Gas-Phase Reactions of Cl Atoms with Propane, *n*-Butane, and Isobutane

DARIUSZ SARZYNSKI, BARBARA SZTUBA

Department of Physical Chemistry, Wroclaw Medical University, Nankier Sq. 1, 50-140 Wroclaw, Poland

Received 31 January 2002; accepted 8 August 2002

DOI 10.1002/kin.10096

ABSTRACT: Using the relative kinetic method, rate coefficients have been determined for the gas-phase reactions of chlorine atoms with propane, *n*-butane, and isobutane at total pressure of 100 Torr and the temperature range of 295–469 K. The Cl_2 photolysis ($\lambda =$ 420 nm) was used to generate Cl atoms in the presence of ethane as the reference compound. The experiments have been carried out using GC product analysis and the following rate constant expressions (in cm^3 $molecule^{-1}$ s^{-1}) have been derived: $(7.4 \pm 0.2) \times 10^{-11}$ exp $[-(70 \pm 11)/T]$, $Cl + C_3H_8 \rightarrow HCl + CH_3CH_2CH_2$; $(5.1 \pm 0.5) \times 10^{-11}$ $\exp[(104 \pm 32)/T]$, $Cl + C_3H_8 \rightarrow HCl + CH_3CHCH_3$; $(7.3 \pm 0.2) \times 10^{-11}$ $\exp[-(68 \pm 10)/T]$, $Cl + n\text{-}C_4H_{10} \rightarrow HCl + CH_3CH_2CH_2CH_2$; $(9.9 \pm 2.2) \times 10^{-11}$ $\exp[(106 \pm 75)/T]$, $Cl + n\text{-}C_4H_{10} \rightarrow HCl + CH_3CH_2CHCH_3$; $(13.0 \pm 1.8) \times 10^{-11}$ $\exp[-(104 \pm 50)/T]$, $Cl + i\text{-}C_4H_{10} \rightarrow HCl + CH_3CHCH_3CH_2$; $(2.9 \pm 0.5) \times 10^{-11}$ $\exp[(155 \pm 58)/T]$, $Cl + i\text{-}C_4H_{10} \rightarrow HCl + CH_3CCH_3CH_3$ (all error bars are $\pm 2\sigma$ precision). These studies provide a set of reaction rate constants allowing to determine the contribution of competing hydrogen abstractions from primary, secondary, or tertiary carbon atom in alkane molecule. © 2002 Wiley Periodicals, Inc. Int J Chem Kinet 34: 651–658, 2002

INTRODUCTION

Reactions of chlorine atoms with hydrocarbons are of great importance for understanding the atmospheric chemistry. It is commonly known that Cl atoms contribute both to the ozone balance and the loss of organics in the troposphere. The role of interaction between chlorine and hydrocarbon chemistry has taken on new importance during last years as the mechanism of chlorine atoms generation in marine troposphere from the reactions of NaCl in sea salt particules had been understood [1–4]. The reactions with Cl atoms have been postulated to be an additional and significant removal process of $\geq C_2$ alkanes in marine troposphere [1,3,5], where the main degradation process of organics is initiated by gas-phase reactions with the OH radicals. Also measurements of hydrocarbons concentration in the Arctic troposphere in springtime have confirmed that the chemistry of hydrocarbons is strongly influenced by chlorine atoms [6,7]. Although numerous kinetic studies of Cl atom reactions with a series of simple alkanes have been reported in the literature [8–20], there are no detailed studies of hydrogen abstraction reactions from individual carbon atoms.

Herein we report on the competitive photochlorination of propane, *n*-butane, and isobutane in the presence of ethane as the reference compound. This study represents part of detailed ongoing investigation on the kinetics and mechanisms of the reactions of Cl atoms with simple alkanes. The main aim of this work was to establish the temperature dependencies of the rate coefficients for reactions of hydrogen abstractions by chlorine atoms from carbons C1 and C2 in propane and

---

Correspondence to: Dariusz Sarzynski; e-mail: darek@bf.uni.wroc.pl.

Contract grant sponsor: State Committee for Scientific Research.
Contract grant number: 498.

n-butane and from carbons C1 and C3 in isobutane. The results comprising the rate coefficients and their temperature dependencies are compared with other literature data.

