Theoretical study of the kinetics of chlorine atom abstraction from chloromethanes by atomic chlorine

Katarzyna Brudnik · Maria Twarda · Dariusz Sarzyński · Jerzy T. Jodkowski

Received: 31 October 2012 / Accepted: 21 January 2013 / Published online: 2 March 2013
© The Author(s) 2013. This article is published with open access at Springerlink.com

Abstract Ab initio calculations at the G3 level were used in a theoretical description of the kinetics and mechanism of the chlorine abstraction reactions from mono-, di-, tri- and tetrachloromethane by chlorine atoms. The calculated profiles of the potential energy surface of the reaction systems show that the mechanism of the studied reactions is complex and the Cl-abstraction proceeds via the formation of intermediate complexes. The multi-step reaction mechanism consists of two elementary steps in the case of CCl₄ + Cl, and three for the other reactions. Rate constants were calculated using the theoretical method based on the RRKM theory and the simplified version of the statistical adiabatic channel model. The temperature dependencies of the calculated rate constants can be expressed, in temperature range of 200–3,000 K as:

\[ k(\text{CH}_3\text{Cl} + \text{Cl}) = 2.08 \times 10^{-11} \times (T/300)^{1.63} \times \exp(-12780/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \]
\[ k(\text{CH}_2\text{Cl}_2 + \text{Cl}) = 2.36 \times 10^{-11} \times (T/300)^{1.37} \times \exp(-10960/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \]
\[ k(\text{CHCl}_3 + \text{Cl}) = 5.28 \times 10^{-11} \times (T/300)^{0.97} \times \exp(-9200/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \]
\[ k(\text{CCl}_4 + \text{Cl}) = 1.51 \times 10^{-10} \times (T/300)^{0.08} \times \exp(-7790/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \]

The rate constants for the reverse reactions CH₃/CH₂Cl/CHCl₂/CCl₃ + Cl₂ were calculated via the equilibrium constants derived theoretically. The kinetic equations allow a very good description of the reaction kinetics. The derived expressions are a substantial supplement to the kinetic data necessary to describe and model the complex gas-phase reactions of importance in combustion and atmospheric chemistry.

Keywords Chemical kinetics · Gas-phase reactions · Reaction mechanism · Chlorine abstraction · Chloromethanes

Introduction

Chlorinated alkanes are used widely in laboratory syntheses and in the chemical industry [1]. As a consequence, they are penetrating into the environment in steadily increasing amounts. Chloroalkanes and products of their environmental reactions are considered toxic and biocumulative species. The chemical inertness and high volatility of chloromethanes mean that they can remain in the atmosphere for a very long time. The products of the atmospheric destruction of chloromethanes have been proven to have a significant impact on chlorine chemistry in the atmosphere and may be involved in various catalytic reaction cycles responsible for the depletion of the stratospheric ozone layer [1, 2].

Monochloromethane (CH₃Cl) is regarded as the most abundant halocarbon in the troposphere, and the largest natural source of stratospheric chlorine [1, 3]. The variability of CH₃Cl in the ice core over the last two millennia suggests a relationship between the concentration of atmospheric CH₃Cl and global mean temperature, which indicates the possibility that a warmer future climate may result in higher tropospheric CH₃Cl levels. Major sources of...
CH₃Cl are biomass burning, oceanic emissions and vegetative emissions. The other chloromethanes occurring in polluted atmosphere, i.e., dichloromethane (CH₂Cl₂), trichloromethane (CHCl₃) and tetrachloromethane (CCl₄), are released primarily from industrial processes [1–5].

The reaction with hydroxyl radical is a major loss pathway for atmospheric chloromethanes. The reactions of Cl atoms with many haloalkanes can also become of some importance because the rate constants for these reactions are distinctly higher than those for the corresponding reactions with OH radicals. Therefore, in the marine boundary layer and in polar regions where the concentration of chlorine atoms is significant, Cl-initiated reactions may play a key role in the decay of many organic compounds in the troposphere.

The sources of chlorine atoms are the photochemically labile chlorine compounds such as Cl₂ and ClNO₂ produced in some aqueous-phase reactions in airborne seawater droplets [1, 2]. Chlorine atoms and their oxides are highly reactive species and can profoundly affect atmospheric composition. The gas-phase reactions of chlorine atoms with the hydrogen-containing atmospheric halocarbons lead to the facile generation of the corresponding free radicals via hydrogen atom abstraction. These reactions also play an important role in the processes of industrial chlorination and incineration of hazardous halogenated wastes, and their kinetics have been the subject of many theoretical and experimental studies [6–8]. Considerably less recognized are the kinetics of chlorine abstraction reactions. To the best of our knowledge, these reactions have not been investigated experimentally. In this study, we present a theoretical analysis of the mechanism and kinetics of the reactions of chloromethanes, CH₄–xClₓ (x=1,2,3 and 4) with atomic chlorine:

\[
CH₄–xClₓ + Cl \rightarrow CH₄–xClₓ–1 + Cl₂
\]

Kinetic information on the reactions indicated in Eq. (1) is very limited. Chlorine abstraction reactions proceed incomparably slower than the analogous H-abstraction processes, and grow in importance only at high temperatures. The kinetics of the reverse processes

\[
CH₄–xClₓ–1 + Cl₂ \rightarrow CH₄–xClₓ + Cl
\]

between chloromethyl radicals and molecular chlorine is considerably better known [6–8]. The reactions indicated in Eq. (−1) indeed also represent chlorine abstraction processes; however, Cl atoms in a molecule of Cl₂ are bound distinctly weaker in comparison with those in chloromethane. In consequence, the reverse reactions (Eq. −1) are relatively fast processes at ambient temperature and their kinetics have been studied experimentally over a wide temperature range, allowing comparison of experimental results with the theoretical kinetic results obtained in this study.

### Computational details

It is well known that the G2 method [9] well reproduces the structural parameters and molecular properties of a wide group of organic compounds. The haloalkanes were studied theoretically using quantum mechanical ab initio methods at various levels of theory. Reliable values relating to thermochemical properties and vibrational frequencies have been obtained using G2 methodology for perhalogenated methanols, methyl hypohalites, halogenated alkyl and alkoxy radicals [10–20]. The G2 method was also used successfully in the theoretical description of the kinetics and mechanism of the abstraction of hydrogen from methanol by halogen atoms [21–23]. We decided to use the G3 method [24] in our investigations. This method provides the same quality of computational results but with a considerable reduction in the time and the levels of calculations required in comparison with the G2 method. All quantum mechanical ab initio calculations were carried out using the Gaussian 09 program package [25]. The geometries of all stationary point structures of the potential energy surface were fully optimized at both the SCF and MP2 levels with the 6–31G(d) basis set. Relative total energies were examined using G3 methodology [24].

