Kinetics of the Reactions of C_2H_5, *n*-C_3H_7, and *n*-C_4H_9 Radicals with Cl_2 at the Temperature Range 190–360 K

ARKKE J. ESKOLA, VLADIMIR A. LOZOVSKY,† RAIMO S. TIMONEN

Laboratory of Physical Chemistry, University of Helsinki, P. O. Box 55 (A. I. Virtasen aukio 1),
Helsinki, FIN-00014, Finland

Received 12 March 2007; revised 22 May 2007; accepted 22 May 2007

DOI 10.1002/kin.20272

ABSTRACT: The kinetics of the $C_2H_5 + Cl_2$, *n*-$C_3H_7 + Cl_2$, and *n*-$C_4H_9 + Cl_2$ reactions has been studied at temperatures between 190 and 360 K using laser photolysis/photoionization mass spectrometry. Decays of radical concentrations have been monitored in time-resolved measurements to obtain reaction rate coefficients under pseudo-first-order conditions. The bimolecular rate coefficients of all three reactions are independent of the helium bath gas pressure within the experimental range (0.5–5 Torr) and are found to depend on the temperature as follows (ranges are given in parenthesis): $k(C_2H_5 + Cl_2) = (1.45 \pm 0.04) \times 10^{-11}\ (T/300\ K)^{-1.73 \pm 0.09}\ cm^3\ molecule^{-1}\ s^{-1}$ (190–359 K), $k(n\text{-}C_3H_7 + Cl_2) = (1.88 \pm 0.06) \times 10^{-11}\ (T/300\ K)^{-1.57 \pm 0.14}\ cm^3\ molecule^{-1}\ s^{-1}$ (204–363 K), and $k(n\text{-}C_4H_9 + Cl_2) = (2.21 \pm 0.07) \times 10^{-11}\ (T/300\ K)^{-2.38 \pm 0.14}\ cm^3\ molecule^{-1}\ s^{-1}$ (202–359 K), with the uncertainties given as one-standard deviations. Estimated overall uncertainties in the measured bimolecular reaction rate coefficients are ±20%. Current results are generally in good agreement with previous experiments. However, one former measurement for the bimolecular rate coefficient of $C_2H_5 + Cl_2$ reaction, derived at 298 K using the very low pressure reactor method, is significantly lower than obtained in this work and in previous determinations. © 2007 Wiley Periodicals, Inc. Int J Chem Kinet 39: 614–619, 2007

---

† Deceased.

Correspondence to: Raimo Timonen; e-mail: raimo.timonen@helsinki.fi.

Contract grant sponsor: Bioscience and Environmental Research Council of the Academy of Finland.

Contract grant sponsor: Maj and Tor Nessling Foundation.

Contract grant sponsor: NoNeCK (Nordic Network for Chemical Kinetics).

INTRODUCTION

The gas phase reactions of carbon-centered free radicals with molecular chlorine are important elementary steps in chlorination processes [1]. Chlorination reactions of saturated hydrocarbons (RH) involve simple two-step free-radical chains that substitute chlorine for hydrogen, constituting an efficient cyclic process for the production of chlorine-containing hydrocarbons.

$$Cl + RH \rightarrow HCl + R \qquad (A)$$

$$R + Cl_2 \rightarrow RCl + Cl \qquad (B)$$

Both these reaction steps appear to be exothermic and have little or no activation energy [2]. Much is known about the reactions of chlorine atoms with saturated hydrocarbons (reaction (A)), partly due to their importance in the atmospheric as well as in the combustion processes and partly because these reactions can be isolated for detailed study relatively easily.

Contrasting the knowledge available on reactions (A), less information is available on the kinetics of the reactions of saturated hydrocarbon free radicals (R) with molecular chlorine (reaction (B)). This is particularly true for the reactions that have been subjected to direct studies [2]. Reactions (B) can also be important in the combustion and incineration processes of chlorinated hydrocarbons, especially under the conditions of incomplete combustion and when the ratio of hydrogen to chlorine is low [3,4].