EXPERIMENTAL

The experiments were carried out in a greaseless, static system, using a cylindrical Pyrex reactor of ca. 250 cm^3 volume (dead volume ~2%) placed at a copper heating block. Chlorine atoms gas-phase reactions with propane, *n*-butane, and isobutane were investigated with ethane as reference over the temperature range of 295–470 K. Temperature was controlled by employing power regulator connected to temperature regulator equipped with Pt-100 resistance sensor. The temperature of the reaction cell was constant to within 0.5°C. Chrome–nickel thermocouple maintained in the half length of the side wall of the reactor was used to measure the temperature. The reactants were introduced into the cell by expansion starting from a mixture of 5% Cl_2 in N_2 followed by pre-made mixture of alkane and reference. Preliminary tests showed that ca. 10-min mixing time was sufficient for the reactants in the cell to reach ambient temperature and confirmed that dark reactions were never observed. In order to test for a possible photolysis or thermal decomposition of the organic reactants, mixtures of organics were irradiated in the absence of Cl_2 at the highest temperature used for more than 60 min. No photolysis or thermal reaction of any of the reactants was observed. Prior to each set of kinetic experiments at temperature above 295 K, tests were performed for dark reactions. Mixtures of organic species and molecular chlorine were prepared and allowed to stand in the dark for at least 60 min. In all the cases, the reaction of the organic species with molecular chlorine was negligible in the absence of photolytic light. In addition, the thermal stability of the reaction products was examined at the highest temperatures applied in the experiments. No destruction products were observed except for 2-chloro-2-methylpropane, which appeared to be unstable at 466 K. All experiments were conducted at total pressure of about 100 Torr while the partial pressure of Cl_2 was varied from 1 to 4 Torr. The mixtures prepared at different ratios of alkane:ethane at least 48 h prior to each set of experiments were stored in a 4 l blackened Pyrex bulbs. Pressure measurements were carried out with a Model 127A MKS Baratron capacitance manometer equipped with two gauges (0–100 and 0–1000 Torr).

The Xe arc lamp (Osram XBO 150W/1 OFR) served as the light source. The optical train consisted of a manually operated shutter, condensing lens, a variable-width slit, and a monochromator. The light from the monochromator was introduced into the cylindrical reactor through its bottom window and after passing through the reactor was reflected back by the mirror placed above the upper window of the reactor. The reaction cell, the feed lines, and the optical assembly were housed in a light-tight enclosure to prevent photolysis initiated by room or stray light. The absence of such reactions was confirmed by repeated blank analyses. Chlorine atoms were generated in their ground state ($Cl(^2P_{3/2}) > 99\%$, $Cl(^2P_{1/2}) < 1\%$ at 298 K) [21] by the photolysis of Cl_2 at 420 nm. The irradiation time (2–20 min) and the slit width (2–20 nm) were varied depending on the reaction temperature in order to avoid higher conversion of reactants.

Product analysis was carried out by thermal conductivity gas chromatography (HP, Model 5890 Series II), using a 25 m-long × 0.32 mm CP-SIL 13CB Chrompack capillary column for halocarbons with temperature–time programming between 30 and 110°C and the heating rate 10°C/min. In all analysis He was used as a carrier gas and 2 ml thermostated gas loop as a sampling unit.

All experiments were conducted below 5% conversion of the reactants when the only products observed were 1-chloropropane and 2-chloropropane, 1-chlorobutane and 2-chlorobutane, and 1-chloro-2-methylpropane and 2-chloro-2-methylpropane for the Cl reactions with propane, *n*-butane, and isobutane, respectively. Calibration curves of relative peak area versus pressure for each reaction product at each reaction temperature were determined by GC analyses of known amounts of original samples diluted with Ar. The linear relationships obtained by the least square method were subsequently used for calculation of the products' pressure in the reactor.

The reactants used in this study had the following stated minimum purities: Propane (99.95%), *n*-butane (99.95%), isobutane (99.95%), and chloroethane (99.7%) from Praxair; ethane (99.97%), 1-chloropropane (99.5%), and 2-chloropropane (99.5%) from Fluka; and 1-chlorobutane (99.5%), 2-chlorobutane (99%), 1-chloro-2-methylpropane (98%), and 2-chloro-2-methylpropane (99%) from Aldrich. 5% Cl_2/N_2 was prepared by Linde. All reaction products except for chloroethane were purified three times, using the freeze-pump-thaw method. All other reactants were used directly from the containers.

RESULTS AND DISCUSSION

The general scheme for gas-phase photochlorination reactions is well established [22–24]. In the case of photochlorination of hydrocarbon RH in the presence of C_2H_6, the reaction sequence may be represented by the following mechanism:

$$Cl_2 \rightarrow 2Cl \tag{1}$$

$$RH + Cl \leftrightarrow R + HCl \tag{2, −2}$$

$$R + Cl_2 \rightarrow RCl + Cl \tag{3}$$

$$C_2H_6 + Cl \leftrightarrow C_2H_5 + HCl \tag{4, −4}$$

$$C_2H_5 + Cl_2 \rightarrow C_2H_5Cl + Cl \tag{5}$$

where RH denotes propane, *n*-butane, or isobutane. Application of the steady-state approximation and the long-chain assumption [25] leads to the following rate expression for the product formation:

$$\frac{d[RCl]}{dt} = k_2[RH]\frac{k_3[Cl][Cl_2]}{k_3[Cl_2] + k_{-2}[HCl]} \tag{6}$$

An analogous rate expression for C_2H_5Cl formation is given by

$$\frac{d[C_2H_5Cl]}{dt} = k_4[C_2H_6]\frac{k_3[Cl][Cl_2]}{k_5[Cl_2] + k_{-4}[HCl]} \tag{7}$$