The rate constants of the reactions studied were analyzed in terms of conventional transition state theory (TST) [26, 27] according to the equation

\[
k_{TST} = \kappa_T \sigma \frac{k_B T}{h} \exp \left( \frac{\Delta S^\ddagger}{R} \right) \exp \left( - \frac{\Delta H^\ddagger}{RT} \right)
\]

where \( \kappa_T \) is the tunneling correction factor, \( \sigma \) denotes a symmetry factor related to degeneracy of the reaction path, and \( k_B \) and \( h \) are the Boltzmann and Planck constants, respectively. \( \Delta S^\ddagger \) is the activation entropy and \( \Delta H^\ddagger \) the activation enthalpy of the reaction under investigation. Values of \( \kappa_T \) were evaluated from the simple Wigner’s expression [26]

\[
\kappa_T \approx 1 - \frac{1}{24} \left( \frac{\hbar \nu^\ddagger}{k_B T} \right)^2
\]

with the imaginary frequencies \( \nu^\ddagger \) of the transition state obtained in the geometry optimization performed at a higher level of theory, i.e., from MP2/6–31G(d) calculations. The vibrational and rotational contributions to the thermodynamic functions were derived by classical harmonic-oscillator rigid-rotor approximation (no free or internal rotation was considered).
Results and discussion

The theoretical investigation of hydrogen abstraction from halomethanes by chlorine atoms shows that the mechanism of these reactions appears to be complex and consists of some consecutive elementary processes with the formation of loosely bound intermediate complexes [21–23]. Therefore, at each level of theory, the potential energy surface of the studied reactions was explored for the possible existence of transition states and intermediate complexes. The geometries of all structures were optimized fully and independently using analytical gradients at the SCF and MP2 levels with the 6–31G(d) basis set. The molecular arrangements and definitions of the structural parameters of the molecular structures taking part in the mechanism of reactions \( \text{CH}_4-x\text{Cl}_x + \text{Cl} \) (\( x=1, 2, 3 \) and 4) are shown in Fig. 1. The results of calculations including the geometrical parameters optimized at the MP2(Full)/6–31G(d) level, the harmonic vibrational frequencies, the rotational constants and the total G3(0 K) energies (ZPE included) for the reactants, products, intermediate complexes and transition states are given in Tables 1 and 2.

Optimized molecular structures

The reactants are highly symmetrical molecular structures. A symmetry of point groups of \( C_{3v}, C_{2v}, C_{3v} \) and \( T_D \) is found for \( \text{CH}_3\text{Cl}, \text{CH}_2\text{Cl}_2, \text{CHCl}_3 \) and \( \text{CCl}_4 \), respectively. The \( \text{C}–\text{H} \) and \( \text{C}–\text{Cl} \) bond lengths obtained in the geometry optimization performed at the MP2(Full)/6–31G(d) level for reactants are very close to one another. The lengths of \( \text{C}–\text{Cl} \) bonds in chloromethanes are within 1.765–1.777 Å whereas \( \text{C}–\text{H} \) bonds cover a narrow range of 1.086–1.088 Å. The differences in the values of the angular parameters, \( \text{H}–\text{C}–\text{H} \) and \( \text{Cl}–\text{C}–\text{H} \) in the reactants do not exceed 1°.

The radical products of the reactions under investigation show more visible differences in structural parameters. Methyl radical (\( \text{CH}_3 \)) is a planar structure with the symmetry of a \( D_{3h} \) point group. Trichloromethyl radical (\( \text{CCl}_3 \)) is also a highly symmetrical structure with a three-fold axis. The equilibrium geometry of \( \text{CCl}_3 \) radical obtained at the MP2/6–31G(d) level corresponds to a \( C_{3v} \) symmetry. The other radicals, chloromethyl (\( \text{CH}_2\text{Cl} \)) and dichloromethyl (\( \text{CHCl}_2 \)) are less symmetrical molecular structures. Either the \( \text{C}–\text{H} \) or the \( \text{C}–\text{Cl} \) bonds in the radical products are a little shorter than their counterparts in the parent chloromethanes.
In contrast, the values of the angular parameters in radical products, Cl–C–H and H–C–H are distinctly greater than those in the corresponding reactants.

Except for tetrachloromethane, the attack of a chlorine atom on molecules of CH₂Cl₂, CH₂Cl₂ and CHCl₃ leads to the formation of the pre-reaction adducts, CH₄-xClₓ…Cl (x=1,2 and 3) denoted by MC1A, MC2A and MC3A for CH₃Cl…Cl, CH₂Cl₂…Cl and CHCl₃…Cl, respectively. The adducts MC1A and MC3A have a Cs symmetry, because the attacking chlorine atom is moving across the symmetry plane of the CH₃Cl or CHCl₃. The geometrical parameters of these molecular complexes retain the values that appear in the isolated reactants. All pre-reaction adducts, CH₃Cl…Cl, CH₂Cl₂…Cl and CHCl₃…Cl, are loose molecular structures with long contact distances between the attacking chlorine and reactant. The vibrational frequencies of MC1A, MC2A and

|                  | CH₃Cl (C₃v) | CH₂Cl₂ (C₂v) | CHCl₃ (C₃v) | CCl₄ (TD) |
|------------------|-------------|--------------|-------------|-----------|
| C-Cl             | 1.7770      | 1.7673       | 1.7648      | 1.7688    |
| C-H              | 1.0877      | 1.0869       | 1.0859      | 1.0859    |
| H-C-Cl           | 108.9063    | 108.2652     | 107.6497    | 109.4712  |
| Cl–C–Cl         | 113.0095    | 111.2297     | 109.4712    | 109.4712  |
| H–C–H           | 110.0290    | 110.7900     | 110.7900    | 110.7900  |
| A                | 157.84728   | 32.625180    | 3.284360    | 3.284360  |
| B                | 13.37535    | 3.291950     | 3.284350    | 3.284350  |
| C                | 13.37530    | 3.048430     | 1.703430    | 1.703430  |
| ν₁               | 700  739    | 728  727     | 258  261    | 218  220   |
| ν₂               | 1,016  1,020 | 691  709    | 258  261    | 218  220   |
| ν₃               | 1,016  1,020 | 752  768    | 360  364    | 311  315   |
| ν₄               | 1,374  1,380 | 889  894    | 652  664    | 311  315   |
| ν₅               | 1,454  1,453 | 1,174  1,172 | 780  774    | 449  452   |
| ν₆               | 1,454  1,453 | 1,295  1,295 | 780  774    | 449  452   |
| ν₇               | 2,917  2,965 | 1,445  1,438 | 1,249  1,238 | 806  783   |
| ν₈               | 3,009  3,071 | 2,980  3,002 | 1,249  1,238 | 806  783   |
| ν₉               | 3,009  3,071 | 3,053  3,079 | 3,043  3,047 | 806  783   |
| Eₒ(G3)          | −499.91251  | −959.37103   | −1,418.82886| −1,878.28323|

|                  | CH₃ (D₃h) | CH₂Cl (Cs) | CHCl₂ (Cs) | CHCl₃ (C₃v) |
|------------------|-----------|------------|------------|-------------|
| C-Cl             | 1.7007    | 1.7029     | 1.7029     | 1.7109      |
| C-H              | 1.0783    | 1.0780     | 1.0809     | 1.0809      |
| H-C-Cl           | 117.4525  | 117.4525   | 116.591    | 116.591     |
| Cl–C–Cl         | 119.0484  | 119.0484   | 119.0484   | 119.0484    |
| H–C–H           | 120.0000  | 122.8962   | 122.8962   | 122.8962    |
| A                | 287.529180| 275.216580 | 47.036420  | 3.377060    |
| B                | 287.529180| 15.849680  | 3.350770   | 3.377030    |
| C                | 143.764590| 15.012400  | 3.135160   | 1.699920    |
| ν₁               | 275  380  | 441  313    | 290  302    | 264  273    |
| ν₂               | 1,375  1,392 | 777  831   | 542  526    | 264  273    |
| ν₃               | 1,375  1,392 | 976  995    | 721  753    | 313  345    |
| ν₄               | 2,933  3,028 | 1,381  1,407 | 863  891    | 484  494    |
| ν₅               | 3,090  3,206 | 2,996  3,074 | 1,228  1,247 | 894  896    |
| ν₆               | 3,090  3,206 | 3,127  3,215 | 3,063  3,113 | 894  896    |
| Eₒ(G3)          | −39.79223 | −499.25600 | −958.71926 | −1,418.18095|

