k_{\rm H}$), D-abstraction from C₂D₅Cl ($k_{\rm D}$), the site-specific rate constants for H-abstraction from α -carbon ($k_{\rm H,\alpha}$) and β -carbon ($k_{\rm H,\beta}$) atoms of C₂H₅Cl were measured in the temperature range of 298–550 K at a total pressure of 100 Torr. The derived temperature dependencies of the rate constants are given by $k_{\rm H} = (2.41 \pm 0.21) \times 10^{-11} \times \exp(-316 \pm 11/T)$, $k_{\rm H,\alpha} = (1.36 \pm 0.09) \times 10^{-11} \times \exp(-202 \pm 8/T)$, $k_{\rm H,\beta} = (1.14 \pm 0.11) \times 10^{-11} \times \exp(-592 \pm 16/T)$ and $k_{\rm D} = (1.58 \pm 0.14) \times 10^{-11} \times \exp(-474 \pm 13/T) \, {\rm cm}^3$ molecule⁻¹ s⁻¹. The values of the kinetic isotope effect, $k_{\rm H}/k_{\rm D}$ were also estimated.

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1. Introduction

The reactions of atomic chlorine may become the major path of the tropospheric oxidation of simple organics. In some conditions, the lifetimes of chlorinated alkanes are determined by chlorine atom reactions. These reactions are very sensitive to temperature and isotopic substitution. Chloroalkanes and products of their atmospheric reactions are considered a toxic, persistent and biocumulative species [1]. Chloroethane (C₂H₅Cl) is a relatively short lived compound that occurs in the Earth's atmosphere as the result of either anthropogenic activity or natural emission [2,3]. However, identification and quantification of the natural and anthropogenic sources of chloroethane are poorly estimated. Ethyl chloride is in common use in the chemical industry as an intermediate. solvent. refrigerant, in flame retardants and foam plastic production [1–3]. The natural sources of C₂H₅Cl include the microbial degradation of other chlorination solvents in soil system and metabolic processes in phytoplankton [2,3].

The dominant loss process of the atmospheric C_2H_5Cl is reaction with OH radicals, coupled with an atmospheric lifetime of about 1 month [2,3]. The radicals CH₃CHCl and CH₂CH₂Cl formed after the H-abstraction from C_2H_5Cl rapidly add molecular oxygen to form the corresponding peroxy radicals. It is well established that the reactions of OH radicals with many organics proceed considerably slower than the analogous reactions of Cl atoms [4,5]. Therefore, in the marine boundary layer and in polar regions where the concentration of chlorine atoms is significant, the reactions of chlorine atoms are growing in importance and may play a key role in

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the decay of many organic compounds in the troposphere [1]. The kinetics of the reaction of chloroethane with chlorine atoms,

$$CH_3CH_2CI + CI \rightarrow CH_3CHCI + HCI$$
(1a)

$$\rightarrow CH_2CH_2Cl + HCl \tag{1b}$$

has been the subject of several experimental [6–17] and theoretical studies [18,19]. Abstraction of an H-atom occurs at two sites, and kinetics of the competitive reaction channels, (1a) and (1b) is described by the rate constants, $k_{\rm H,\alpha}$ and $k_{\rm H,\beta}$, respectively. Results of the experimental investigations show substantial scatter in the values of the measured rate constants, with distinct, however, domination of the H-abstraction from the $-CH_2CI$ group of chloroethane. The reported values of $k_{\rm H,\alpha}$ at room temperature cover a range of $(3.0-8.1) \times 10^{-12} \, {\rm cm}^3$ molecule⁻¹ s⁻¹ [7,8,13,15,16] and are about four times higher than the values of $k_{\rm H,\beta}$, which describes the H-abstraction from the $-CH_3$ group.

In this Letter we present measurements of the site-specific, $k_{H,\alpha}$ and $k_{H,\beta}$, and overall $k_H = k_{H,\alpha} + k_{H,\beta}$ rate constants for the hydrogen abstraction reaction CH₃CH₂Cl + Cl using the relative rate technique. The experiments were performed in the temperature range of 298–550 K to examine the temperature dependence of the rate constants and the values of the activation energy available in literature. The reaction of the entirely deuterated chloroethane,

$$CD_3CD_2Cl + Cl \rightarrow CD_3CDCl + DCl$$
(2a)

$$\rightarrow CD_2CD_2Cl + DCl \tag{2b}$$

was also included in our kinetic investigation. The independent measurements of the overall rate constant $k_D = k_{2a} + k_{2b}$ for reactions (2a) and (2b) enabled us to determine the kinetic isotope



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effect (KIE) defined by the ratio of $k_{\rm H}/k_{\rm D}$, and its dependence on temperature. KIE values can provide useful information for interpreting the stable isotope composition of the organic compounds in the atmosphere [20,21].