The rate ratio for products formation can be obtained by dividing Eq. (6) by (7):

$$\frac{\frac{d[RCl]}{dt}}{\frac{d[C_2H_5]}{dt}} = \frac{k_2[RH]}{k_4[C_2H_6]}\frac{1 + \frac{k_{-4}[HCl]}{k_5[Cl_2]}}{1 + \frac{k_{-2}[HCl]}{k_3[Cl_2]}} \tag{8}$$

For initial conditions or if conversion with respect to Cl_2 is not significant (in other words, concentration of HCl is very low), the reverse reactions (−2) and (−4) are unimportant and may be neglected in relation to the steps (3) and (5). Under these conditions, it can be also assumed that the ratio $[RH]/[C_2H_6]$ is almost equal to the ratio of initial concentrations $[RH]_0/[C_2H_6]_0$ and Eq. (8) can be integrated giving

$$\frac{k_2}{k_4} = \frac{[C_2H_6]_0}{[RH]_0}\frac{[RCl]}{[C_2H_5Cl]} \tag{9}$$

where k_2 denotes the rate coefficient for the reaction of hydrogen atom abstraction from the primary or secondary carbon in the molecules of propane and *n*-butane, and from the primary or tertiary carbons in the molecule of isobutane.

Relative rate determinations of the kinetics of the system described above were conducted using GC product analysis which allowed to discriminate between two pathways of hydrogen abstraction from molecules of propane, *n*-butane, and isobutane. All experimental results for reactions of Cl with propane, *n*-butane, and isobutane are summarized in Table I. Absolute values of k_2 were calculated from the rate constant ratios $k_2{}^{prim}/k_4$, $k_2{}^{sec}/k_4$, and $k_2{}^{tert}/k_4$, using an Arrhenius expression for the reference reaction of Cl atoms with ethane

$$k_4 = (8.6 \pm 0.5) \times 10^{-11} \times \exp[-(135 \pm 26)/T]\,\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

determined for the temperature range of 292–600 K [8], where $k_2{}^{prim}$ and $k_2{}^{sec}$ denote the rate coefficients of abstraction of hydrogen atoms from all primary and secondary carbon atoms in propane or *n*-butane molecules, respectively; $k_2{}^{tert}$ denotes the rate coefficient of the abstraction of tertiary hydrogen in isobutane. Based on these values the simple Arrhenius expressions are derived for each of the reactions studied and listed in Table II. The Arrhenius plots are shown in Figs. 1–3 for Cl reactions with propane, *n*-butane, and isobutane, respectively.

Reaction of Cl with Propane

It is well known from the thermochemical data [26] that the primary and secondary hydrogen abstraction from propane leading to the formation of *n*-propyl and isopropyl radical are both exothermic at 298 K by 8.9 kJ mol^{-1} and 18.9 kJ mol^{-1}, respectively. The difference in the exothermicity of radical formations indicates greater stability of a secondary radical than that of a primary radical. Experimental data obtained show that the attack of chlorine is faster and the activation energy lower in the case of β-hydrogen than those for α-hydrogen abstraction (Table II). Derived simple Arrhenius expressions show very weak temperature dependence with a positive value of activation energy for hydrogen abstraction from primary carbon of propane and negative one for hydrogen abstraction from secondary carbon (Table II and Fig. 1). The data were also fitted to a modified Arrhenius expression of the form $k = BT^n e^{-Ea/RT}$ (cm^3 molecule^{-1} s^{-1}) yielding $k_2{}^{prim} = (3.53 \pm 8.84) \times 10^{-10} \times T^{(-0.227\pm0.362)}$ $\exp[-(154.49 \pm 134.22)/T]$ and $k_2{}^{sec} = (3.41 \pm 9.08) \times 10^{-10} \times T^{(-0.274\pm0.384)}$ $\exp[(3.84 \pm 143.08)/T]$ (the errors represent 2σ). The results obtained for both primary and secondary hydrogen abstractions are shown by dotted line in Fig. 1. Again, the activation energy for the hydrogen abstraction from a primary carbon is slightly positive but practically equal to zero for the hydrogen abstraction from a secondary carbon.

Table I Rate Parameters for Competitive Photochlorination of Propane, *n*-Butane, and Isobutane

