Kinetics of Reactions of Cl Atoms with Ethane, Chloroethane, and 1,1-Dichloroethane

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Reactions of Cl atoms with ethane (1), chloroethane (2), and 1,1-dichloroethane (3) were studied experimentally with the discharge flow/resonance fluorescence technique over wide ranges of temperatures and at pressures between 2.3 and 9.2 Torr. Results of earlier investigations of the reactions of Cl atoms with ethane and chloroethanes are analyzed and compared with the results of the current work. The rate constants of the reaction of Cl atoms with ethane obtained in the current study ($k_1 = (4.91 \times 10^{-12})T^{0.47} \exp(-82\ \mathrm{K}/T)$ cm^3 molecule^{-1} s^{-1}, 299−1002 K) agree with the results of earlier determinations. Combination of the temperature dependence of k_1 obtained in the current work with the existing (mostly at lower temperatures) literature data results in the expression $k_1 = (7.23 \times 10^{-13})T^{0.70} \exp(+117\ \mathrm{K}/T)$ cm^3 molecule^{-1} s^{-1} (203−1400 K). Rate constants of the reactions of Cl atoms with chloroethane and 1,1-dichloroethane demonstrate different temperature dependences in the low-temperature (room temperature to 378 K) and the high-temperature (484−810 K) regions. The differences are due to the regeneration of Cl atoms at higher temperatures as a consequence of the fast thermal decomposition of radical products with a chlorine atom in the β position. This information enables quantitative differentiation between the site-specific reaction channels. The results of the current study, combined with those of earlier relative-rate experiments, were used to derive expressions for the temperature dependences of the rates of the site-specific abstraction channels: $k_{2a}(T) = (2.76 \pm 0.28) \times 10^{-11} \exp(-455 \pm 44\ \mathrm{K}/T)$ (296−810 K), $k_{2b}(T) = (1.92 \pm 0.47) \times 10^{-11} \exp(-789 \pm 84\ \mathrm{K}/T)$ (296−378 K), $k_{3a}(T) = (1.46 \pm 0.21) \times 10^{-11} \exp(-733 \pm 58\ \mathrm{K}/T)$ (293−810 K), and $k_{3b}(T) = (2.98 \pm 1.42) \times 10^{-11} \exp(-1686 \pm 160\ \mathrm{K}/T)$ (293−378 K) cm^3 molecule^{-1} s^{-1}, where channels a and b signify abstraction of hydrogen atoms in the α and β positions, respectively.

I. Introduction

Reactions of Cl and H atoms with chlorinated hydrocarbons (CHCs) are among the most important and sensitive reactions in the combustion and incineration of CHCs.[1−9] In CHC/O_2 and CHC/hydrocarbon/O_2 flames, reactions of Cl and H atoms with CHCs together with unimolecular decomposition are the major channels of consumption of CHCs.[1−5,7−14] As a part of a project directed at the elucidation of the kinetics of these important reactions, we recently reported[15−18] the results of our experimental and computational studies of the reactions of H and Cl atoms with methane and chlorinated methanes, and the reactions of H atoms with ethane and three chlorinated ethanes. In the current work, we extend such kinetic studies to the reactions of Cl atoms with ethane and two chlorinated ethanes (C_2H_5Cl and CH_3CHCl_2) conducted over wide ranges of temperatures:

$$\mathrm{Cl} + \mathrm{C_2H_6} \rightarrow \mathrm{HCl} + \mathrm{C_2H_5}\ (299{-}1002\ \mathrm{K}) \tag{1}$$

$$\mathrm{Cl} + \mathrm{C_2H_5Cl} \rightarrow \mathrm{HCl} + \mathrm{CH_3CHCl}\ (296{-}810\ \mathrm{K}) \tag{2a}$$

$$\rightarrow \mathrm{HCl} + \mathrm{CH_2CH_2Cl} \tag{2b}$$

$$\mathrm{Cl} + \mathrm{CH_3CHCl_2} \rightarrow \mathrm{HCl} + \mathrm{CH_3CCl_2}\ (293{-}810\ \mathrm{K}) \tag{3a}$$

$$\rightarrow \mathrm{HCl} + \mathrm{CH_2CHCl_2} \tag{3b}$$

The numbers in parentheses indicate the experimental temperature ranges of the current work.