2. Experimental

The gas phase reactions of chlorine atoms with chloroethane and deuterated chloroethane- d_5 were investigated using reactions with chloromethane as the reference in the temperature range of 298–550 K. The experiments were carried out in a greaseless static system using a cylindrical quartz 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 K during the experiment.

The reactants were introduced into the cell by expansion, starting from the mixture of C₂H₅Cl in CH₃Cl or C₂D₅Cl in CH₃Cl followed by the mixture of Cl_2 in N_2 to a total pressure of 100 Torr. The mixtures of C₂H₅Cl with CH₃Cl or C₂D₅Cl with CH₃Cl were kept for 12 h before the first use. The ratio of concentrations of C₂H₅Cl or C₂D₅Cl to CH₃Cl were around 1:2 in all experiments. In the case of investigations of the kinetics of $C_2H_5Cl + Cl$ at the temperature 550 K, the ratio of concentrations of C₂H₅Cl to CH₃Cl was around 1:1. All experiments were carried out at a total pressure of 100 Torr with the partial pressure of Cl₂ varying from 4.5 to 4.9 Torr. At the temperature of 298 and 529 K the set of experiments for reactions of C₂H₅Cl + Cl and C₂D₅Cl + Cl has been repeated at a total pressure of 750 Torr. The partial pressure of C₂H₅Cl and C₂D₅Cl were in the range of 1.6-1.7 Torr, and for CH₃Cl were in the range 3.3-3.4 Torr in all experiments. Only for the reaction of C₂H₅Cl + Cl at the temperature 550 K the partial pressure of C₂H₅Cl and CH₃Cl were in the range 2.3–2.4 and 2.6–2.7 Torr, respectively. The mixture of Cl₂ in N_2 were prepared (at least 24 h before the first use) from pure Cl_2 (>99.5%) and N₂ (>99.999%) and stored in a 4 L blackened Pyrex bulb. The reactants C₂H₅Cl, C₂D₅Cl and CH₃Cl were used directly from the lecture bottles to prepare the mixtures C₂H₅Cl/CH₃Cl and C₂D₅Cl/CH₃Cl. The mixtures were stored under vacuum in the light-tight Pyrex containers. The compounds CH₂ClCH₂Cl, CH₃₋ CHCl₂ and CH₂Cl₂ (the primary photolysis products of the reactions $C_2H_5Cl + Cl$ and $CH_3Cl + Cl$) were degassed using the freeze-pumpthaw method and stored under vacuum in light-tight small containers. These compounds were used for calibration of the primary reaction products of the photolysis system $C_2H_5Cl/CH_3Cl + Cl_2/N_2$, when relative rate method based on the products analysis was used. 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 line consisted of a manually operated shutter, a condensing lens, a variable-width slit, and monochromator with a Czerny–Tunner 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 were used as a Cl atoms source. At this wavelength the molar extinction coefficient for Cl₂ is the highest [22]. The irradiation time (0.25–15 min) and band width (5, 10, 15 or 20 nm) were 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 gas chromatography (HP, Model 5890 Series II) with thermal conductivity detector using 30 m long × 0.53 mm Restek Rt-Q-PLOT capillary column with temperature programming between 80 and 200 °C with helium as the carrier gas.

Before and after experiments the calibrations of the peak areas of either reactants, $(C_2H_5Cl, C_2D_5Cl \text{ and } CH_3Cl)$ or products $(CH_2-ClCH_2Cl, CH_3CHCl_2 \text{ and } CH_2Cl_2)$ vs. their partial pressures were determined by GC analysis. The reactants used in this study and their minimal stated purity were as follows: C_2H_5Cl (99.7%), C_2D_5Cl (>98%), CH_3Cl (>99.5%), CH_2Cl_2 (99.8%), Cl_2 (>99.5%) from Aldrich, CH_2ClCH_2Cl (>99.9%) and CH_3CHCl_2 (>99.3%) from Fluka, N_2 (>99.999%) from BOC.

3. Results and discussion

The kinetics of the reaction $C_2H_5Cl + Cl$ was analyzed using the related rate method. This experimental approach is based on the competition between two reactants reacting with the same reactive species. The H-abstraction from chloromethane by chlorine atoms,

$$CH_3Cl + Cl \rightarrow CH_2Cl + HCl$$
 (3)

was selected as the reference reaction. If two reactants C_2H_5Cl (or C_2D_5Cl) and CH_3Cl react with chlorine atoms, and assuming that reaction with Cl atoms is the only significant loss for both reactants, it can be shown that,

$$\ln \frac{\left[C_2 X_5 C I\right]_0}{\left[C_2 X_5 C I\right]_t} = \frac{k_X}{k_3} \cdot \ln \frac{\left[C H_3 C I\right]_0}{\left[C H_3 C I\right]_t}$$
(4)

where k_3 denotes the rate constant for the reaction (3), k_X is the overall rate constant describing decay of the reactant C₂X₅Cl (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 relative rate constant ratio k_X/k_3 can easily be derived from the slope of the plot $\ln([C_2X_5CI]_0/[C_2X_5CI]_t)$ vs. $\ln([CH_3CI]_0/[CH_3CI]_t)$, and finally the value of k_X when k_3 is known with sufficient accuracy.