Table 1 Molecular properties of the reactants and products of the reactions under investigation calculated at the G3 level. The vibrational frequencies νi (cm⁻¹) obtained at the SCF/6–31G(d) level and scaled by 0.8929 (first column), derived in the MP2(full)/6–31G(d) calculations (second column) were scaled by 0.94 for reactants and products. Experimental frequencies [28–32] are given in parenthesis.

*G3 molecular parameters: geometrical structure optimized at the MP2(Full)/6–31G(d) level, (bond lengths in Å, valence and dihedral angles in degrees), rotational constants ABC in GHz, the total G3-energies in a.u. at 0 K (ZPE included).
Table 2  Molecular properties of structures taking part in the mechanism of reaction under investigation derived at the G3 level\textsuperscript{a}

|                 | MC1A (C\textsubscript{3v}) | MC1B (C\textsubscript{3v}) | MC2A | TS1 (C\textsubscript{3v}) | MC2B (C\textsubscript{3v}) | MC3A (C\textsubscript{s}) | TS2 (C\textsubscript{3v}) | MC3B (C\textsubscript{s}) | TS3 (C\textsubscript{3v}) | MC4B (C\textsubscript{3v}) | TS4 (C\textsubscript{3v}) | MC4A (C\textsubscript{3v}) |
|----------------|-----------------------------|-----------------------------|------|---------------------------|-----------------------------|-----------------------------|---------------------------|-----------------------------|---------------------------|-----------------------------|---------------------------|-----------------------------|
| ClCl\textsubscript{0} | 3.1706                      | 2.0952                      | 2.032 | 5.1473                    | 2.1118                      | 2.032                       | 3.4875                    | 2.1344                      | 2.0222                    | 2.1589                      | 2.024                     | 2.1747                      |
| CCl\textsubscript{0}  | 1.7794                      | 2.3218                      | 3.0624| 1.7675                    | 2.2707                      | 3.0366                      | 1.7682                    | 2.2175                      | 3.0234                    | 2.1747                      | 3.0465                    | 2.1807                      |
| CH\textsubscript{1}   | 1.0880                      | 1.0810                      | 1.0791| 1.7675                    | 1.6944                      | 1.6989                      | 1.6989                    | 1.7036                      | 1.7014                    | 1.7198                      | 1.7104                    | 1.7104                      |
| CCl\textsubscript{1}  | 1.0879                      | 1.0810                      | 1.0791| 1.0866                    | 1.0822                      | 1.0793                      | 1.0857                    | 1.0841                      | 1.0818                    | 1.7198                      | 1.7104                    | 1.7104                      |
| CH\textsubscript{2}   | 1.0879                      | 1.0810                      | 1.0791| 1.0866                    | 1.0822                      | 1.0793                      | 1.0857                    | 1.0841                      | 1.0818                    | 1.7198                      | 1.7104                    | 1.7104                      |
| CCl\textsubscript{2}  | 1.0879                      | 1.0810                      | 1.0791| 1.0866                    | 1.0822                      | 1.0793                      | 1.0857                    | 1.0841                      | 1.0818                    | 1.7198                      | 1.7104                    | 1.7104                      |
| CH\textsubscript{3}   | 1.0879                      | 1.0810                      | 1.0791| 1.0866                    | 1.0822                      | 1.0793                      | 1.0857                    | 1.0841                      | 1.0818                    | 1.7198                      | 1.7104                    | 1.7104                      |
| CH\textsubscript{4}   | 1.0879                      | 1.0810                      | 1.0791| 1.0866                    | 1.0822                      | 1.0793                      | 1.0857                    | 1.0841                      | 1.0818                    | 1.7198                      | 1.7104                    | 1.7104                      |

\textsuperscript{a} G3 molecular parameters: geometrical structure optimized at the MP2(Full)/6-31G(d) level, (bond lengths in Å, valence and dihedral angles in degrees), rotational constants ABC in GHz, the vibrational frequencies $\nu_i$ (cm\textsuperscript{-1}) obtained at the MP2/6-31G(d) level and scaled by 0.940

\textsuperscript{b} The total G3-energies in kJmol\textsuperscript{-1} at 0 K (ZPE included) calculated towards the G3-energy of the respective reactants' energy

\textsuperscript{0}E(G3)
MC3A from \( \nu_4 \) up are almost identical with the corresponding frequencies in the isolated reactants. The transition states (CH\(_4\)\(_x\)Cl\(_{x-1}\)…Cl…Cl)\(^x\), denoted by TS\(_x\) (\( x=1,2,3 \) and 4) describe the chlorine abstraction from CH\(_4\)…Cl\(_2\) by Cl atom. All transition states are reactant-like structures. In reactions CH\(_2\)Cl+Cl and CCl\(_4\)+Cl, the attacking Cl atom is approaching CH\(_2\)Cl and CCl\(_4\) along the C–Cl\(_0\) bond. The angle of C–Cl\(_0\)–Cl is then equal to 180° and the three-fold axis of the reactant molecule (CH\(_2\)Cl or CCl\(_4\)) is retained in the structure of transition states TS1 and TS4, which have the symmetry of a C\(_{3v}\) point group. Both TS2 and TS3 are molecular structures with the C–Cl\(_0\)/Cl\(_0\)–Cl bonds breaking/forming located in the symmetry plane of the transition state. The attack of the chlorine atom at the TS2 and TS3 structures is nearly collinear, with values of the angle C–Cl\(_0\)–Cl of 177° and 176° found for TS2 and TS3, respectively. The calculated lengths of the breaking bonds C–Cl\(_0\) are 30 % longer than those in the parent reactants. The length of C–Cl\(_0\) decreases with the increase in the number of chlorine atoms in the reactant molecule. The Cl\(_0\)/Cl–Cl bonds formed are only 4–7 % longer than the Cl–Cl bond in molecular chlorine. The values of the other structural parameters of the transition states TS\(_x\) are close to their counterparts in the isolated reactants.