No. of Runs	Average Temp (K)	$k_2^{\mathrm{prim}}/k_4{}^a$	$k_2^{\mathrm{sec}}/k_4{}^a$	$k_2^{\mathrm{prim}\ a,b,c,d}$	$k_2^{\mathrm{sec}\ a,b,c,d}$
$Cl + C_3H_8/C_2H_6$					
30	298.6	1.06 ± 0.03	1.31 ± 0.03	$(5.8 \pm 0.2) \times 10^{-11}$	$(7.2 \pm 0.2) \times 10^{-11}$
28	328.0	1.04 ± 0.02	1.24 ± 0.03	$(5.9 \pm 0.1) \times 10^{-11}$	$(7.1 \pm 0.1) \times 10^{-11}$
23	365.0	1.02 ± 0.02	1.16 ± 0.01	$(6.1 \pm 0.1) \times 10^{-11}$	$(6.9 \pm 0.08) \times 10^{-11}$
25	412.3	1.00 ± 0.04	1.08 ± 0.04	$(6.2 \pm 0.3) \times 10^{-11}$	$(6.7 \pm 0.3) \times 10^{-11}$
28	467.7	0.97 ± 0.04	0.97 ± 0.04	$(6.3 \pm 0.3) \times 10^{-11}$	$(6.3 \pm 0.2) \times 10^{-11}$
$Cl + C_4H_{10}/C_2H_6$					
22	295.4	1.06 ± 0.07	2.59 ± 0.13	$(5.8 \pm 0.4) \times 10^{-11}$	$(14.1 \pm 0.7) \times 10^{-11}$
27	325.5	1.06 ± 0.08	2.41 ± 0.16	$(6.0 \pm 0.4) \times 10^{-11}$	$(13.7 \pm 0.9) \times 10^{-11}$
23	365.2	1.02 ± 0.04	2.26 ± 0.13	$(6.1 \pm 0.2) \times 10^{-11}$	$(13.4 \pm 0.8) \times 10^{-11}$
20	411.7	1.04 ± 0.03	2.18 ± 0.12	$(6.2 \pm 0.2) \times 10^{-11}$	$(13.5 \pm 0.7) \times 10^{-11}$
26	469.4	0.97 ± 0.06	1.85 ± 0.12	$(6.3 \pm 0.4) \times 10^{-11}$	$(11.9 \pm 0.8) \times 10^{-11}$
		$k_2^{\mathrm{prim}}/k_4{}^a$	$k_2^{\mathrm{tert}}/k_4{}^a$	$k_2^{\mathrm{prim}\ a,b,c,d}$	$k_2^{\mathrm{tert}\ a,b,c,d}$
$Cl + i\text{-}C_4H_{10}/C_2H_6$					
25	297.5	1.71 ± 0.04	0.92 ± 0.06	$(9.3 \pm 0.2) \times 10^{-11}$	$(5.0 \pm 0.3) \times 10^{-11}$
25	327.1	1.60 ± 0.06	0.81 ± 0.10	$(9.1 \pm 0.3) \times 10^{-11}$	$(4.6 \pm 0.6) \times 10^{-11}$
43	364.0	1.65 ± 0.23	0.76 ± 0.10	$(9.8 \pm 1.3) \times 10^{-11}$	$(4.5 \pm 0.6) \times 10^{-11}$
19	411.6	1.65 ± 0.05	0.69 ± 0.13	$(10.2 \pm 0.3) \times 10^{-11}$	$(4.3 \pm 0.8) \times 10^{-11}$
26	466.6	1.59 ± 0.11	–[e]	$(10.3 \pm 0.7) \times 10^{-11}$	–[e]

[a] The indicated errors are experimental uncertainties ($\pm 2\sigma$ precision) and do not take into account the uncertainties in the rate constant k_4.

[b] Placed on an absolute basis by use of an Arrhenius expression for the reaction of the Cl atoms with ethane [8].

[c] In cm^3 molecule^{-1} s^{-1} units.

[d] k_2^{prim} and k_2^{sec} denote the rate coefficients for the abstraction of hydrogen atom from all primary and secondary carbon atoms in alkane molecule, respectively.

[e] The 2-chloro-2-methylpropane is not stable at 466.6 K.

The first experimental study of Cl + propane reaction and its rate temperature dependence was published by Lewis et al. [9] who used absolute rate method:

$$k = (1.36 \pm 0.13) \times 10^{-10} \exp[(44 \pm 25)/T]\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

They reported a negative activation energy for the overall reaction studied by low-pressure discharge flow-resonance fluorescence technique in temperature range of 220–607 K. Our value of an overall rate coefficient for $Cl + C_3H_8$ reaction calculated as the sum of measured rate coefficients for hydrogen abstraction from primary and secondary carbons, $k = (1.3 \pm 0.04) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (at 298.6 K) is approximately 15% lower than the rate factor found by Lewis. Moreover, the overall rate coefficient was found to be invariant with temperature over the range 298–412 K as shown in Table I, decreasing only at temperature 467.7 K to slightly lower value of $(1.26 \pm 0.05) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Our experimental observations are consistent with those reported recently by Taatjes and co-workers [8] who observed no temperature dependence of overall rate coefficient in the temperature range of 292–700 K.

Table II A Summary of Arrhenius Parameters

Reaction[a]	A (10^{11} cm^3 molecule^{-1} s^{-1})[b]	E_a/R (K)[b]
$Cl + C_3H_8 \rightarrow CH_3CH_2CH_2 + HCl$	7.4 ± 0.2	70 ± 11
$Cl + C_3H_8 \rightarrow CH_3CHCH_3 + HCl$	5.1 ± 0.5	-104 ± 32
$Cl + C_4H_{10} \rightarrow CH_3CH_2CH_2CH_2 + HCl$	7.3 ± 0.2	68 ± 10
$Cl + C_4H_{10} \rightarrow CH_3CH_2CHCH_3 + HCl$	9.9 ± 2.2	-106 ± 75
$Cl + i\text{-}C_4H_{10} \rightarrow CH_3CHCH_3CH_2 + HCl$	13.0 ± 1.8	104 ± 50
$Cl + i\text{-}C_4H_{10} \rightarrow CH_3CCH_3CH_3 + HCl$	2.9 ± 0.5	-155 ± 58

[a] $Cl + C_2H_6 \rightarrow C_2H_5Cl + HCl$ as a primary standard.