Eq. (4) enables a determination of the overall rate constants, $k_{\rm H}$ and $k_{\rm D}$, which describe the rate of decay of the respective reactants, C_2H_5Cl and C_2D_5Cl in their reactions with atomic Cl. The estimation of the site-specific rate constants, $k_{\rm H,\alpha}$ and $k_{\rm H,\beta}$ needs a comparison of the rate of formation of the given channel product of reaction (1), i.e. CH₃CHCl or CH₂CH₂Cl with the rate of formation of the product of the reference reaction (3).

The general scheme for gas-phase photochlorination reactions is well established [23–25]. In the case of photochlorination of C_2H_5Cl in the presence of CH_3Cl , the radical products of the reactions (1a), (1b) and (3) are only consumed in reaction with molecular chlorine,

$$CH_3CHCl + Cl_2 \rightarrow CH_3CHCl_2 + Cl \tag{5a}$$

$$CH_2CH_2Cl + Cl_2 \rightarrow CH_2ClCH_2Cl + Cl$$
(5b)

$$CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl \tag{5c}$$

because of the large excess of Cl₂ in the reaction system. The monitoring of the rate of formation of CH₃CHCl₂, CH₂ClCH₂Cl and CH₂Cl₂ enables a determination of the site-specific rate constants based on the assumption that dichloromethane and both dichloroethanes are only formed in the reactions (5a), (5b), and (5c), so that $[C_2H_5Cl]_0 = [C_2H_5Cl]_t + [CH_3CHCl_2]_t + [CH_2ClCH_2Cl]_t$ and $[CH_3Cl]_0 =$ $[CH_3Cl]_t + [CH_2Cl_2]_t$. At the low conversion of reactants of reactions (1a), (1b) and (3) the site-specific rate constants, $k_{H,\alpha}$ and $k_{H,\beta}$, can be easily derived from the expressions:

$$\frac{k_{\mathrm{H},\alpha}}{k_3} = \frac{[\mathrm{CH}_3\mathrm{Cl}]_0}{[\mathrm{C}_2\mathrm{H}_5\mathrm{Cl}]_0} \cdot \frac{[\mathrm{CH}_3\mathrm{CH}\mathrm{Cl}_2]_t}{[\mathrm{CH}_2\mathrm{Cl}_2]_t} \tag{6a}$$

and

$$\frac{k_{\mathrm{H},\beta}}{k_3} = \frac{[\mathrm{CH}_3\mathrm{Cl}]_0}{[\mathrm{C}_2\mathrm{H}_5\mathrm{Cl}]_0} \cdot \frac{[\mathrm{CH}_2\mathrm{Cl}\mathrm{CH}_2\mathrm{Cl}]_t}{[\mathrm{CH}_2\mathrm{Cl}_2]_t}$$
(6b)

In all our experiments the highest conversion of the C₂H₅Cl was always lower than 10% (usually it was around 5%). The conversion of CH₃Cl was always lower than that for C₂H₅Cl. The above expressions give an opportunity for an additional comparison of the values of the overall rate constant, $k_{\rm H}$ calculated as the sum of $k_{\rm H,\alpha} + k_{\rm H,\beta}$ with values obtained from Eq. (4).

The reference reaction $CH_3Cl + Cl$ was the subject of many experimental studies [4,5] but only four of them cover the temperature range of this Letter. The kinetic results obtained by Sarzyński et al. [26] in our laboratory can be considered the best compromise for all reported experimental points obtained below 500 K. Therefore, we decided to use the expression derived in that study,

$$k_3 = (1.7 \pm 0.1) \times 10^{-11} \times \exp(-1040 \pm 10/T)$$
 cm³molecule⁻¹s⁻¹ (7)

which describes the temperature dependence of k_3 obtained using the same apparatus, the same temperature range and analogous experimental methodology as for the studied $C_2H_5Cl/C_2D_5Cl + Cl$ reaction systems.

To test for possible photolysis or thermal decomposition of the organic reactants, mixtures of the organics (C₂H₅Cl, C₂D₅Cl and CH₃Cl) were irradiated in the absence of Cl₂ at the highest temperature used for more than 60 min. The same procedure was repeated for the products of the reactions (CH₃CHCl₂, CH₂ClCH₂Cl and CH₂Cl₂). No photolysis or thermal reaction of the reactants or products were observed. Prior to each set of experiments at temperatures above 298 K. test for a dark reaction were performed. Prepared mixtures of organic species (reactants or products) and molecular chlorine were allowed to stand in a dark for at least 60 min. At the temperature of 451 K and lower, the reaction of organic species with molecular chlorine were negligible in the absence of photolytic light. No products of a thermal reaction were detected. At the highest temperatures of this study the thermal decomposition of Cl₂ was observed. At these temperatures, in some experiments with low conversion of the reactants, the thermal decomposition of Cl₂ was used as the Cl-atom source.