The post-reaction adducts, CH\(_4\)…xCl\(_{x-1}\)...Cl\(_2\), designated by MCxB (\( x=1,2,3 \) and 4), are intermediates consisting of two subunits: radical CH\(_4\)…Cl\(_{x-1}\) and molecular chlorine Cl\(_2\) bonded in a molecular complex. All molecular complexes, MCxB keep the symmetry of their respective transition states TS\(_x\), so that MC1B and MC4B have a C\(_{3v}\) symmetry whereas MC2B and MC3B possess a C\(_s\) symmetry. The vibrational frequencies of these adducts are very close to the corresponding frequencies in the isolated radical product and Cl\(_2\).

In standard G3 approach, the vibrational frequencies are obtained in geometry optimization performed at the SCF/6–31G(d) level and scaled by 0.8929 to take into account their overestimation [24]. The vibrational frequencies derived in this way reproduce the experimental frequencies well and give a correct estimation of the zero-point energy of the reactants and products. However, the optimized structures for either intermediate complexes or transition states derived at the SCF and MP2 levels show substantial differences in both geometrical parameters and vibrational frequencies. Therefore, our kinetic analysis of the studied reactions was based on the MP2(Full)/6–31G(d)-frequencies as the more credible ones. The value of the scaling factor for the MP2-frequencies was found by comparing the available experimental [28–33] and calculated MP2 frequencies for reactants and products. As can be seen from Table 1, using a value of the scaling factor of 0.940 leads to the best agreement of the MP2 and experimental frequencies [28–33]. Therefore, this

scaling factor was used to calculate the vibrational frequencies of all molecular structures taking part in the mechanism of the studied reactions.

**Reaction energetics**

The G3 method allows reliable estimation of the reaction energetics. The accuracy of these estimations based on the G3-energies is usually considered to be better than 6 kJ mol\(^{-1}\). The enthalpy of formation, \( \Delta H^f_{298} \) can be evaluated directly as the G3 enthalpy of the formation reaction of CH\(_4\)Cl\(_y\) from the elemental reference compounds such as C\(_{2g}\)H\(_{2g}\) and C\(_{2g}\)Cl\(_{2g}\), i.e., C\(_{2g}\)+(x/2)H\(_{2g}\)+(y/2)Cl\(_{2g}\)→CH\(_4\)Cl\(_y\), and taking into account that the elemental standard state of carbon is graphite. An alternative approach involved the total G3-energy for the atomization reaction CH\(_4\)Cl\(_y\)→C\(_{2g}\)+xH\(_{2g}\)+yCl\(_{2g}\) in combination with the calculated and experimental values of the enthalpy of formation of the gaseous atoms, such as \( \Delta H^f_{298} \) (C\(_{2g}\)) = 716.7 kJ mol\(^{-1}\), \( \Delta H^0_{298} \) (H\(_{2g}\)) = 218.0 kJ mol\(^{-1}\) and \( \Delta H^0_{298} \) (Cl\(_{2g}\)) = 121.3 kJ mol\(^{-1}\) [6, 7].

Table 3 compares the values of \( \Delta H^0_{298} \) of the reactants and products of the studied reactions derived on the basis of the total G3-energy calculated for the formation of CH\(_4\)Cl\(_y\) (a) or for its atomization reaction (b). The results presented show that the calculated values of \( \Delta H^0_{298} \) in both approaches (a) and (b) are in very good agreement with the experimental estimates for CH\(_4\)Cl, CH\(_2\)Cl\(_2\), CH\(_3\) and CH\(_2\)Cl. However, the heat of reaction \( \frac{1}{2} \)Cl\(_2\)→Cl calculated at the G3 level is associated with an error of 2.4 kJ mol\(^{-1}\) at 298 K with respect to the experimental estimate. This is the primary cause of the sizable errors in the values of \( \Delta H^0_{298} \) calculated by the formation of CH\(_4\)Cl\(_y\) for molecular structures containing three or more chlorine atoms. The calculations of \( \Delta H^0_{298} \) for CH\(_4\)Cl\(_y\) (y>2) on the basis of the G3-energy for the atomization reaction reproduce the experimental estimates considerably better [34–37]. The greatest difference between the calculated and experimental value of \( \Delta H^0_{298} \) occurs for CCl\(_4\). However, the values of \( \Delta H^0_{298} \) obtained by the latter method are closer to experimental estimates for CCl\(_4\) as well as the other reactants and products of the studied reactions. This leads to the conclusion that this method is the most suitable approach in calculations of the enthalpy of formation of chlorine-containing species.

The reaction enthalpy was calculated directly from the total G3-energy of the reactants and products. The calculated values of reaction enthalpy do not depend on the method used to calculate the enthalpy of formation. Figure 2 shows that all investigated reactions are highly endothermic processes. The reaction enthalpy \( \Delta H^r_{298} \) of 107.1 kJ mol\(^{-1}\) calculated at the G3 level for reaction CH\(_4\)Cl+Cl → CH\(_3\)+Cl\(_2\) at room temperature is in excellent agreement with the experimental value of 107.1±0.9 kJ mol\(^{-1}\) [7]. The theoretical value of \( \Delta H^r_{298} \) of 92.9 kJ mol\(^{-1}\) for CH\(_2\)Cl+...
Cl ↔ CH₂Cl + Cl₂ is also very close to that of 91.4 ± 5.6 kJ mol⁻¹ [7] derived from the experimentally estimated values of ΔH_f²⁹⁸ of the reactants and products.

In the case of the reaction CHCl₃ + Cl ↔ CHCl₂ + Cl₂, the calculated value of ΔH_f²⁹⁸ of 77.0 kJ mol⁻¹ at 298 K is 6 kJ mol⁻¹ higher than the experimental estimate [7]. A more visible difference between the calculated and experimental values of ΔH_f²⁹⁸ occurs for CCl₄ + Cl ↔ CCl₃ + Cl₂. The calculated heat of this reaction of 57.2 kJ mol⁻¹ distinctly overestimates the experimental value of 45.6 kJ mol⁻¹ [7] derived at room temperature. This is due to the sizable difference between the theoretical and experimental values of the enthalpy of formation of CCl₄.

### Reaction mechanism

The mechanism of the reactions under investigation appears to be complex and consists of some consecutive elementary processes related with the formation of loosely bound intermediate complexes. The profiles of the potential energy surface are shown in Fig. 2. All reactions studied are highly endothermic. Except for reaction CCl₄ + Cl, the mechanism of Cl-abstraction proceeds in accordance with a three-step reaction mechanism

\[
\text{CH}_x\text{Cl}_y + \text{Cl} \rightarrow \text{CH}_x\text{Cl}_y\text{...Cl} \rightarrow \text{CH}_x\text{Cl}_y\text{...Cl}_2
\]

where \( x = 1, 2 \) and 3. The first and third elementary processes are recombination and unimolecular dissociation, while the second is related to an energy barrier. The pre-reaction adducts formed in the first elementary step are loose molecular complexes. The most stable structure is the adduct CH₃Cl…Cl denoted as MC1A. Its dissociation energy to reactants is 15.2 kJ mol⁻¹. The other pre-reaction complexes are considerably less bonded. The next elementary step leads, via TSx, to the molecular complex MCxB, which dissociates to the final channel products, CH₄-xCl_x+Cl₂.

The calculated energy barriers for the second step are high, which implies small values of the rate constants for the studied reactions at ambient temperature. It is interesting that the height of the energy barrier is very close to the reaction heat, and both decrease as the number of chlorine atoms in the reactant molecule increases.