The temperature behavior of the fast reaction 1 has been studied by a number of groups (refs 19−26 and references therein) with generally good agreement between the results of different studies. Reviews of these data can be found, for example, in refs 27 and 28. The current study extends the temperature range of direct experimental studies of reaction 1 by sensitive flow techniques to 1002 K, almost to the high-temperature range covered by shock-tube-based methods.[26] Although reactions 2 and 3 have been studied before,[22,29−37] earlier studies were confined to relatively low temperatures, where research was stimulated by the importance of these reactions for atmospheric chemistry; most of these studies involved indirect determinations of rate constants. Only one direct determination of the rate constants of reactions 2 and 3 as functions of temperature is available in the literature.[35]

In the current study, the kinetics of reactions 1−3 was investigated by the discharge flow technique with resonance fluorescence detection of Cl atoms. The excellent sensitivity of the method (detection limit of $<10^8$ atoms cm^{-3}) permits experiments with very low initial Cl concentrations ($\leq 10^{11}$ atoms cm^{-3}), thus ensuring the absence of any complications due to potential fast secondary reactions. The rate constants of reactions 1−3 were obtained as functions of temperature in direct experiments. In reactions 2 and 3, different temperature dependences were obtained in the low-temperature (296−378 K) and the high-temperature (484−810 K) regions. The differences are due to the regeneration of Cl atoms at higher temperatures as a consequence of the fast thermal decomposition of radical products with a Cl atom in the β position. This information enables quantitative differentiation between the site-specific reaction channels. In particular, the current study

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provides the first direct determination of the rate constant of the abstraction of a hydrogen atom in the α position in reactions 2 and 3. The information obtained on the site-specific and the overall rate constants, combined with the results of earlier relative-rate studies,[29,32,34] was used to derive expressions for the temperature dependences of the rates of the individual reaction channels.

The paper is organized as follows: Section I (current) is an introduction. The experimental method, procedures, and results are reported in section II. The results are discussed in section III. Brief conclusions are given in section IV.

II. Experimental Section

Rate constant measurements were conducted in a heatable tubular flow reactor under pseudo-first-order conditions with a large excess of molecular substrate. Cl atoms were detected by resonance fluorescence, and their decay was measured as a function of contact time over wide ranges of experimental conditions.

II.1. Experimental Apparatus. Details of the experimental apparatus have been described previously in connection with our investigation of reactions of H atoms with methane and chloromethanes;[15] modifications introduced to enable studies of Cl atom reactions have been presented in ref 18. Thus, only a brief description of the apparatus is given here. Cl atoms were generated in a sidearm of a heated tubular quartz reactor by a 2.45 GHz microwave discharge in a Cl_2/He mixture. Chlorine atoms formed in the discharge area were carried through the reactor by a flow of helium, and their concentration was monitored by resonance fluorescence in the detection zone located downstream. The molecular substrate ($C_2H_{6-X}Cl_X$) was introduced through a quartz movable injector. Care was taken to ensure that, under all experimental conditions used in the current work, the plug flow approximation was valid. The only exception to the plug flow approximation was the minor contribution of axial and radial diffusion of Cl atoms; diffusional corrections had to be introduced into the experimentally obtained atom decay rates (vide infra). The uniformity of the temperature profiles in the working zone of the reactor (15−30 cm in length) was no worse than 0.5% of T.