The kinetics of the reactions $C_2H_5Cl + Cl$ and $C_2D_5Cl + Cl$ was investigated at five temperatures in the temperature range of 298-529 K, and at a nearly constant total pressure of 100 Torr. The reaction C₂H₅Cl + Cl has been also studied at the temperature 550 K. At the temperatures of 298 and 529 K, the experiments were also repeated at a total pressure of 750 Torr in order to check the pressure dependence of the rate constants. No pressure dependence of the rate constants of the reactions under investigation was observed in the range of pressures 100-750 Torr. Figure 1 shows sample kinetic data obtained from the experiments performed at 451 K plotted according to Eq. (4) for the reaction of Cl atoms with C₂H₅Cl and C₂D₅Cl measured with respect to CH₃Cl + Cl. The results of the measurements were analyzed using least squares procedure which allowed zero point offset. The linearity of the plots shown in the Figure 1 supports the assumption that the organic reactants are consumed only in reaction with chlorine atoms.

The final products of the reactions $C_2H_5Cl + Cl$ and $CH_3Cl + Cl$ obtained at very low conversions of reactants were identified by comparison with chromatograms of GC standards of CH_3CHCl_2 ,



Figure 1. Relative rate data obtained at 451 K and a pressure of 100 Torr for the reactions of Cl atoms with C_2H_5Cl (\bigcirc) and C_2D_5Cl (\square) using CH₃Cl as the reference compound.

CH₂ClCH₂Cl and CH₂Cl₂. Any secondary reaction products were not detected under our experimental conditions. Results of the kinetic measurements performed at six temperatures (298, 337, 383, 451, 529 and 550 K) are gathered in Table 1.

The Arrhenius plots for the reaction channels C_2H_5 -Cl + Cl \rightarrow CH₃CHCl + HCl and C_2H_5 Cl + Cl \rightarrow CH₂CH₂Cl + HCl are shown in Figure 2. The temperature dependence of the site-specific rate constants, $k_{H,\alpha}$ and $k_{H,\beta}$ corresponding to the H-abstraction from α or β carbon atoms of C_2H_5 Cl can be expressed in the temperature range of 298–550 K as:

$$\begin{split} k_{\rm H,\alpha} &= (1.36\pm0.09)\times10^{-11}\times \exp(-202\pm8/T) \quad {\rm cm}^3{\rm molecule}^{-1}{\rm s}^{-1} \quad (8{\rm a}) \\ k_{\rm H,\beta} &= (1.14\pm0.11)\times10^{-11}\times \exp(-592\times16/T) \quad {\rm cm}^3{\rm molecule}^{-1}{\rm s}^{-1} \quad (8{\rm b}) \end{split}$$

where the error limits represent 2σ statistical uncertainties. The reported experimental results presented in Figure 2 show distinct domination of the H_{α} -reaction channel. Our average room temperature value of the site-specific rate constant, $k_{\mathrm{H},\alpha}$ of $(6.8\pm0.7)\times10^{-12}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ can be compared with the other estimates. The value of the overall rate constant, $k_{\rm H}$ of $(7.6 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K is obtained by Bryukov et al. [16]. The values of the ratio $k_{\rm H,\alpha}/k_{\rm H,\beta}$ obtained in different experimental studies are very close to each other. With the widely accepted value of $k_{\rm H,\alpha}/k_{\rm H,\beta}$ of 82% at room temperature the result of measurements of Bryukov et al. [16] corresponds to value of $k_{\rm H,\alpha}$ of $(6.3\pm0.4)\times10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$ at 296 K. This is in good agreement with value of $k_{\rm H,\alpha}$ derived in this study. This is also similar to the result of $(6.0 \pm 0.7) \times 10^{-12}$ obtained by Maricq et al. [13], and that of $(5.8\pm0.2)\times10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$ derived by Niedzielski et al. [8]. The value of the overall rate constant $k_{\rm H}$ of $(8.1 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ of Dobis and Benson [15] is}$ equivalent to $k_{\rm H,\alpha}$ -value of $(6.6 \pm 0.4) \times 10^{-12} \,\rm cm^3 \,molecule^{-1} \, s^{-1}$ which is very close to our evaluation of $k_{H,\alpha}$. The values of the overall rate constant, $k_{\rm H}$ describing the decay of C₂H₅Cl in the reaction with Cl atoms of $(1.15 \pm 0.15) \times 10^{-11}$ [9] and $(1.19 \pm 0.17) \times 10^{-11} [10] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ obtained at } 295 \text{ K by}$