The reactions of carbon-centered hydrocarbon free radicals with molecular chlorine are interesting also from the view of basic research. Already some time ago, Timonen and Gutman [5] performed the first direct measurements of the $CH_3 + Cl_2$, $C_2H_5 + Cl_2$, i-C_3H_7 + Cl_2, and t-$C_4H_9 + Cl_2$ reactions as a function of temperature employing laser photolysis/photoionization mass spectrometry method (LP-PIMS). Importantly, although the obtained temperature dependence of the $CH_3 + Cl_2$ reaction was positive ($E_a = 2.2 \pm 0.5$ kJ/mol), activation energies of the other reactions were negative or about zero, i.e., $E_a(C_2H_5 + Cl_2) = -1.3 \pm 0.5$ kJ/mol, $E_a(i\text{-}C_3H_7 + Cl_2) = -2.0 \pm 1.0$ kJ/mol, and $E_a(t\text{-}C_4H_9 + Cl_2) = 0 \pm 0.6$ kJ/mol [5]. At room temperature, bimolecular rate coefficients of these reactions are $k(CH_3 + Cl_2)_{298\ K} = (2.0 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, $k(C_2H_5 + Cl_2)_{298\ K} = (19 \pm 4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, $k(i\text{-}C_3H_7 + Cl_2)_{298\ K} = (57 \pm 11) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, and $k(t\text{-}C_4H_9 + Cl_2)_{298\ K} = (44 \pm 9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively. It is especially interesting to note that $C_2H_5 + Cl_2$ reaction at 298 K is about 10 times faster than that of the $CH_3 + Cl_2$. This is in contradiction with the recent determination of these reactions by Dobis and Benson [6]. They employed the very low-pressure reactor (VLPR) method and derived $k(CH_3 + Cl_2) = (3.4 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k(C_2H_5 + Cl_2) = (1.05 \pm 0.05) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K by following the product (CH_3Cl, C_2H_5Cl) formation kinetics [6]. Although the value obtained by Dobis and Benson [6] for the $CH_3 + Cl_2$ is close to that measured by Timonen and Gutman [5], the bimolecular reaction rate coefficient for the $C_2H_5 + Cl_2$ reaction derived by Dobis and Benson is about one twentieth of the value measured by Timonen and Gutman. In addition, the value derived by Dobis and Benson for the $C_2H_5 + Cl_2$ reaction is about three times smaller than the value they obtained for the $CH_3 + Cl_2$ reaction, which is in opposite with the observation by Timonen and Gutman for these reactions, as discussed above.

Using a relative rate method (UV radiation to produce radicals and FTIR spectroscopy to detect stable products), Kaiser et al. [7] measured reaction rate coefficient ratios $k(C_2H_5 + O_2)/k(C_2H_5 + Cl_2)$ as a function of helium pressure at 298 K. Combining the value for this ratio with the bimolecular reaction rate coefficient of the $C_2H_5 + O_2$ reaction obtained from direct measurements [8] at 298 K and under about 5 Torr He pressure, Kaiser et al. [7] derived $k(C_2H_5 + Cl_2)_{298\ K} = (16 \pm 2.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. This value is in good agreement with that of Timonen and Gutman [5]. Employing similar method as Kaiser et al. above, Tyndall et al. [9] determined the rate coefficient ratio $k(n\text{-}C_4H_9 + O_2)/k(n\text{-}C_4H_9 + Cl_2)$ at 296 K and pressures 10 and 700 Torr N_2. No pressure dependency was observed. Combining the obtained value for this ratio with the available direct determination of the bimolecular reaction rate coefficient for the n-$C_4H_9 + O_2$ reaction [10] at 298 K, Tyndall et al. derived $k(n\text{-}C_4H_9 + Cl_2)_{298\ K} = 23 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

To obtain deeper understanding of the reasons affecting the reactivity of radicals, it is profitable to systematically investigate a series of reactions in which only one parameter (e.g., radical substitution) is changed at a time. In the present study, we have performed the systematic work among the reactions of alkyl-substituted methyl radicals with Cl_2 and we describe the direct experimental measurements for reactions (1)–(3).