Three reactors were used in these experiments: a quartz reactor with an internal diameter (i.d.) of 1.93 cm, a quartz reactor with i.d. = 3.19 cm, and a Pyrex reactor with i.d. = 4.66 cm. The reactor surface, the surface of the movable injector, and the inside of the discharge tube were treated to reduce heterogeneous loss of Cl atoms by first soaking in a 5% aqueous solution of ammonium bifluoride for 30 min with subsequent rinsing with distilled water and then by the method of Sepehrad et al.[38] This procedure, essentially, results in a very thorough cleaning of the glass surface. The resultant values of the first-order wall loss rate constant, k_w, were always below 20 s^{-1}. Typical values of k_w were ~2−8 s^{-1}. Reactors of different diameters were used to rule out potential contributions of heterogeneous reactions to the rate constant values obtained in the experiments (vide infra).

Cl atom resonance fluorescence was induced by light from a discharge flow resonance lamp[39,40] and detected by a solar blind photomultiplier (EMR model 542-G-09, peak of sensitivity in the 115−170 nm spectral interval). CaF_2 windows (cutoff 123 nm) and a gas optical filter (1 Torr of N_2O, optical path length 3 cm)[40,41] were used to block potential radiation from H and O atoms (121.6 and 130.2−130.6 nm, respectively) while transmitting the Cl resonance lines at 135−139 nm. The sensitivity of the atom detection system to Cl atoms was determined by titration with Br_2 (the rate constant of the Cl + Br_2 reaction is $\geq 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}).[42,43] The sensitivity limit (defined by unity signal-to-noise ratio) was $<10^8$ atoms cm^{-3}.

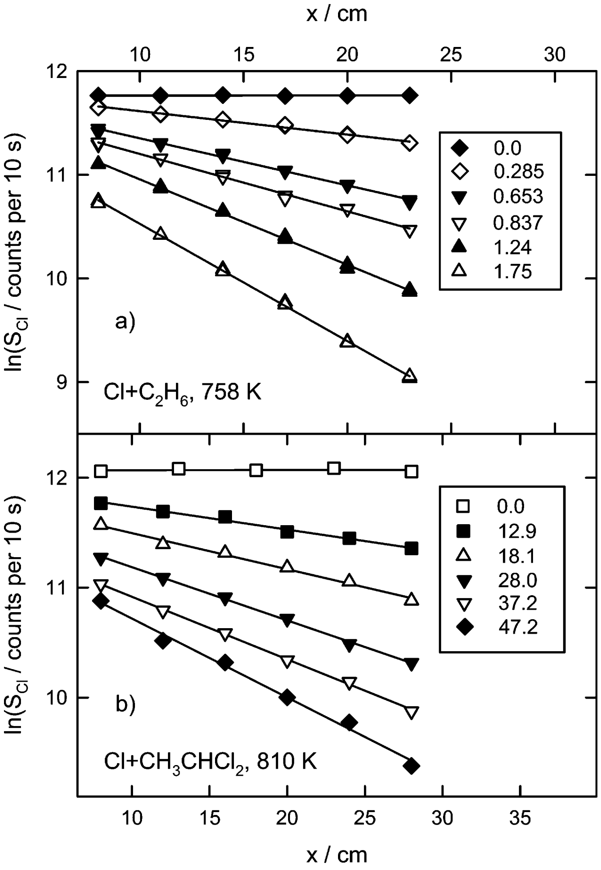

Figure 1. Examples of experimentally obtained ln(S_{Cl}) vs x dependences. Data from experiments 9 on Cl + C_2H_6 and 15 on Cl + CH_3CHCl_2 (see Tables 1 and 2). Numbers are the concentrations of the $C_2H_{6-X}Cl_X$ substrate (10^{12} molecules cm^{-3}).

Molecular substrates ($C_2H_{6-X}Cl_X$) were stored undiluted in Pyrex reservoirs. Flows of these reagents into the reactor were determined by measuring the pressure drop over time in a calibrated volume. To ensure the absence of interference from heterogeneous absorption and desorption processes on the walls of the vacuum manifold, it was verified that the measured flows were independent of the surface-to-volume ratio of the calibrated volume. Flows of molecular chlorine to the atom-producing discharge were measured in a similar way. The dissociation efficiency of the discharge was in the 20−50% range, which resulted in the concentrations of undissociated Cl_2 in the reactor being no more than a factor of 2 higher than the initial Cl atom concentrations.