Table 1	
The measured rate constant ratios $k_{\rm H,\alpha}/k_3$, $k_{\rm H,\beta}/k_3$, $k_{\rm H}/k_3$, and $k_{\rm D}/k_3$, the absolute values of $k_{\rm H,z}$, $k_{\rm H,\beta}$, $k_{\rm H}$ and $k_{\rm D}$, and the derived values of the kinetic isotope effect $k_{\rm H}/k_{\rm D}$. ^a

Т	$k_{\mathrm{H},\alpha}/k_3$	$k_{\mathrm{H},\mathrm{\beta}}/k_{\mathrm{3}}$	$k_{\rm H}/k_3$	$k_{\rm D}/k_3$	$10^{12} imes k_{ m H,lpha}$	$10^{12} imes k_{ m H, eta}$	$10^{12} imes (k_{\mathrm{H},lpha}$ + $k_{\mathrm{H},eta})$	$10^{12} imes k_{ m H}$	$10^{12} \times k_{\rm D}$	$k_{\rm H}/k_{\rm D}$
(K)					(cm ³ molecul	(cm ³ molecule ⁻¹ s ⁻¹)				
298	13.3 ± 0.8	2.94 ± 0.18	16.0 ± 0.6	6.34 ± 0.21	6.90 ± 0.78	1.52 ± 0.17	8.42 ± 0.95	8.32 ± 0.75	3.29 ± 0.11	2.55 ± 0.22
298 ^b	13.1 ± 0.6	2.94 ± 0.22	15.2 ± 0.5	5.98 ± 0.11	6.79 ± 0.67	1.52 ± 0.19	8.31 ± 0.86	7.86 ± 0.67	3.10 ± 0.22	2.61 ± 0.14
337	9.81 ± 0.43	2.61 ± 0.11	12.5 ± 0.4	5.03 ± 0.16	7.58 ± 0.56	2.01 ± 0.14	9.60 ± 0.70	9.63 ± 0.61	3.89 ± 0.24	2.47 ± 0.17
383	7.32 ± 0.18	2.20 ± 0.10	9.86 ± 0.23	4.05 ± 0.07	8.22 ± 0.47	2.47 ± 0.19	10.7 ± 0.7	11.1 ± 0.6	4.54 ± 0.24	2.39 ± 0.10
451	5.26 ± 0.15	1.85 ± 0.06	7.31 ± 0.17	3.29 ± 0.06	8.88 ± 0.57	3.13 ± 0.22	12.0 ± 0.8	12.4 ± 0.7	5.55 ± 0.30	2.19 ± 0.14
529	3.87 ± 0.15	1.57 ± 0.07	5.71 ± 0.16	2.72 ± 0.05	9.20 ± 0.72	3.73 ± 0.30	12.9 ± 1.0	13.6 ± 0.9	6.46 ± 0.38	2.05 ± 0.11
529 ^b	3.88 ± 0.12	1.50 ± 0.06	5.65 ± 0.07	2.69 ± 0.04	9.22 ± 0.66	3.56 ± 0.28	12.8 ± 0.9	13.4 ± 0.7	6.38 ± 0.36	2.06 ± 0.08
550	3.66 ± 0.12	1.45 ± 0.05	5.38 ± 0.06		9.38 ± 0.70	3.73 ± 0.27	13.0 ± 1.0	13.8 ± 0.7		
550	3.69 ± 0.10	1.53 ± 0.05			9.48 ± 0.63	3.93 ± 0.29				

^a With 2σ statistical uncertainties.

^b Experiments were performed at a total pressure of 750 Torr.



Figure 2. Arrhenius plots for the reaction channels: $C_2H_5CI + CI \rightarrow CH_3CHCI + HCI$ (α -channel) and $C_2H_5CI + CI \rightarrow CH_2CH_2CI + HCI$ (β -channel). The error limits represent 2σ . The results of relative experiments of Niedzielski et al. [8] obtained using the temperature dependence of the rate constant for the reference reaction $CH_4 + CI$ given by Keyser [30] are denoted by the dotted line. The dashed line describes results of Niedzielski et al. [8] converted on the base of the temperature dependence of k($CH_4 + CI$) derived by Pilgrim et al. [31].

Wallington et al. [9,10] corresponds to the highest experimentally estimated values of $k_{\rm H,\alpha}$ of $(9.4 \pm 1.2) \times 10^{-12}$ and $(9.7 \pm 1.4) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, respectively. On the other hand, the value of $(3.0 \pm 0.6) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ obtained by Tschuikow-Roux et al. [7] is distinctly lower than the other estimates and gives the bottom limit of the experimental results of $k_{\rm H,\alpha}$ at 298 K. Therefore, our evaluation of $k_{\rm H,\alpha}$ value at 298 K seems to be realistic, taking into account dispersion of the experimental results.