$$C_2H_5 + Cl_2 \rightarrow C_2H_5Cl + Cl \qquad (1)$$

$$n\text{-}C_3H_7 + Cl_2 \rightarrow n\text{-}C_3H_7Cl + Cl \qquad (2)$$

$$n\text{-}C_4H_9 + Cl_2 \rightarrow n\text{-}C_4H_9Cl + Cl \qquad (3)$$

Current study represents the first direct measurements for reactions (2) and (3). All reactions have been determined as a function of temperature to obtain information on the temperature dependencies. This work also extends the temperature range in which $R + Cl_2$ reactions have been studied to 190 K (i.e., significantly below room temperature).

EXPERIMENTAL

Details of the experimental apparatus used have been described previously [11], and so only a brief overview is given here. The radical $R(R = C_2H_5$, n-C_3H_7, or n-$C_4H_9)$ was generated from an appropriate precursor along the flow reactor by pulsed unfocused exciplex laser (ELI-76E) photolysis at 193 nm. The gas mixture flowing through the tubular, temperature-controlled reactor coupled with a photoionization mass spectrometer (PIMS) contained the radical precursor ($<$0.10%), Cl_2 in various amounts ($<$0.10%), and an inert carrier gas (He) in large excess ($>$99.8%). The employed reactor tubes with 8- and 17-mm inner diameters (i.d.) were made of seamless stainless steel and Pyrex-glass and were coated with halocarbon wax. The gas flow rates at used pressures (0.5–5 Torr of He) and temperatures (190–363 K) were typically about 4–6 m s^{-1} inside the reactor, which means that the gas mixture passes the uniformly cooled (heated) zone in about 80 ms. The gas was continuously sampled through a 0.4-mm-diameter hole at the side of the reactor and formed into a beam by a conical skimmer before it entered a vacuum chamber containing PIMS. As the gas beam traversed the ion source, a portion was selectively photoionized and the ions formed were mass selected in the quadrupole mass spectrometer (Extrel, C-50/150-QC/19 mm rods). The selected ions were detected by an off-axis electron multiplier.

Ionization radiation in the PIMS was provided by a chlorine lamp (8.9–9.1 eV) for C_2H_5, n-C_3H_7, and n-C_4H_9 radicals. Temporal ion signals were recorded by a multichannel scaler (EG&G Ortec MCS plus) from 10 ms before each laser pulse up to 80 ms following the pulse. Typically, a profile from 3000–10,000 repetitions was accumulated at about 5 Hz frequency before the least-squares method was used to fit an exponential function, $[R]_t = [R]_0 \times \exp(-k't)$, to the data. Here, $[R]_t$ is the signal proportional to the radical concentration at time t and k' is the first-order rate coefficient.

The C_2H_5 radicals were generated either from $C_2H_5NO_2$ as

$$C_2H_5NO_2 + h\nu(193\text{ nm}) \rightarrow C_2H_5 + NO_2 \quad (4a)$$

$$\rightarrow \text{Other products} \quad (4b)$$

or from C_2H_5Br [5] as

$$C_2H_5Br + h\nu(193\text{ nm}) \rightarrow C_2H_5 + Br \quad (5a)$$

$$\rightarrow \text{Other products} \quad (5b)$$

The n-C_3H_7 radicals were produced either from n-$C_3H_7NO_2$ as

$$n\text{-}C_3H_7NO_2 + h\nu(193\text{ nm}) \rightarrow n\text{-}C_3H_7 + NO_2 \quad (6a)$$

$$\rightarrow \text{Other products} \quad (6b)$$

or from n-C_3H_7Br [12] as

$$n\text{-}C_3H_7Br + h\nu(193\text{ nm}) \rightarrow n\text{-}C_3H_7 + Br \quad (7a)$$

$$\rightarrow \text{Other products} \quad (7b)$$

whereas n-C_4H_9 radicals were produced from n-C_4H_9Br [12] as

$$n\text{-}C_4H_9Br + h\nu(193\text{ nm}) \rightarrow n\text{-}C_4H_9 + Br \quad (8a)$$