[b] The indicated errors are two least-squares standard deviations ($\pm 2\sigma$ precision).

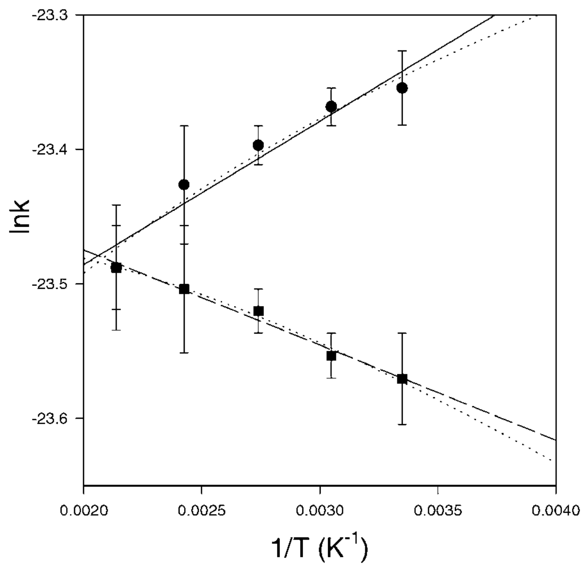

Figure 1 Simple Arrhenius plots for reaction $Cl + C_3H_8 \rightarrow CH_3CHCH_3 + HCl$ (filled circles and solid line), $Cl + C_3H_8 \rightarrow CH_3CH_2CH_2 + HCl$ (filled squares and interrupted line), and modified Arrhenius plots for both reactions (dotted line).

There is also a very good agreement between our rate coefficient and the newest value of $(1.33 \pm 0.08) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K reported by Hitsuda et al. [17] for the reaction of $Cl(^2P_{3/2})$ with C_3H_8 measured by direct experimental technique.

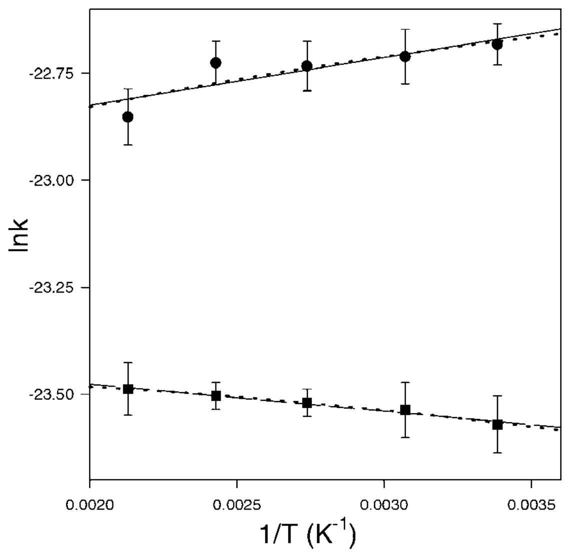

Figure 2 Simple Arrhenius plots for the reaction $Cl + n$-butane $\rightarrow CH_3CHCH_2CH_3 + HCl$ (filled circles and solid line), $Cl + n$-butane $\rightarrow CH_3CH_2CH_2CH_2 + HCl$ (filled squares and the interrupted line), and modified Arrhenius plots for both reactions (dotted line).

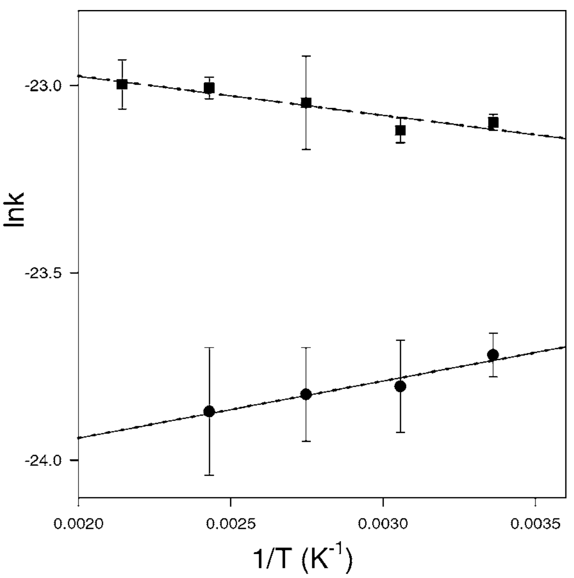

Figure 3 Simple Arrhenius plots for the reaction $Cl +$ isobutane $\rightarrow CH_3CCH_3CH_3 + HCl$ (filled circles and solid line), $Cl +$ isobutane $\rightarrow CH_3CHCH_3CH_2 + HCl$ (filled squares and interrupted line), and modified Arrhenius plots for both reactions (dotted line).