The temperature dependence of $k_{\rm H,\alpha}$ was studied by various experimental techniques in a wide temperature range of 280– 810 K, and the reported values of the activation energy are very similar to that of 3.4–3.8 kJ mol⁻¹ [7,8,16]. The results of our measurements predict a weaker temperature dependence of $k_{\rm H,\alpha}$ corresponding to the activation energy of 1.7 kJ mol⁻¹ for H_{α}-abstraction. The experiments of Bryukov et al. [16] were performed over the widest temperature range but their results indicate a non-Arrhenius behavior of the kinetics of reaction $C_2H_5Cl + Cl$. The similar curvature of the Arrhenius' plots were also reported by Bryukov et al. [27] for reactions of chloromethanes CH_3Cl, CH_2Cl_2 and $CHCl_3$ with atomic chlorine. Unfortunately, there are no other credible measurements which can verify the results of the high-temperature experiments of Bryukov et al. [27] obtained for reactions of chloromethanes with chlorine atoms. The other experimental studies [26,28,29] do not confirm non-Arrhenius behavior of the kinetics of these reactions at temperatures below 500 K.

The quality of results obtained by the relative rate method is determined by the reliability of the reference kinetic parameters. 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. The relative rate study of the H_{α} -abstraction was conducted by Tschuikow-Roux et al. [7] and Niedzielski et al. [8] in the temperature range of 280-368 K using the results of kinetic investigations of Keyser [30] for the reference reaction $CH_4 + Cl$. The temperature dependence of $k(CH_4 + Cl)$ derived by Keyser [30] is steeper than that found in the recent measurements [4,5]. The most credible description of the kinetics of CH_4 + Cl in this temperature range is that given by Pilgrim et al. [31], which can be utilized to conversion of the results of Niedzielski et al. [8]. Converted this way, the results of measurements of Niedzielski et al. [8] denoted by the dashed line in Figure 2, predict a distinctly weaker dependence on temperature of $k_{\rm H,\alpha}$ than that given in their study (marked by a dotted line).

The abstraction of the hydrogen from the β carbon atom of C₂H₅Cl proceeds considerably slower than the H_{\alpha}-abstraction. The value of $k_{\rm H,\beta}$ of $(1.5 \pm 0.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ derived in this study at room temperature is over four times lower compared with $k_{\rm H,\alpha}$. This corresponds to the ratio of $k_{\rm H,\alpha}/(k_{\rm H,\alpha} + k_{\rm H,\beta})$ at 298 K of 82%, exactly the same as obtained by Tschuikow-Roux et al. [7] and Orlando and Tyndall [14]. Our room temperature value of $k_{\rm H,\beta}$ is in good agreement with the estimates of $(1.3 \pm 0.1) \times 10^{-12}$ of Bryukov et al. [16], of $(1.2 \pm 0.1) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ obtained by Tschuikow-Roux et al. [7] and Niedzielski et al. [8].

The kinetics of H_{β} -abstraction from C_2H_5Cl by Cl atoms was previously studied in a wide temperature range of 220–1650 K [7,8,16,17]. The temperature dependencies of $k_{H,\beta}$ expressed in the Arrhenius form show some differences in the reported values of both the pre-exponential factor and activation energy. The reported values of the activation energy cover range of 4.4– 7.2 kJ mol⁻¹. These differences can be related with the regeneration of Cl atoms at higher temperatures as a consequence of the fast thermal decompositions of radical products with a chlorine atom in the β position. For this reason the measurements of the site-specific rate constant, $k_{H,\beta}$ performed by Bryukov et al. [16] were limited to the temperature range of 296–378 K. We did not observe the thermal decomposition of CH₂CH₂Cl under our experimental conditions, probably because of the high concentration of Cl₂ molecules resulting in the very high rate of the reaction CH₂. CH₂Cl + Cl₂. In addition, the H_β-abstraction channel product, CH₂. ClCH₂Cl was always detected among the photoreaction products. Our value of the activation energy of 4.9 kJ mol⁻¹ is very close to the most recently derived of 4.4 kJ mol⁻¹ by Wakamatsu and Hida-ka [17] and of 4.7 kJ mol⁻¹ by Orlando and Tyndall [14].