$$\rightarrow \text{Other products} \quad (8b)$$

Experiments were conducted under conditions where only two significant reactions consumed R

$$R + Cl_2 \rightarrow \text{Products} \quad (B)$$

$$R \rightarrow \text{Heterogeneous loss} \quad (C)$$

The first-order decay rate of reaction (C), the wall reaction rate coefficient k_{wall}, consists of all first-order processes occurring in the reaction mixture and on the reactor wall without the added molecular reactant. It was measured by reducing the precursor concentration and/or laser intensity until the rate obtained for this reaction no longer depended on these factors, and the exponential fit to the temporal ion signal showed no deviation from the first-order decay. When these conditions were achieved, it was presumed that all radical–radical processes had only negligible rates compared to the first-order processes occurring in the system.

The first-order rate coefficient (k') was then measured as a function of the Cl_2 concentration ($[Cl_2]$), which was always much higher (>15 times) than [R], resulting in pseudo-first-order reaction kinetics. Since the only significant processes consuming R during these experiments were the reaction with Cl_2 (B) and disappearance in the mainly heterogeneous reaction (C), the bimolecular reaction rate coefficient $k(R + Cl_2)$ could be obtained from the slope of the k' versus $[Cl_2]$ plot. In Fig. 1, typical plots at 203, 298, and 358 K are shown for the $C_2H_5 + Cl_2$ reaction. An

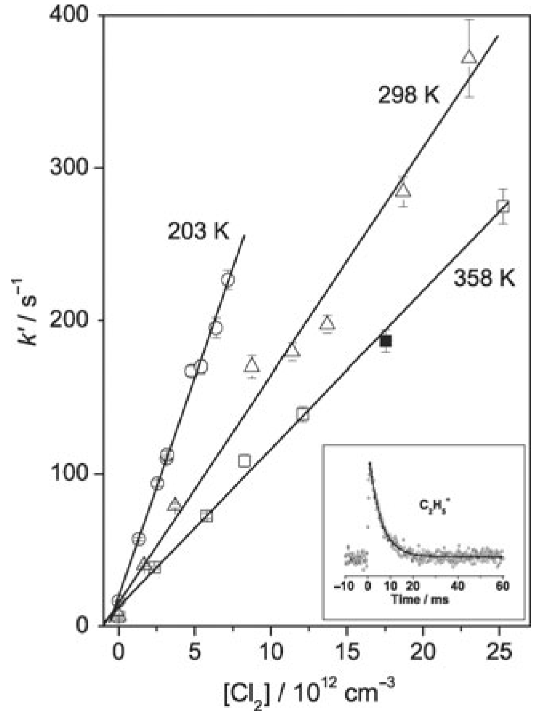

Figure 1 Plots of first-order C_2H_5 decay rate coefficients k' versus $[Cl_2]$ at $T = 203$, 298, and 358 K at about 1 Torr pressure employing the 17-mm i.d. reactor tube. Inset shows actual ion signal profile for the C_2H_5 decay in the presence of $[Cl_2] = 1.75 \times 10^{13}$ cm^{-3}. The corresponding decay rate is $k' = 188 \pm 5$ s^{-1} and is shown as the solid square in the plot. Uncertainty is one-standard deviation (1σ).

example of the C_2H_5 radical signal decay is shown at the lower right corner of Fig. 1.

Radical precursors, C_2H_5Br (Sigma-Aldrich Finland, Helsinki, Finland; purity $\geq$98%), $C_2H_5NO_2$ (Sigma-Aldrich Finland; purity $\geq$96%), n-C_3H_7Br (Sigma-Aldrich Finland; purity $\geq$99%), n-$C_3H_7NO_2$ (Sigma-Aldrich Finland; purity $\geq$98%), and n-C_4H_9Br (Sigma-Aldrich Finland; purity >98%) were degassed before use. Helium (Messer Suomi Oy, Tuusula, Finland; purity 99.9996%) and chlorine (Messer Suomi Oy; purity 99.8%) were employed as supplied.