To our best knowledge, there is only one report concerning the rates of hydrogen abstraction from individual carbon atoms in propane molecule. Tyndall and co-workers [13] using FTIR spectroscopy determined the relative rates of Cl atoms attack on propane at 298 K. The yields of 1- and 2-chloropropane formation are $(43 \pm 3)\%$ and $(57 \pm 3)\%$, respectively. These values are in excellent agreement with corresponding results obtained in this work, $(45 \pm 2)\%$ and $(55 \pm 2)\%$.

A comparison of room temperature values of rate coefficient for Cl + propane reaction is shown in Table III.

Reaction of Cl with *n*-Butane

Analogously to propane, the primary and secondary hydrogen abstraction from *n*-butane leading to the formation of *n*-butyl and *s*-butyl radical are both exothermic at 298 K by 7.0 kJ mol^{-1} and 18.9 kJ mol^{-1}, respectively [26]. The greater stability of a secondary radical is confirmed by experimental data. The attack of chlorine atom is faster and activation energy lower in the case of β-hydrogen than for α-hydrogen abstraction (Table II). Relative rate constants ratios, k_2^{prim}/k_4 determined for reactions system $Cl + n$-butane/ethane appeared to be nearly the same (≈ 1) as in the case of previously discussed system Cl + propane/ethane (Table I). This finding leads to the conclusion that the attack of chlorine atom on the hydrogen attached to primary carbon in propane and butane molecule is equally fast. The simple Arrhenius expressions show very weak temperature dependence with the positive

Table III Overall Room Temperature Rate Coefficients for the Reaction of Cl Atoms with Propane, *n*-Butane, and Isobutane Obtained in This Work and Comparison to Recent Literature Data

k (10^{-10} cm^3 molecule^{-1} s^{-1})[a]	Pressure (Torr)	Method[b]	Reference
Cl + C_3H_8			
1.51(±0.06)	1–3	FFD/RF	[9]
1.38(±0.05)	10	LP/cwIRLPA	[8]
1.23(±0.10)	1	FFD/RF	[15]
1.31(±0.03)	60	LP/RF	[10]
1.34(±0.05)	760	RR	[11]
1.27(±0.02)	760	RR	[12]
1.60(±0.04)	760	RR	[16]
1.33(±0.08)	1.5	LP/LIF	[17]
1.37			[18] (IUPAC)
1.40			[19] (JPL)
1.30(±0.04)	100	RR	This work
Cl + *n*-Butane			
2.25(±0.10)	1–3	FFD/RF	[9]
1.97	760	RR	[11]
1.94	740	RR	[14]
1.94	760	RR	[12]
2.11(±0.18)	1	FFD/RF	[15]
2.25(±0.06)	60	LP/RF	[10]
2.20(±0.30)	700	RR	[13]
2.15(±0.15)	45, 48	LP/RF	[13]
1.91(±0.20)	60	LP/IR	[20]
2.18			[18] (IUPAC)
1.99(±0.13)	100	RR	This work
Cl + Isobutane			
1.46(±0.06)	1–3	FFD/RF	[9]
1.37(±0.02)	760	RR	[11]
1.51(±0.09)	740	RR	[16]
1.30(±0.01)	760	RR	[12]
1.40(±0.08)	760	FFD/RF	[15]
1.43			[18] (IUPAC)
1.43(±0.05)	100	RR	This work

[a] The indicated errors are uncertainties (±2σ precision).

[b] FFD/RF: Fast flow discharge–resonance fluorescence; LP/cwIRLPA: Laser photolysis-continous wave infrared long-path absorption; LP/RF: Laser photolysis–resonance fluorescence; RR: Relative rate method; LP/LIF: Laser photolysis–laser induced fluorescence; LP/IR: Laser photolysis–infrared diode laser absorption.

value of activation energy for hydrogen abstraction from primary carbon of *n*-butane and negative one for hydrogen abstraction from secondary carbon (Table II and Fig. 2). Fitting the results to a modified Arrhenius expression yields $k_2{}^{\text{prim}} = (3.53 \pm 7.57) \times 10^{-10} \times T^{(-0.229\pm0.310)}$ $\exp[-(147.05 \pm 114.55)/T]$ and $k_2{}^{\text{sec}} = (7.28 \pm 148.43) \times 10^{-10} \times T^{(-0.228\pm2.946)}$ $\exp[(1.314 \pm 1081.56)/T]$ (k in cm^3 molecule^{-1} s^{-1}, errors are ±2σ precision). Their logarithmic plots shown in Fig. 2 reveal slightly positive E_a for the hydrogen abstraction from primary carbons and E_a close to zero for the hydrogen abstraction from secondary carbons.

Lewis et al. [9] published the first experimental determination of absolute rate coefficients of reaction Cl + *n*-butane at temperatures 298, 422, and 598 K. Their Arrhenius expression

$$k = (2.15 \pm 0.10) \times 10^{-10} \times \exp[(12 \pm 26)/T]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

exhibits weak negative temperature dependence of the overall rate coefficient. The room temperature rate coefficient $k = (2.25 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} is slightly higher than our value of $(1.99 \pm 0.13) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} calculated as the sum of the rate coefficients for hydrogen abstraction from primary and secondary carbons in *n*-butane molecule. Our simple Arrhenius equation for overall rate coefficient $(1.7 \pm 0.2) \times 10^{-10}$ $\exp[(56 \pm 53)/T]$ cm^3 molecule^{-1} s^{-1} exhibits stronger negative temperature dependence than that determined by Lewis and coworkers [9].