The values of the overall rate constant, $k_{\rm H}$ can be calculated as the sum of the site-specific rate constants, $k_{\rm H,\alpha}$ and $k_{\rm H,\beta}$ associated with the H_{\alpha} and H_{\beta} reaction channels. However, $k_{\rm H}$ can also be evaluated from measurements of the decay rate of reactants, C₂H₅Cl and CH₃Cl according to Eq. (4). As it is shown in Table 1, the values of the overall rate constant, $k_{\rm H}$ derived from Eq. (4) and those obtained from Eqs. (6a) and (6b) as the sum of $k_{\rm H,\alpha}$ and $k_{\rm H,\beta}$ are very similar. The greatest differences do not exceed 3% and 5% at 451 and 529 K, respectively. The temperature dependence of the average overall rate constant, $k_{\rm H}$ calculated on the base of Eq. (4) and (6) can be expressed in the form:

$$k_{\rm H} = (2.41 \pm 0.21) \times 10^{-11} \times \exp(-316 \pm 11/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$
 (9)

in the temperature range of 298–550 K. The Arrhenius plot comparing available results of kinetic measurements is shown in Figure 3. Our average room temperature value of $k_{\rm H}$ is $(8.2 \pm 0.8) \times 10^{-12} \,{\rm cm}^3$ molecule⁻¹ s⁻¹ is very close to $(8.0 \pm 0.6) \times 10^{-12} \,{\rm cm}^3$ molecule⁻¹ s⁻¹ obtained by Wine and Semmes [6], of $(8.1 \pm 0.4) \times 10^{-12} \,{\rm cm}^3$ molecule⁻¹ s⁻¹ of Dobis and Benson [15], and that of $(7.6 \pm 0.4) \times 10^{-12} \,{\rm cm}^3$ molecule⁻¹ s⁻¹ of Bryukov et al. [16]. It is also in reasonable agreement with $(7.1 \pm 0.4) \times 10^{-12} \,{\rm cm}^3$ molecule⁻¹ s⁻¹ derived as the sum of $k_{\rm H,\alpha}$ and $k_{\rm H,\beta}$ values of Niedzielski et al. [8] and that of $(6.8 \pm 1.4) \times 10^{-12} \,{\rm cm}^3$ molecule⁻¹ s⁻¹ determined by Kaiser et al. [11]. The results of measurements of Wallington et al. of $(1.15 \pm 0.15) \times 10^{-11} \,{\rm cm}^3$ molecule⁻¹ s⁻¹ [9]

and $(1.19 \pm 0.17) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [10] are distinctly overestimated.

The reported temperature dependence of the overall rate constant $k_{\rm H}$ shows some divergence. The values of the activation energy of $k_{\rm H}$ cover the range of 2.6–6.2 kJ mol⁻¹ [6–8,14,16]. Our value of 2.6 kJ mol⁻¹ indicates a weak temperature dependence of the overall rate constant, $k_{\rm H}$. Except for findings of Bryukov et al. [16] the temperature dependence of $k_{\rm H}$ derived in this study very well describes the reported results of kinetic measurements performed over a wide temperature range and using different experimental techniques. A comparison of the values of the overall rate constant $k_{\rm H}$ and the site-specific rate constants, $k_{\rm H,\alpha}$ and $k_{\rm H,\beta}$ is given in Table 1. The differences in values of $k_{\rm H}$ derived from measurements of the rate of reactants decay and products formation are small, do not exceed 5% at the highest temperature of this Letter. This indirectly proves that the thermal decomposition of CH₂₋ CH₂Cl radicals is only negligible under our experimental conditions. C₂H₄ was not detected among the stable products of the reaction studied.

The temperature dependence of the rate constant, k_D for the reaction of entirely deuterated chloroethane- d_5 with chlorine atoms was determined by measurements of the rate of decay of C_2D_5Cl in the reaction with Cl atoms. The reaction of $CH_3Cl + Cl$ was also used as the reference. All experimental data are gathered in Table 1. The kinetic analysis of the experimental results leads to the following Arrhenius expression,

$$k_{\rm D} = (1.58 \pm 0.14) \times 10^{-11} \times \exp(-474 \pm 13/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$
 (10)

valid in the temperature range of 298–529 K. The abstraction of deuterium from C_2D_5Cl by Cl atom proceeds distinctly more slowly than H-abstraction from C_2H_5Cl and is related with the higher activation energy. Figure 4 shows, however, that the increase in activation energy is small, especially when compared to that observed for



Figure 3. Arrhenius plot for the $C_2H_5Cl + Cl$ reaction comparing the available results of kinetic measurements. The solid line corresponds to the plot of Eq. (9). Results of Niedzielski et al. [8] are denoted by the dotted and dashed lines analogously as in Figure 2.



Figure 4. Comparison of the temperature dependence of the rate constants, $k_{\rm H}$ and $k_{\rm D}$ for C₂H₅Cl/C₂D₅Cl + Cl reaction systems. The diamonds (\diamond) and (\blacklozenge) denotes values of $k_{\rm H}$ in the temperature range of 298–550 K obtained from Eqs. (4) and (6), respectively. The symbols (\bigcirc) corresponds to values of $k_{\rm D}$ derived from Eq. (4) in the range of 298–529 K.

the reactions of deuterated chloromethanes, $CH_3Cl/CD_3Cl + Cl$, CH_2 - $Cl_2/CD_2Cl_2 + Cl$ and $CHCl_3/CDCl_3 + Cl$ [26,28,29].