RESULTS AND DISCUSSION

The measured bimolecular reaction rate coefficients for the C_2H_5, n-C_3H_7, and n-C_4H_9 radical reactions with Cl_2 are given in Table I along with their statistical uncertainties (1σ) and experimental conditions. The estimated overall uncertainties in the measured bimolecular reaction rate coefficients are ±20%. These arise mainly from the uncertainties in determining the reactant concentrations and from the uncertainties in the first-order rate coefficients. Linear least-squares fits of an expression $k = \tilde{A} \times (T/300\ \mathrm{K})^n$ to the experimental results are also given in Table I. In this expression, T is temperature in K, and $\tilde{A}$ and n are empirical parameters. Corresponding fits of an Arrhenius expression ($k = A \times \exp(-E_a/RT)$) are $k(C_2H_5 + Cl_2) = (3.21 \pm 0.29) \times 10^{-12} \times \exp(3.70 \pm 0.19\ \mathrm{kJ\ mol^{-1}}/RT)$ cm^3 $molecule^{-1}$ s^{-1}, $k(n\text{-}C_3H_7 + Cl_2) = (4.43 \pm 0.63) \times 10^{-12} \times \exp(3.54 \pm 0.31\ \mathrm{kJ\ mol^{-1}}/RT)$ cm^3 $molecule^{-1}$ s^{-1}, and $k(n\text{-}C_4H_9 + Cl_2) = (2.65 \pm 0.47) \times 10^{-12} \times \exp(5.23 \pm 0.38\ \mathrm{kJ\ mol^{-1}}/RT)$ cm^3 $molecule^{-1}$ s^{-1}, with the uncertainties given as one-standard deviations. Double logarithmic plots of the bimolecular rate coefficients for the C_2H_5, n-C_3H_7, and n-C_4H_9 radical reactions with Cl_2 are shown in Fig. 2. Also shown are results from previous studies of these reactions for comparison.

Measurements were carried out at various pressures to investigate possible contributions of three-body processes. Changing pressures between 0.5 and 5 Torr (He) did not change bimolecular rate coefficients in any of the $R + Cl_2$ reactions studied. Therefore, no three-body processes are likely to be present in any significant extent in these reactions.

Wallington et al. [13] also studied the reactions of ethyl radicals with O_2 and Cl_2 at 295 K using the relative rate method (UV radiation to produce radicals and FTIR spectroscopy to detect stable products). At 700 Torr total pressure (mainly N_2), they obtained $k(C_2H_5 + Cl_2)/k(C_2H_5 + O_2) = 1.99 \pm 0.14$. Combining this result with the preferred value for the bimolecular rate coefficient of the $C_2H_5 + O_2$ reaction at 298 K and 1 bar pressure ($k(C_2H_5 + O_2)_{298\ \mathrm{K,1\ bar}} = 7.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) [14] results in $k(C_2H_5 + Cl_2)_{298\ \mathrm{K,1\ bar}} = (13.9 \pm 1.0) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for the $C_2H_5 + Cl_2$ reaction under these conditions. This value is in an excellent agreement with the current result at 300 K, $k(C_2H_5 + Cl_2)_{300\ \mathrm{K}} = (1.45 \pm 0.04) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, which clearly indicates that the rate of this reaction is independent of buffer gas density over wide pressure range. Also the value obtained by Kaiser et al. [7], $k(C_2H_5 + Cl_2)_{298\ \mathrm{K,5\ Torr}} = (16 \pm 2.5) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, is in an excellent agreement with the current result (see Fig. 2). The bimolecular rate coefficient obtained by Timonen and Gutman [5] at 298 K, $k(C_2H_5 + Cl_2)_{298\ \mathrm{K}} = (19 \pm 4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, is slightly higher than the value measured in the current determination. On the other hand, the activation energy they have obtained for this reaction, $E_a(C_2H_5 + Cl_2)$ [5] $= -1.3 \pm 0.5$ kJ/mol^{-1}, is less negative than obtained in this work,