A flow of CF_4 with concentrations in the (3.1−20) × 10^{14} molecules cm^{-3} range was added to the carrier gas through an inlet located upstream from the reaction zone to ensure fast equilibration[44] of the ground and the excited spin−orbit states of the Cl atom. Literature values of the room-temperature quenching rate coefficient range from 0.23 × 10^{-10} to 1.5 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}.[45−47] Therefore, the large concentrations of CF_4 used in the current work keep the rate of spin−orbit equilibration much faster than the rates of the reactions under study.

II.2. Reaction Rate Measurements. All experiments to measure the rate constants of reactions 1−3 were conducted under conditions of an excess of molecular substrate. Initial concentrations of Cl atoms in the detection zone were in the

TABLE 1: Conditions and Results of Experiments To Measure Rate Constants of the Reactions of Cl Atoms with Ethane and Chloroethane (Reactions 1 and 2)

no.[a]	T/K	P[b]/Torr	$[C_2H_{6-X}Cl_X]$[c] range/10^{12}	$[CF_4]$[c]/10^{14}	k_0[d]/s^{-1}	V[e]/m s^{-1}	$[Cl]_0$[c]/10^{10}	$((k' - k'_{OBS})/k'_{OBS}))_{max}$[f]	k_i[g]/10^{-11}
				$Cl + C_2H_6 \rightarrow HCl + C_2H_5$ (1)					
1	299	3.78	1.55−5.88	13.5	0.1 ± 7.4	32.7	2.8	0.045	5.23 ± 0.20
2	299	2.47	0.66−4.62	7.5	3 ±16	24.5	8.9	0.033	5.46 ± 0.56
3	346	3.64	1.18−5.00	5.2	−3.8 ± 7.6	35.8	3.9	0.036	6.14 ± 0.26
4*	402	2.45	0.14−2.59	10.1	3.6 ± 1.0	14.1	1.8	0.054	6.94 ± 0.60
5	426	4.73	0.71−4.24	16.9	−6 ± 11	39.0	3.2	0.029	6.88 ± 0.40
6*	498	2.45	0.12−2.4	8.3	−0.1 ± 8.5	17.5	3.7	0.049	7.66 ± 0.63
7	604	5.99	0.62−2.52	16.0	−7.2 ± 7.3	35.5	3.2	0.018	8.27 ± 0.46
8*	707	4.02	0.34−3.12	5.5	−6 ± 12	27.9	5.4	0.046	9.44 ± 0.58
9+	758	4.08	0.285−1.75	9.2	1.7 ± 2.6	14.5	1.9	0.079	10.03 ± 0.26
10+	758	4.11	0.33−1.81	6.2	−3.5 ± 7.4	14.5	0.86	0.080	9.93 ± 0.68
11*	855	4.00	0.32−3.87	3.1	0 ± 13	33.3	6.1	0.056	10.68 ± 0.63
12	1002	9.22	0.60−4.19	11.7	14 ± 14	57.3	2.4	0.028	11.63 ± 0.60
				$Cl + C_2H_5Cl \rightarrow HCl + C_2H_4Cl$ (2)					
1	296	4.29	10.9−36.9	12.0	−1.3 ± 9.4	31.0	3.0	0.048	0.76 ± 0.04
2	320	2.85	4.25−21.1	9.6	5 ± 10	23.3	6.9	0.024	0.82 ± 0.07
3	346	3.60	4.14−28.9	11.0	0.6 ± 6.4	34.8	2.6	0.032	0.97 ± 0.04
4	378	3.94	3.24−27.8	13.0	9 ± 11	37.9	5.4	0.034	1.05 ± 0.07
5*	378	4.03	2.88−12.1	19.2	4.8 ± 5.6	7.3	1.5	0.109	1.04 ± 0.08
6	484	7.26	5.28−20.2	9.0	2.7 ± 5.2	29.2	4.3	0.031	1.11 ± 0.04
7*	494	4.03	1.54−14.0	5.6	6.8 ± 7.0	9.6	1.5	0.098	1.07 ± 0.09
8	523	5.88	4.73−30.0	16.7	6 ± 11	44.7	2.7	0.029	1.08 ± 0.06
9	557	4.32	2.55−14.1	14.3	0 ± 10	31.2	2.8	0.014	1.12 ± 0.11
10	604	5.91	2.61−16.0	6.6	6 ± 13	35.7	4.6	0.017	1.27 ± 0.13
11	713	7.52	4.6−23.8	16.0	10 ± 15	51.2	3.3	0.025	1.45 ± 0.10
12*	758	4.06	1.32−9.78	7.7	5.6 ± 6.7	14.4	1.6	0.075	1.68 ± 0.12
13	810	7.24	2.99−10.9	17.5	−0.4 ± 7.9	39.2	1.9	0.011	1.65 ± 0.12