The abstraction of deuterium from deuterated chloroethanes was studied in detail by Tschuikow-Roux's research group [7,8,32–34] in the temperature range 280–367 K to establish the kinetic isotope effects (KIE) for the abstraction of the primary and secondary hydrogen/deuterium atoms. The values of the site-specific rate constants, $k_{D,\alpha}$ and $k_{D,\beta}$ derived by Tschuikow-Roux and Niedzielski [32] show distinct domination of the D_{α} abstraction channel. Their ratio of $k_{\mathrm{D},\alpha}/k_{\mathrm{D},\beta}$ of 12.1 obtained at 298 K is threefold greater than value of $k_{\rm H,\alpha}/k_{\rm H,\beta}$. In consequence, values of KIE at room temperature for H/D-abstraction from the α - and β -carbons in CH₃CH₂Cl and CD₃CD₂Cl show distinct difference. Tschuikow-Roux and Niedzielski [32] show that the values of KIE for the H_{α}/D_{α} -abstraction from CH₃CH₂Cl/CD₃CD₂Cl by Cl atoms are found around 2.0 in the temperature range of 281-367 K. The kinetic study of Niedzielski et al. [8] for the reaction of chloroethane-1-d₁, CH₃CHDCl with Cl also confirm very weak temperature dependence of KIE for the α -abstraction. Their results of KIE for α -abstraction of 1.85₅ at 280 K, 1.83 at 298 K and 1.66 at 365 K are close to the other estimates [7,32-34]. The abstraction of hydrogen or deuterium from the β -carbon of CH₃CH₂Cl/CD₃CD₂Cl is related to distinctly higher values of KIE compared to the abstraction from α -carbon atom. The values of KIE for the β abstraction obtained by Tschuikow-Roux and Niedzielski [32] are of 6.2, 5.8 and 4.9 at 281, 298 and 367 K, respectively. This is in line with the rule that for two hydrogen abstraction channels the higher isotope effect will be observed for the one with the higher activation energy.

Figure 5 shows a comparison of the temperature dependence of the overall KIE obtained in this study expressed by $k_{\rm H}/k_{\rm D}$ with values of $(k_{\rm H,\alpha} + k_{\rm H,\beta})/(k_{\rm D,\alpha} + k_{\rm D,\beta})$ derived by Tschuikow-Roux et al. [7] denoted by the dashed line. The values of the overall KIE are closer to values of $k_{\rm H,\alpha}/k_{\rm D,\alpha}$ than $k_{\rm H,\beta}/k_{\rm D,\beta}$ because of distinct domination of the α -abstraction channel. Our room temperature value of KIE



Figure 5. Comparison of the values of the kinetic isotope effect k_H/k_D for $C_2H_5Cl/C_2D_5Cl + Cl$ obtained by Tschuikow-Roux et al. [7] (dashed line), with results derived in this study (\bigcirc) and values of KIE obtained by Sarzyński et al. [35] for $C_2H_5Br/C_2D_5Br + Cl$ (...) reaction systems.

of 2.6 ± 0.2 is in good agreement with that of 2.3 ± 0.3 obtained by Tschuikow-Roux et al. [7]. The overall KIE values only weakly depend on temperature. At the temperature of 529 K, our value of the overall KIE, described by the ratio $k_{\rm H}/k_{\rm D}$, diminishes to 2.05 ± 0.09. However, in contrast to our measurements, the results of Tschuikow-Roux et al. [7] predict a very small increase of the overall KIE with increasing temperature. Their value of $(k_{\rm H,\alpha} + k_{\rm H,\beta})/(k_{\rm D,\alpha} + k_{\rm D,\beta})$ of 2.31 derived at 280 K increases to 2.34 at 368 K.

The values of KIE derived in this study can be compared with those obtained for the $C_2H_5Br/C_2D_5Br + Cl$ reaction system [35] denoted in Figure 5 by the dotted line. The abstraction of hydrogen or deuterium by Cl atoms from chloroethane proceeds faster than from bromoethane. The value of KIE for C₂H₅Br/C₂D₅Br + Cl of 3.2 ± 0.8 at 298 K decreases to 2.0 ± 0.4 when the temperature rises to 529 K [35]. The temperature dependence of KIE for bromoethane is considerably stronger than that found for chloroethane. All the changes in the molecular properties of the reactants related to the substitution of a hydrogen atom by deuterium are reflected in the values of the rate constant. An explanation and a detailed interpretation of the derived values of the KIE is difficult without the theoretical investigations which enable insight into the molecular structure and properties of the reactants during the reaction. The experimental results presented in this Letter 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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