Table I Results and Conditions of the Experiments[a] Used to Measure the Bimolecular Rate Coefficients of the Reaction $R + Cl_2 \rightarrow$ Products ($R = C_2H_5$, n-C_3H_7, and n-C_4H_9)

T (K)	P^b (Torr)	10^{-12} [Cl_2] (cm^{-3})	k^c_{wall} (s^{-1})	10^{-12} k^d (cm^3 s^{-1})
		$C_2H_5 + Cl_2 \rightarrow C_2H_5Cl + Cl$		
190	1.1^e	1.5–4.7	10	33.3 ± 1.1
203	1.2^f	1.4–7.2	14	28.6 ± 0.9
223	1.2^f	2.2–8.3	16	23.8 ± 1.3
244	$1.1^{e,f}$	3.0–13.5	12	18.5 ± 1.3
267	1.2	2.7–12.1	12	18.1 ± 1.0
298	1.1	1.7–23.0	8	14.9 ± 0.8
336^g	1.0	3.9–20.0	11	12.5 ± 0.3
359^g	1.0	2.4–25.2	6	10.3 ± 0.3
$k(C_2H_5 + Cl_2) = (1.45 \pm 0.04) \times 10^{-11}$ $(T/300\ K)^{-1.73 \pm 0.09}$ cm^3 molecule^{-1} s^{-1}				
		n-$C_3H_7 + Cl_2 \rightarrow n$-$C_3H_7Cl + Cl$		
204	1.1	1.5–6.3	18	32.6 ± 1.8
220	1.0	1.6–5.0	6	30.5 ± 0.9
230	5.4	4.8–17.2	51^h	30.5 ± 1.9
244	$1.1^{e,f}$	1.6–5.9	16	29.0 ± 1.1
267	1.0	1.4–10.4	16	19.8 ± 0.8
297	$1.0^{e,f}$	2.1–10.0	13	17.5 ± 0.9
330^i	1.0	2.1–15.4	8	16.4 ± 0.5
355^i	1.0	1.7–14.1	5	14.8 ± 0.4
363	4.6	4.9–18.8	33^h	14.2 ± 1.3
$k(n\text{-}C_3H_7 + Cl_2) = (1.88 \pm 0.06) \times 10^{-11}$ $(T/300\ K)^{-1.57 \pm 0.14}$ cm^3 molecule^{-1} s^{-1}				
		n-$C_4H_9 + Cl_2 \rightarrow n$-$C_4H_9Cl + Cl$		
202	1.0	1.4–4.1	26	52.8 ± 2.1
221	1.0	1.5–3.9	17	50.1 ± 2.9
244	1.0	1.7–4.9	17	35.4 ± 1.1
267	1.0	1.4–6.4	9	29.5 ± 1.0
299	$1.2^{e,f}$	2.0–6.9	7	22.7 ± 1.0
324	1.1	3.0–12.1	17	16.9 ± 0.4
359	1.0^f	2.4–11.4	12	15.0 ± 0.4
$k(n\text{-}C_4H_9 + Cl_2) = (2.21 \pm 0.07) \times 10^{-11}$ $(T/300\ K)^{-2.38 \pm 0.14}$ cm^3 molecule^{-1} s^{-1}				

[a] $C_2H_5NO_2$, n-$C_3H_7NO_2$, and n-C_4H_9Br used as precursors for C_2H_5, n-C_3H_7, and n-C_4H_9 radicals employing 193 nm radiation, unless otherwise stated. Range of precursor concentrations used: $(0.7–2.4) \times 10^{12}$ molecule cm^{-3} for $C_2H_5NO_2$, $(0.5–2.1) \times 10^{12}$ molecule cm^{-3} for n-$C_3H_7NO_2$, and $(4.5–27) \times 10^{12}$ molecule cm^{-3} for n-C_4H_9Br.

[b] Helium used as a buffer gas.

[c] Pyrex-glass reactor tube with 17-mm inner diameter (i.d.) coated with halocarbon wax used, unless otherwise stated.