In the case of the reactions CCl₄ + Cl, the CI-abstraction process requires only two elementary steps as

\[
\text{CCl}_4 + \text{Cl} \rightarrow \text{CCl}_3\ldots\text{Cl}_2 \rightarrow \text{CCl}_3 + \text{Cl}_2
\]

The intermediate complex, CCl₃…Cl₂ denoted as MC4B formed in the first elementary step dissociates into the final reaction products, trichloromethyl radical CCl₃ and molecular chlorine Cl₂. The energy barrier for this reaction of 62.2 kJ mol⁻¹ is the lowest among the reactions studied. Therefore, the reaction CCl₄ + Cl should be the fastest process among the reactions under investigation.

---

**Table 3** Comparison of experimental ΔH_f²⁹⁸ (exp.) and theoretical ΔH_f²⁹⁸ (calc.) values of the enthalpy of formation of the reactants and products of the studied reactions obtained at the G3 level

| Molecular system | ΔH_f²⁹⁸ (calc.) (kJ mol⁻¹) | ΔH_f²⁹⁸ (exp.) (kJ mol⁻¹) |
|------------------|---------------------------|--------------------------|
|                  | Formation reaction of CHₓClᵧ | Atomization reactionb     |
| CH₃Cl            | -80.6                     | -81.1                    | -82.0 ± 0.7   |
| CH₂Cl₂           | -95.9                     | -93.0                    | -95.4 ± 2.5   |
| CHCl₃            | -108.7                    | -102.5                   | -103.3 ± 1.3  |
| CCl₄             | -112.1                    | -102.5                   | -95.8 ± 2.5   |
| CH₃              | 145.4                     | 142.6                    | 146.4 ± 0.3   |
| CH₂Cl            | 115.9                     | 116.4                    | 117.3 ± 3.1   |
| CHCl₂            | 87.1                      | 91.0                     | 89.0 ± 3.0    |
| CCl₃             | 64.0                      | 71.2                     | 71.1 ± 2.5    |
| Cl               | 118.9                     | 121.301 ± 0.008          |

a Calculated from G3-energy for the formation reaction of CHₓClᵧ from the elemental reference compounds

b Calculated from G3-energy for the atomization reaction of CHₓClᵧ

c From Ref. [7] and papers cited therein
Rate constant calculations

There are some theoretical kinetic models for describing the kinetics of a bimolecular reaction, which involve the formation of intermediate molecular complexes [21, 38, 39]. Assuming that the intermediates formed are loosely bound complexes, their collisional stabilization can, at a first approximation, be omitted in the description of the reaction rate. A method for the rate constant calculation for a bimolecular reaction that proceeds through the formation of pre- (MCxA) and post-reaction (MCxB) complexes has been applied successfully to describe the kinetics of many H-abstraction reactions [21–23]. The general equation, which takes into account the rotational energy, is derived from RRKM theory. According to this formalism, the rate coefficient \(k\) for the three-step reaction mechanism, such as for Eq. (4) with formation of the pre-reaction and post-reaction adducts, can be expressed as

\[
k = \frac{Q_{RC1}}{Q_{Cl}} \int_{E_{TSx}}^{\infty} \frac{W_{MCxA}(E,J) \times W_{TSx}(E,J)}{W_{MCxA}(E,J)+W_{TSx}(E,J)} \times \exp(-E/RT)dE
\]

where \(Q_{RC1}\) and \(Q_{Cl}\) are the partition functions of chloromethane \(CH_{x-1}Cl_{x}\) (\(x=1,2,3\) and 4) and atomic chlorine, respectively, with the center of mass partition function factored out of the product \(Q_{RC1}Q_{Cl}\) and included in \(z\) together with the partition functions of those inactive degrees of freedom that are not considered by the sums of the states under the integral. \(E_{TSx}\) is the threshold energy towards the reactants \(CH_{x-1}Cl_{x}+Cl\), whereas \(W_{TSx}(E,J)\), \(W_{MCxA}(E,J)\), and \(W_{TSx}(E,J)\) denote the sum of the states at energy less than or equal to \(E\) and with angular momentum \(J\) for the transition state \(TSx\) and the activated complexes for the unimolecular dissociations of MCxA and MCxB, respectively. All computational effort is then related to calculating the sum of the states, \(W(E,J)\) This calculation depends on the level at which the conservation of angular momentum is considered and is discussed in detail in Refs. [21, 22].

Equation 6 can be used directly in the description of kinetics of the reactions \(CH_{3}Cl+Cl\), \(CH_{2}Cl_{2}+Cl\) and \(CHCl_{3}+Cl\). In the case of the two-step mechanism such as for the reaction \(CCl_{4}+Cl\), one must replace \(W_{MC4A}(E,J)\) by \(W_{TSd}(E,J)\) and omit the first fraction under the integral in Eq. (6).

The results of direct calculations [13, 20–22] show that the dominant contribution to the rate constant is given by states with energy \(E\) not higher than \(E_{TSx}+3RT\). In the case of a sizable (compared with RT) energy barrier \(V_{TSx}\) the value of the product of the microcanonical branching fractions at an energy slightly higher than \(V_{TSx}\) becomes close to unity and the TST rate constant \(k_{TST}\) is then a good approximation of the exact rate coefficient, especially at ambient temperatures [13, 20–22].

Reaction system \(CH_{3}Cl+Cl\)

The values of the calculated rate constants are given in Table 4. The height of the energy barrier is clearly the major factor determining the magnitude of the rate constant and its dependence on temperature. Figure 2 shows that the Cl-abstraction from \(CH_{3}Cl\) by Cl atoms is related with a high energy barrier of 106 kJ\(mol^{-1}\). The calculated value of the rate constant at 298 K is of \(4.5 \times 10^{-30}\) \(cm^3molecule^{-1}s^{-1}\). This value is 17 orders of magnitude lower than the rate constant for the competitive reaction of H-abstraction from \(CH_{3}Cl\) by atomic chlorine [40]. This is the major reason of the lack of experimental measurements of rate constants for Cl-abstraction from \(CH_{3}Cl\). The kinetics of the reverse reaction \(CH_{3}+Cl_{2}\) are considerably better recognized [4–6]. The values of the rate constant for this reaction calculated via the equilibrium constant obtained theoretically are also given in Table 4. The values of the rate constants, \(k(CH_{3}Cl+Cl)\) and \(k(CH_{3}+Cl_{2})\) calculated in the temperature range of 200–3,000 K, can be expressed as:

\[
k(CH_{3}Cl+Cl) = 2.08 \times 10^{-31} \times (T/300)^{1.63} \times \exp(-12780/T) \ cm^3molecule^{-1}s^{-1}
\]

(7)

\[
k(CH_{3}+Cl_{2}) = 6.70 \times 10^{-15} \times (T/300)^{1.31} \times \exp(270/T) \ cm^3molecule^{-1}s^{-1}
\]

(8)

The calculated values of \(k(CH_{3}+Cl_{2})\) are compared with available experimental results in Fig. 3. The inset shows the temperature dependence of the calculated \(k(CH_{3}Cl+Cl)\). The room temperature value of the rate constant \(k(CH_{3}Cl+Cl)\) is very low: 2.0 \times 10^{-24} \ cm^3molecule^{-1}s^{-1}. However, the values of \(k(CH_{3}Cl+Cl)\) depend strongly on temperature. The increase in temperature from 200 K to 1,000 K results in a rise in the value of \(k(CH_{3}Cl+Cl)\) by over 20 orders of magnitude. The calculated values of \(k(CH_{3}Cl+Cl)\) are 4.7 \times 10^{-16} and 1.1 \times 10^{-11} \ cm^3molecule^{-1}s^{-1} at 1,000 K and 3,000 K, respectively.