There is a very good agreement between our room temperature rate coefficient and the values of 1.97×10^{-10} cm^3 molecule^{-1} s^{-1} [11] and 1.94×10^{-10} cm^3 molecule^{-1} s^{-1} [14] derived by Atkinson and Aschmann by carrying out a least-squares fit of absolute rate coefficients for Cl atoms reactions with the C_2—C_4 alkanes to their rate constant ratios determined for the alkane/*n*-butane pairs. The latter value of the rate coefficient is identical with the value estimated with a standard deviation of 11% by Hooshiyar et al. [12].

Tyndall and co-workers [13] have reported the relative yields of the 1- and 2-chlorobutane formation, which reflect the extent of initial attack at each site of *n*-butane. They obtained the yields of 1- and 2-chlorobutane formation (29 ± 2)% and (71 ± 3)%, respectively, which are in excellent agreement with our corresponding values of (29 ± 2)% and (71 ± 4)%.

Summary of the overall room temperature rate coefficients of the Cl atoms reaction with *n*-butane including the value recommended by Atkinson [18] is presented in Table III. These results are shown to be consistent with the uncertainty better than 15% with our value of absolute room temperature rate constant measured as the sum of both hydrogen abstractions from primary and secondary carbons in *n*-butane molecule.

Analogous trends in temperature dependence were observed, slightly positive temperature dependence for abstraction of hydrogen attached to primary carbon and slightly negative for hydrogen abstraction from secondary carbon.

Reaction of Cl with Isobutane

Calculated from the thermochemical data [26] the enthalpy of the primary and tertiary hydrogen abstraction from isobutane by chlorine atoms are both exothermic at 298 K by 9.4 kJ mol^{-1} and 31.4 kJ mol^{-1}, respectively. The difference in the enthalpy of two pathways of hydrogen abstraction is higher than in the case of propane and *n*-butane. As can be seen in Table I, isobutane was found to react with Cl slower than *n*-butane did. The overall rate constant of the Cl atoms reaction with isobutane determined in this work (calculated as the sum of the rate coefficients for hydrogen abstraction from primary and tertiary carbons in isobutane) exhibits negligible temperature dependence whereas the very weak opposite temperature influence was observed for the individual hydrogen abstraction reactions. The corresponding simple Arrhenius equations derived from kinetic measurements have been plotted in Fig. 3 and Arrhenius parameters are presented in Table II. The kinetic results were also fitted to a modified Arrhenius form and the following temperature dependence of the rate constants were derived: $k_2{}^{\mathrm{prim}} = (1.00 \pm 31.60) \times 10^{-10} \times T^{(0.038 \pm 2.281)} \exp[-(90.63 \pm 1692.07)/T]$ and $k_2{}^{\mathrm{sec}} = (3.03 \pm 2.39) \times 10^{-11} \times T^{(-0.002 \pm 0.117)} \exp[(151.31 \pm 94.50)/T]$. The units of the rate constants are cm^3 molecule^{-1} s^{-1} and the quoted uncertainties are 2σ. The modified Arrhenius expressions plotted in Fig. 3 show slightly positive activation energy for the hydrogen abstraction from primary carbons and slightly negative one for the hydrogen abstraction from tertiary carbon.

A comparison of the rate coefficient determined in this work to other literature data presented in Table III shows good agreement within 10%.

Comparison of Results Obtained Experimentally and by an Estimation Method

The overall rate constants of Cl atoms with propane, *n*-butane, and isobutane at room temperature determined in this work (given in Table III) are also in good agreement with the results obtained by an estimation method developed by Atkinson and Aschmann [14]. This method allowed room temperature rate constants for the reactions of Cl atoms with alkanes to be calculated. The calculations were based on the estimation of primary, secondary, and tertiary C—H group rate constants, which depend on the identity of the alkyl substituents around these groups. The lowest value of 2.9×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K, resulting from data in Table I, corresponds to the CH_3 group rate constant predicted by Atkinson and Aschmann [14]. The same values of $k_2{}^{\mathrm{prim}}$ were found by us both for propane and *n*-butane in agreement with an estimated value of 2.62×10^{-11} cm^3 molecule^{-1} s^{-1} [14] for primary group rate constant related to the Cl atom reactions with C_3 and C_4 alkanes. The rate coefficient for primary hydrogen atoms abstraction in molecule of isobutane equal to 3.10×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K is only slightly higher than analogous value for propane and *n*-butane. Thus, the influence of tertiary carbon atom on the value of hydrogen abstraction rate constant seems to be of no significance. Similar values of secondary group rate constants (within the experimental uncertainties range) were found in the case of hydrogen atoms abstraction from propane and *n*-butane, 7.20×10^{-11} cm^3 molecule^{-1} s^{-1} and 7.05×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively. In the case of tertiary hydrogen atom abstraction in isobutane, our experimental rate coefficient is 18% lower than an estimated value.