[d] Statistical uncertainties shown are 1σ; estimated overall uncertainties are about ±20%.

[e] A few decay rates measured at three times higher buffer gas pressure ($3 \times P$); however, no dependence on pressure was observed.

[f] A few decay rates measured at $0.5 \times P$; however, no dependence on pressure was observed.

[g] C_2H_5Br (193 nm) used as a precursor, concentration range $(2.1–2.9) \times 10^{13}$ molecule cm^{-3}.

[h] Stainless steel reactor tube with 8-mm i.d. coated with halocarbon wax.

[i] n-C_3H_7Br (193 nm) used as a precursor, concentration range $(0.6–1.3) \times 10^{13}$ molecule cm^{-3}.

$E_a = -3.70 \pm 0.19$ kJ mol^{-1}. Similar differences were also observed in the context of $C_2H_3 + Cl_2$ reaction measurements [11]. We are unable to propose any probable reason for these differences. However, a significantly more pronounced difference exists between current results, which are in good agreement with previous determinations discussed above, and that obtained by Dobis and Benson [6] for the $C_2H_5 + Cl_2$ reaction (see Fig. 2). Their bimolecular rate coefficient at 298 K is lower than other values with a factor of 10 or more.

The value derived by Tyndall et al. [9] for the n-$C_4H_9 + Cl_2$ reaction, $k(n\text{-}C_4H_9 + Cl_2)_{298\ K} = 23 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, is in an excellent agreement with the current determination $k(n\text{-}C_4H_9 + Cl_2)_{300\ K} = (2.21 \pm 0.07) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Finally, to gain understanding of the reasons affecting the reactivity of the alkyl radicals in $R + Cl_2$ reactions, it is instructive to make comparison among the reactions of alkyl-substituted methyl radicals with Cl_2 when R substitution is

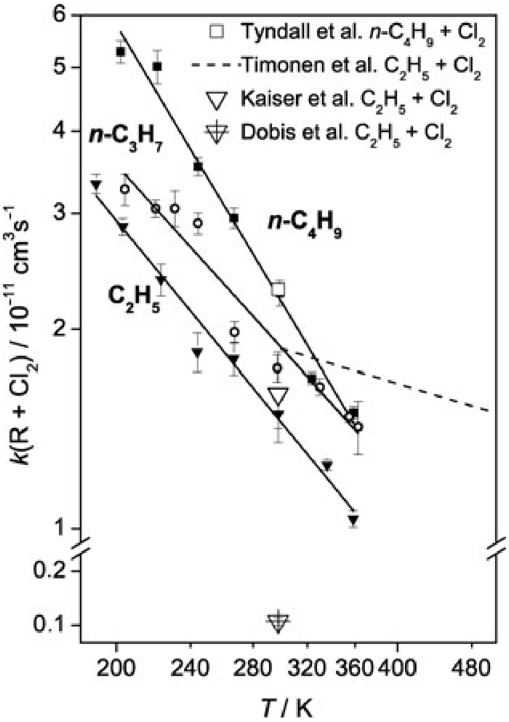

Figure 2 Double logarithmic plots of bimolecular rate coefficients for $C_2H_5 + Cl_2$, n-$C_3H_7 + Cl_2$, and n-$C_4H_9 + Cl_2$ reactions versus T. Fittings to the current data are shown with solid lines. Bimolecular rate coefficients for comparison are taken from Dobis and Benson [6], Kaiser et al. [7], and Tyndall et al. [9]. For $C_2H_5 + Cl_2$ reaction, only fitting of the bimolecular rate coefficients given by Timonen and Gutman [5] is shown as a broken line for clarity.