The reverse reaction has been studied experimentally over a wide temperature range. Figure 3 compares our calculated values of \(k(CH_{3}+Cl_{2})\) with the experimental results of Eskola et al. [41] performed in the range of 188–500 K, Timonen et al. [42] at 298–423 K, Timonen and Gutman [43] at 296–712 K, and those of Kovalenko and Leone [44] studied at 298 K. The results of Timonen et al. [42] are distinctly underestimated. The other experimental measurements are consistent and show only little dispersion. The calculated values of \(k(CH_{3}+Cl_{2})\) can be considered the best compromise between
Table 4  Rate constant calculated for the Cl-abstraction reactions CH₄···Clₓ+Cl⁻→CH₄···Clₓ⁻+Cl₂ and their reverse processes

| T (K) | CH₂Cl+Cl⁻→CH₂+Cl₂ | CCl₃+Cl⁻→CCl₃+Cl₂ |
|-------|---------------------|---------------------|
|       | k(CH₂Cl+Cl⁻) (cm³molecule⁻¹s⁻¹) | k₁(CH₂Cl+Cl⁻) (cm³molecule⁻¹s⁻¹) | logK₂⁰ | k(CH₂+Cl₂) (cm³molecule⁻¹s⁻¹) | k₁(CH₂+Cl₂) (cm³molecule⁻¹s⁻¹) | logK₂⁰ | k(CH₂Cl+Cl⁻) (cm³molecule⁻¹s⁻¹) | k₁(CH₂Cl+Cl⁻) (cm³molecule⁻¹s⁻¹) | logK₂⁰ | k(CH₂+Cl₂) (cm³molecule⁻¹s⁻¹) | k₁(CH₂+Cl₂) (cm³molecule⁻¹s⁻¹) | logK₂⁰ |
|-------|---------------------|---------------------|--------|---------------------|---------------------|--------|---------------------|---------------------|--------|---------------------|---------------------|--------|
| 200   | 2.21×10⁻⁻³⁹         | 2.44×10⁻⁻³⁹         | -26.8131 | 1.39×10⁻⁻¹²             | 2.60×10⁻⁻³⁵         | 3.24×10⁻⁻³⁵             | -22.0543 | 2.83×10⁻⁻¹³             |
| 250   | 9.42×10⁻⁻³⁴         | 1.02×10⁻⁻³³         | -21.2130 | 1.51×10⁻⁻¹²             | 1.73×10⁻⁻³⁰         | 2.00×10⁻⁻³⁰             | -17.2029 | 2.70×10⁻⁻¹³             |
| 298   | 4.49×10⁻⁻³⁰         | 4.81×10⁻⁻³⁰         | -17.5717 | 1.65×10⁻⁻¹²             | 2.42×10⁻⁻₂⁷         | 2.70×10⁻⁻²⁷             | -14.0551 | 2.71×10⁻⁻¹³             |
| 300   | 5.90×10⁻⁻³⁰         | 6.31×10⁻⁻³⁰         | -17.4547 | 1.66×10⁻⁻¹²             | 3.06×10⁻⁻₂⁷         | 3.41×10⁻⁻²⁷             | -13.9541 | 2.71×10⁻⁻¹³             |
| 350   | 3.26×10⁻⁻²⁷         | 3.48×10⁻⁻²⁷         | -14.7538 | 1.83×10⁻⁻¹²             | 6.72×10⁻⁻²⁵         | 7.40×10⁻⁻²⁵             | -11.6244 | 2.80×10⁻⁻¹³             |
| 400   | 3.92×10⁻⁻²⁵         | 4.18×10⁻⁻²⁵         | -12.7171 | 2.03×10⁻⁻¹²             | 3.98×10⁻⁻²³         | 4.38×10⁻⁻²³             | -9.8716  | 2.95×10⁻⁻¹³             |
| 450   | 1.69×10⁻⁻²³         | 1.81×10⁻⁻²³         | -11.1257 | 2.24×10⁻⁻¹²             | 4.95×10⁻⁻²²         | 1.09×10⁻⁻²²             | -8.5049  | 3.12×10⁻⁻¹³             |
| 500   | 3.35×10⁻⁻²⁲         | 3.81×10⁻⁻²²         | -8.9479  | 2.48×10⁻⁻¹²             | 1.29×10⁻⁻²⁰         | 1.46×10⁻⁻²⁰             | -7.4096  | 3.32×10⁻⁻¹³             |
| 600   | 3.56×10⁻⁻²⁰         | 3.94×10⁻⁻²⁰         | -7.9238  | 2.98×10⁻⁻¹²             | 6.48×10⁻⁻¹⁹         | 7.57×10⁻⁻¹⁹             | -5.7646  | 3.77×10⁻⁻¹³             |
| 700   | 1.01×10⁻⁻¹⁸         | 1.15×10⁻⁻¹⁸         | -6.5450  | 3.53×10⁻⁻¹²             | 1.10×10⁻¹⁷          | 1.34×10⁻¹⁷             | -4.5896  | 4.28×10⁻⁻¹³             |
| 800   | 1.28×10⁻⁻¹⁷         | 1.51×10⁻⁻¹⁷         | -5.5099  | 4.13×10⁻⁻¹²             | 9.39×10⁻⁻¹⁷         | 1.20×10⁻¹⁷             | -3.7099  | 4.82×10⁻⁻¹³             |
| 900   | 9.40×10⁻⁻¹⁷         | 1.15×10⁻⁻¹⁶         | -4.7054  | 4.77×10⁻⁻¹²             | 5.06×10⁻⁻¹⁶         | 6.80×10⁻⁻¹⁶             | -3.0280  | 5.41×10⁻⁻¹³             |
| 1000  | 4.70×10⁻⁻¹⁶         | 5.96×10⁻⁻¹⁶         | -4.0630  | 5.44×10⁻⁻¹²             | 1.97×10⁻⁻¹⁵         | 2.78×10⁻⁻¹⁵             | -2.4848  | 6.03×10⁻⁻¹³             |
| 1500  | 6.44×10⁻⁻¹⁴         | 9.90×10⁻⁻¹⁴         | -2.1559  | 9.26×10⁻⁻¹²             | 1.24×10⁻⁻¹³         | 2.21×10⁻⁻¹³             | -0.8807  | 9.50×10⁻⁻¹³             |
| 2000  | 8.01×10⁻⁻¹³         | 1.48×10⁻⁻¹²         | -1.2290  | 1.37×10⁻⁻¹¹             | 1.04×10⁻⁻¹²         | 2.27×10⁻⁻¹²             | -0.1083  | 1.35×10⁻⁻¹²             |
| 2500  | 3.73×10⁻⁻¹²         | 8.10×10⁻⁻¹²         | -0.6918  | 1.85×10⁻⁻¹¹             | 3.85×10⁻⁻¹²         | 9.96×10⁻⁻¹²             | 0.3353   | 1.79×10⁻⁻¹²             |
| 3000  | 1.05×10⁻⁻¹¹         | 2.65×10⁻⁻¹¹         | -0.3470  | 2.35×10⁻⁻¹¹             | 9.31×10⁻⁻¹²         | 2.81×10⁻⁻¹¹             | 0.6173   | 2.26×10⁻⁻¹²             |