At higher temperatures Cl atom reaction rate constants show similar trends with the number of carbon atoms in the alkane.

CONCLUSIONS

We determined the contribution of competing abstraction of primary, secondary, and/or tertiary hydrogen atoms from propane, butane, and isobutane by Cl atom attack using the relative kinetic method with product formation analysis.

Attempted fitting of the experimental results to a modified Arrhenius expression leads to the conclusion that the temperature dependence of each reaction studied is described by a simple Arrhenius equation. As expected, these dependencies are very weak; however, interesting differences in their direction have been observed. First, the abstraction of primary hydrogen atoms from alkane molecule undergoes with the very low positive values of activation energy. In the case of secondary hydrogen atoms abstraction from propane and *n*-butane, a simple Arrhenius expression gives slightly negative value of activation energy, whereas a modified Arrhenius form gives E_a practically equal to zero. Slightly negative value of activation energy was determined from both Arrhenius forms for the abstraction of tertiary hydrogen atoms in isobutane molecule.

On the basis of our experimental results we postulate the formation of very weakly bounded complex during the abstraction of secondary or tertiary hydrogen atom by Cl atom, but further work is needed to explain fully this experimental finding.

We thank Dr. Andrzej Drys for his help in statistical analysis of experimental data.

BIBLIOGRAPHY

1. Finlayson-Pitts, B. J. Res Chem Int 1993, 19, 235.
2. Graedel, T. E.; Keene, W. C. Global Biogeochem Cycles 1995, 9, 47.
3. Finlayson-Pitts, B. J. J Geophys Res 1993, 98, 14991.
4. Leu, M. Y.; Timonen, R. S.; Keyser, L. F.; Yung, Y. T. J Phys Chem 1995, 99, 13203.
5. Singh, H. B.; Kasting, J. F. J Atmos Chem 1988, 7, 261.
6. Jobson, B. J.; Niki, H.; Yokouchi, Y.; Bottenheim, J.; Hopper, F.; Leaitch, R. J Geophys Res 1994, 99, 25355.
7. Keiser, B. N.; Sideris, T.; Niki, H.; Bottenheim, J.; Leaitch, R. Atmos Environ 1993, 27, 2979.
8. Pilgrim, J. S.; McIlroy, A.; Taatjes, C. A. J Phys Chem 1997, 101, 1873.
9. Lewis, R. S.; Sander, S. P.; Wagner, S.; Watson, R. T. J Phys Chem 1980, 84, 2009.
10. Mellouki, A. J Chim Phys 1998, 95, 513.
11. Atkinson, R.; Aschmann, S. M. Int J Chem Kinet 1985, 17, 33.
12. Hooshiyar, P. A.; Niki, H. Int J Chem Kinet 1995, 27, 1197.
13. Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Dill, M.; Kaiser, E. W. Int J Chem Kinet 1997, 29, 43.
14. Aschmann, S. M.; Atkinson, R. Int J Chem Kinet 1995, 27, 613.
15. Beichert, P.; Wingen, L.; Lee, J.; Vogt, R.; Ezell, M. J.; Ragains, M.; Neavyn, R.; Finlayson-Pitts, B. J. J Phys Chem 1995, 99, 13156.
16. Wallington, T. J.; Skewes, L. M.; Siegl, W. O.; Wu, C. H.; Japar, S. M. Int J Chem Kinet 1988, 20, 867.
17. Hitsuda, K.; Takahashi, K.; Matsumi, Y.; Wallington, T. J. Chem Phys Lett 2001, 346, 16.
18. Atkinson, R. J Phys Chem, Ref Data 1997, 26, 221.
19. DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation No. 12; JPL Publication, 1997, 97-4.
20. Qian, H.; Turton, D.; Seakins, D. W.; Pilling, M. J. Int J Chem Kinet 2002, 34, 86.
21. Ravishankara, A. R.; Wine, P. H. J Chem Phys 1980, 72, 25.
22. Chiltz, G.; Goldfinger, P.; Huybrechts, G.; Martens, G.; Verbecke, G. Chem Rev 1963, 63, 35.
23. Daiton, F. S.; Ayscough, P. B. In Photochemistry and Reaction Kinetics; Ashmore, P. G.; Daiton, F. S.; Sugden, T. M. (Eds.); Cambridge University Press: London, 1967; p. 64.
24. Fettis, G. C.; Knox, J. H. In Progress in Reaction Kinetics, Vol. 2; Porter, G. (Ed.); Pergamon Press and Macmillan Co.: New York, 1964; p. 1.
25. Tschuikow-Roux, E.; Yano, T.; Niedzielski, J. J Phys Chem 1984, 88, 1408.
26. NIST, Chemical Kinetics Database on the Web, Public Beta Release 1.1, Standard Reference Database 17, Version 7.0 (Web Version), http://kinetics.nist.gov/; IUPAC Subcommittee for Gas Kinetic Data Evaluation, http://www.iupac-kinetic.ch.cam.ac.uk/.