systemically changed. A good choice is to perform comparison at about 300 K temperature. Starting from the above-mentioned methyl radical + Cl_2 reaction with the value given by Timonen and Gutman [5], $k(CH_3 + Cl_2)_{298\ K} = (2.0 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (direct measurement of Kovalenko and Leone [15] at room temperature, $(1.5 \pm 0.1) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, also supported this value), it can be readily noted that the $C_2H_5 + Cl_2$ reaction ($k(C_2H_5 + Cl_2)_{298\ K} = (1.45 \pm 0.04) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) is about 10 times faster than $CH_3 + Cl_2$ reaction. However, the substitution of β-hydrogen in the ethyl radical with the methyl group (i.e., forming n-propyl radical) has only a small effect: $k(n\text{-}C_3H_7 + Cl_2)_{300\ K}/k(C_2H_5 + Cl_2)_{300\ K} \approx 1.30$. Substituting γ-hydrogen in the n-propyl radical with the methyl group (i.e., forming n-butyl radical) has even a smaller effect: $k(n\text{-}C_4H_9 + Cl_2)_{300\ K}/k(n\text{-}C_3H_7 + Cl_2)_{300\ K} \approx 1.18$. Additional kinetic studies are in progress to improve our understandings of the reactivities of substituted alkyl radicals in their reactions with Cl_2. Currently, we are working with $CH_3 + Cl_2$ and $CD_3 + Cl_2$ reactions.

CONCLUSIONS

The bimolecular rate coefficients of the $C_2H_5 + Cl_2$, n-$C_3H_7 + Cl_2$, and n-$C_4H_9 + Cl_2$ reactions were measured as a function of temperature, and no experimental evidences on activation barriers were observed for any of the reactions studied. Arrhenius activation energies of these reactions, $E_a(C_2H_5 + Cl_2) = -3.70 \pm 0.19$ kJ mol^{-1}, $E_a(n\text{-}C_3H_7 + Cl_2) = -3.54 \pm 0.31$ kJ mol^{-1}, and $E_a(n\text{-}C_4H_9 + Cl_2) = -5.23 \pm 0.38$ kJ mol^{-1}, are more negative than expected and are comparable with those of R + HBr reactions [12]. The current results of the direct measurements for the $C_2H_5 + Cl_2$ and n-$C_4H_9 + Cl_2$ reactions performed at few Torr pressures are in excellent agreement with bimolecular rate coefficients derived previously using the relative rate method at low and high pressures.

BIBLIOGRAPHY

1. Kroschwitz, J. I.; Howe-Grant, M. (Eds). Encyclopedia of Chemical Technology, 4th ed.; Wiley: New York, 1993; Vol. 5.
2. NIST Chemical Kinetics Database (Web version), release 1.4; National Institute of Standards and Technology: Gaithersburg, MD.
3. Tsang, W. Combust Sci Technol 1990, 74, 99–116.
4. Procaccini, C.; Bozzelli J. W.; Longwell, J. P.; Smith, K. A.; Sarofim, A. F. Environ Sci Technol 2000, 34, 4565–4570.
5. Timonen, R. S.; Gutman, D. J Phys Chem 1986, 90, 2987–2991.
6. Dobis, O.; Benson S. W. Z Phys Chem 2001, 215, 283–304.
7. Kaiser, E. W.; Wallington, T. J.; Andino, J. M. Chem Phys Lett 1990, 168, 309–313.
8. Slagle, I. R.; Feng, Q.; Gutman, D. J Phys Chem 1984, 88, 3648–3653.
9. Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Dill, M.; Kaiser, E. W. Int J Chem Kinet 1997, 29, 43–55.
10. Lenhardt, T. M.; McDade, C. E.; Bayes, K. D. J Chem Phys 1980, 72, 304–310.
11. Eskola, A. J.; Timonen, R. S. Phys Chem Chem Phys 2003, 5, 2557–2561.
12. Seetula, J. A.; Slagle, I. R. J Chem Soc, Faraday Trans 1997, 93, 1709–1719.
13. Wallington, T. J.; Andino, J. M.; Kaiser, E. W.; Japar, S. M. Int J Chem Kinet 1989, 21, 1113–1122.
14. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J. Atmos Chem Phys 2006, 6, 3625–4055.
15. Kovalenko, L. J.; Leone, S. R. J Chem Phys 1984, 80, 3656–3667.