The equilibrium constant K_p calculated for the reaction enthalpy corrected by -6.0 kJ mol⁻¹ to obtain value of ΔH°₂₉₈ of 71.0 kJ mol⁻¹ (see text)
the available estimates. The predicted temperature dependence of the rate constants, $k(\text{CH}_3\text{Cl}+\text{Cl})$ and $k(\text{CH}_3+\text{Cl}_2)$ expressed by Eqs. (7) and (8) allows a description of the kinetics of the reactions $\text{CH}_3\text{Cl}+\text{Cl}$ and $\text{CH}_3+\text{Cl}_2$ over a wide temperature range.

Reaction system $\text{CH}_2\text{Cl}_2+\text{Cl}$

The profiles of the potential energy surface presented in Fig. 2 show that Cl abstraction from $\text{CH}_2\text{Cl}_2$ by Cl atoms is also related to a high energy barrier of 90 kJmol$^{-1}$. This implies a low values of the rate constants $k(\text{CH}_2\text{Cl}_2+\text{Cl})$. The calculated value of $k(\text{CH}_2\text{Cl}_2+\text{Cl})$ at 298 K of $2.4 \times 10^{-27}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ is over 1,000 times higher than the value of $k(\text{CH}_2\text{Cl}+\text{Cl})$ at the same temperature. The height of the energy barrier is lower by 16 kJmol$^{-1}$ than that calculated for $\text{CH}_3\text{Cl}+\text{Cl}$. As a consequence, values of $k(\text{CH}_2\text{Cl}_2+\text{Cl})$ increase a little more weakly with temperature than values of $k(\text{CH}_3\text{Cl}+\text{Cl})$. The calculated values of $k(\text{CH}_2\text{Cl}_2+\text{Cl})$ are $2.0 \times 10^{-15}$ and $9.3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 1,000 K and 3,000 K, respectively.

To the best of our knowledge there is no experimental information on the kinetics of $\text{CH}_2\text{Cl}_2+\text{Cl}$. However, the reverse reaction $\text{CH}_2\text{Cl}+\text{Cl}_2$ has been studied experimentally [45–47] in the temperature range 201–873 K. Figure 4 compares our theoretical results with the results of the experimental investigations of Seetula [45], Seetula et al. [46] and Eskola et al. [47] by (black squares) with those obtained theoretically in this study. Solid line Plot of Eq. (10). Inset Temperature dependence of $k(\text{CH}_2\text{Cl}_2+\text{Cl})$ from Eq. (9).

The results of our calculations reproduce the experimentally estimated values of $k(\text{CH}_2\text{Cl}+\text{Cl}_2)$ very well at low temperatures.
temperatures, i.e., below 400 K. At higher temperatures, our values of \(k(\text{CH}_2\text{Cl}_2+\text{Cl}_2)\) are slightly lower compared with the experimental results. The difference between the experimental and theoretical results increases with increasing temperature. The experimental value of \((9.22\pm0.54)\times10^{-13}\) \(\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\) obtained by Seetula et al. [46] at 719 K is two times higher than the \(4.4\times10^{-13}\) \(\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\) derived from Eq. (10). This may be an effect of the treatment of the lowest degrees of freedom of the transition state TS2 as harmonic vibrations. However, it should be emphasized that the theoretically derived values of \(k(\text{CH}_2\text{Cl}_2+\text{Cl}_2)\) and \(k(\text{CH}_2\text{Cl}_2+\text{Cl})\) describe very well the kinetics of the chlorine abstraction reactions \(\text{CH}_2\text{Cl}_2+\text{Cl}\) and \(\text{CH}_2\text{Cl}_2+\text{Cl}_2\) at temperatures not higher than ambient.

**Reaction system \(\text{CHCl}_3+\text{Cl}\)**

The calculated energy barrier of 75 kJmol\(^{-1}\) for reaction \(\text{CHCl}_3+\text{Cl}\) is lower by 15 and 31 kJmol\(^{-1}\) than those derived for \(\text{CH}_2\text{Cl}_2+\text{Cl}\) and \(\text{CH}_2\text{Cl}_2+\text{Cl}_2\), respectively. This indicates that chlorine abstraction proceeds more easily from a reactant with a greater number of chlorine atoms. The height of the energy barrier for chlorine abstraction decreases by 15 kJ mol\(^{-1}\) for any subsequent chlorine atom inserted into the chloromethane molecule. However, the energy barrier for \(\text{CHCl}_3+\text{Cl}\) is still high, which implies a low value of the rate constant \(k(\text{CHCl}_3+\text{Cl})\) at room temperature. The calculated value of \(k(\text{CH}_2\text{Cl}_2+\text{Cl})\) at 298 K is of \(2.0\times10^{-24}\) \(\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\). This value is over 3 and 6 orders of magnitude higher than the calculated at the same temperature values of \(k(\text{CH}_2\text{Cl}_2+\text{Cl})\) and \(k(\text{CH}_2\text{Cl}_2+\text{Cl}_2)\), respectively. The derived temperature dependence of \(k(\text{CHCl}_3+\text{Cl})\) can be expressed in the temperature range 200–3,000 K as,

\[
k(\text{CHCl}_3+\text{Cl}) = 5.28\times10^{-11}\times(T/300)^{0.97}\times\exp(-9200/T) \quad \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}
\]

(11)

According to the sizable energy barrier, the reaction \(\text{CHCl}_3+\text{Cl}\) becomes important only at very high temperatures. Experimental information is available only for the reverse process, \(\text{CHCl}_3+\text{Cl}_2\) [45, 46]. Figure 5 shows a comparison of the temperature dependence of the rate constant \(k(\text{CHCl}_3+\text{Cl}_2)\) derived theoretically with that from experimental findings [45, 46]. The dashed line denotes the values of the rate constant \(k(\text{CHCl}_3+\text{Cl}_2)\) obtained via the calculated equilibrium constant. The calculated values of \(k(\text{CHCl}_3+\text{Cl}_2)\) distinctly overestimate the experimental results of Seetula [45] and Seetula et al. [46], especially at low temperatures.

It is worth noting that a comparison of the theoretical and experimental values of \(k(\text{CHCl}_3+\text{Cl}_2)\) is indeed the only way to verify, albeit indirectly, the calculated values of both \(k(\text{CH}_2\text{Cl}_2+\text{Cl}_2)\) and \(k(\text{CHCl}_3+\text{Cl})\), on the condition that the calculated equilibrium constants are realistic. The calculated reaction enthalpy at room temperature for \(\text{CHCl}_3+\text{Cl}\rightarrow\text{CHCl}_2+\text{Cl}_2\) is of 77.0 kJmol\(^{-1}\), whereas the experimentally estimated one is 71.0 kJmol\(^{-1}\) [7]. The correction of the reaction enthalpy by \(-6.0\) kJmol\(^{-1}\) at any temperature should lead to more realistic values of the equilibrium constant, and finally to a more reliable rate constant \(k(\text{CHCl}_2+\text{Cl}_2)\). The values of \(k(\text{CHCl}_2+\text{Cl}_2)\) after reduction by a factor of \(\exp(6.0\) kJmol\(^{-1}/RT)\), shown in Fig. 5 (solid line), can be expressed by

\[
k(\text{CHCl}_2+\text{Cl}_2) = 6.81\times10^{-14}\times(T/300)^{1.00}\times\exp(-370/T) \quad \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}
\]

(12)

The corrected values of the rate constant, \(k(\text{CHCl}_2+\text{Cl}_2)\), reproduce the experimental results very well. Agreement between experimental and calculated values of \(k(\text{CHCl}_2+\text{Cl}_2)\) is excellent over a wide temperature range. This also confirms the reliability of the values of the rate constant, \(k(\text{CHCl}_3+\text{Cl})\), calculated in this study.
Reaction system CCl₄+Cl

Figure 2 shows that the lowest energy barrier of 62 kJmol⁻¹ was found for the reaction of CCl₄+Cl. The calculated value of \( k(\text{CCl}_4+\text{Cl}) \) of \( 6.2\times10^{-22} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) at 298 K is over 300 times higher than the value of \( k(\text{CHCl}_3+\text{Cl}) \) at the same temperature (see Table 4). The sizable energy barrier for CCl₄+Cl results in the distinct temperature dependence of \( k(\text{CCl}_4+\text{Cl}) \). The values of \( k(\text{CCl}_4+\text{Cl}) \) and \( k(\text{CCl}_3+\text{Cl}_2) \) for the reverse reaction calculated via the equilibrium constant can be expressed in the form

\[
\begin{align*}
\frac{k(\text{CCl}_4+\text{Cl})}{\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}} & = 1.51 \times 10^{-10} \times (T/300)^{0.58} \times \exp(-7790/T) \\
\frac{k(\text{CCl}_3+\text{Cl}_2)}{\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}} & = 1.43 \times 10^{-11} \times (T/300)^{1.51} \times \exp(-550/T)
\end{align*}
\]

The kinetics of reaction CCl₄+Cl have been studied experimentally by Seetula [45] and DeMare and Huybrechts [48]. Their investigations were, however, performed in different temperature ranges, and the reported temperature dependencies of \( k(\text{CCl}_4+\text{Cl}) \) expressed in the Arrhenius form show distinct differences in both the pre-exponential factor and the activation energy, which makes it difficult to compare the experimental and theoretical values of \( k(\text{CCl}_4+\text{Cl}) \). There is no experimental information on the kinetics of the reverse reaction CCl₃+Cl₂. The reaction CCl₄+Cl is one of the processes involved in the pyrolysis of CCl₄ in the gas-phase. Huybrechts et al. [49] studied the pyrolysis of CCl₄ in terms of modeling by computer simulations and optimizations of the kinetic parameters of the elementary processes taking part in the mechanism of the investigated pyrolysis. The Arrhenius parameters derived from the kinetic model of Huybrechts et al. [49] allow a description of the kinetics of the reaction CCl₄+Cl in the temperature range 300–800 K. The value of \( 4.9\times10^{-22} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) derived at 300 K by Huybrechts et al. [49] is lower than our estimate of \( 7.3\times10^{-22} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \). The similar difference between our result for the value of \( k(\text{CCl}_4+\text{Cl}) \) and that derived by Huybrechts et al. [49] is maintained at temperatures below 800 K. This agreement can be considered as satisfactory taking into account the uncertainties of the kinetic modeling procedure.

Summary

The main aim of the present study was to perform a theoretical analysis of the kinetics of chlorine abstraction from chlorinated methanes, CH₃Cl, CH₂Cl₂, CHCl₃ and CCl₄ by chlorine atoms. Theoretical investigations based on ab initio calculations of the CH₄-xClₓ+Cl→CH₄-xClₓ-1+Cl₂ (x=1,2,3 and 4) reaction systems at the G3 level were performed to gain insight into the reaction mechanism. Kinetic information on these reactions is very limited. The results of the calculations also allow an estimation of the reaction energetics and the molecular properties of the structures taking part in the reaction mechanism.

The calculated values of the enthalpy of formation of the reactants and products are in good agreement with the reported values estimated experimentally. All the studied reactions are strongly endothermic processes, with calculated values of reaction enthalpy at 298 K of 107.1, 92.9, 77.0 and 57.2 kJmol⁻¹ for CH₃Cl+Cl, CH₂Cl₂+Cl, CHCl₃+Cl and CCl₄+Cl, respectively. The calculated profiles of the potential energy surface show that the mechanism of the reactions studied is complex and that Cl-abstraction proceeds via the formation of intermediate complexes. The multi-step reaction mechanism consists of two elementary steps in the case of CCl₄+Cl, and three steps for the other reactions. The heights of the energy barrier relative to the Cl-abstraction by Cl atoms from CH₃Cl, CH₂Cl₂, CHCl₃ and CCl₄ are 106, 90, 75 and 62 kJmol⁻¹, respectively. The differences in energy barriers are reflected in the values of the rate constants. The rate constants calculated at 298 K are \( 4.5\times10^{-30}, 2.4\times10^{-27}, 2.0\times10^{-24} \) and \( 6.2\times10^{-22} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) for reactions CH₃Cl/CH₂Cl₂/CHCl₃/CCl₄+Cl, respectively. The rate constants for the reverse reactions CH₃/CH₂Cl/CHCl₂/CCl₃+Cl have also been calculated using the equilibrium constants derived theoretically. The ordering of the values of the calculated rate constants for the reverse reactions is quite the opposite of their counterparts in the forward direction. The highest value of \( 1.7\times10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) at 298 K is found for \( k(\text{CH}_3+\text{Cl}_2) \), the lowest one is \( k(\text{CCl}_3+\text{Cl}_2) = 2.1\times10^{-14} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \). The calculated values of the rate constants describe the kinetics of the reverse reactions well. An especially good agreement between the calculated and reported values of the rate constants was reached for reactions CH₃+Cl₂, CH₂Cl+Cl₂ and CHCl₂+Cl₂. In the temperature range of 200–400 K, the theoretically derived kinetic parameters for these reactions allow the reaction kinetics to be described with an accuracy no worse than that given by various kinetic data evaluations.

This confirms the reliability of the theoretically derived kinetic expressions, which represent a substantial supplement to the kinetic data necessary for the description and modeling of the complex gas-phase reactions of importance in combustion and atmospheric chemistry.

Acknowledgements This research was supported by Wroclaw Medical University under grant No. ST-694. The Wroclaw Center of Networking and Supercomputing is acknowledged for the generous allotment of computer time.