[a] Experiment number. A quartz reactor with i.d. = 3.19 cm was used in experiments marked with an asterisk, a Pyrex reactor with i.d. = 4.66 cm was used in experiments marked with a plus sign, and a quartz reactor with i.d. = 1.93 cm was used in unmarked experiments. [b] Reactor pressure. [c] Units of concentrations are molecules cm^{-3}. [d] Zero-abscissa intercept on the k' vs $[C_2H_{6-X}Cl_X]$ dependence. [e] Average flow velocity. [f] Maximum relative value of the diffusion correction. [g] Units of rate constants are cm^3 $molecule^{-1}$ s^{-1}. Error limits represent statistical uncertainties and are reported as 2σ. Maximum estimated systematic uncertainties are 8% of the rate constant value (see the text).

range (0.9−9) × 10^{10} atoms cm^{-3}. Exact knowledge of the Cl atom concentrations is not needed for the determination of rate constants because all experiments were conducted under pseudo-first-order conditions. The rate of heterogeneous loss of Cl atoms on the walls of the reactor and the movable injector (0.5−17 s^{-1}) was regularly measured using the method described in ref 18 (in the absence of molecular substrate).

The time of contact between the molecular substrate and Cl atoms was varied by changing the position of the movable injector. The effective first-order rate constant values, k'_{OBS}, were obtained from the dependences of the Cl atom fluorescence signal, S_{Cl}, on the distance between the tip of the movable injector and the detection zone. Examples of experimentally obtained $\ln(S_{Cl})$ vs x dependences are presented in Figure 1. The observed values of k'_{OBS} were corrected for axial and radial diffusion of Cl atoms.[48−50] The values of the Cl atom diffusion coefficient in He were calculated using the

$$D = 0.0237T^{1.75} \text{ Torr cm}^2 \text{ s}^{-1} \qquad \text{(I)}$$

formula.[51] This correction for atom diffusion never exceeded 11% of k'_{OBS}. A more detailed description of the experimental procedure and the diffusion correction is given in ref 18.

The bimolecular rate constants of reactions 1−3 were obtained from the slopes of the linear dependences of k' on the concentration of substrate, $[C_2H_{6-X}Cl_X]$:

$$k' = k_i[C_2H_{6-X}Cl_X] + k_0 \qquad \text{(II)}$$

Here, k_i is the bimolecular rate constant of the reaction under study (i = 1−3) and k_0 is the zero-abscissa intercept of the k' vs $[C_2H_{6-X}Cl_X]$ dependence. The k_0 intercept appears due to the nonnegligible losses of Cl atoms on the surfaces of the reactor and the movable injector and can acquire both positive and negative values.[15] The values of k_0 obtained in the current study were minor compared with the first term in eq II (see Table 1), and uncertainties in k_0 were generally comparable with the k_0 values. Examples of experimentally obtained k' vs $[C_2H_{6-X}Cl_X]$ dependences are presented in Figure 2.

Gases used in the experiments were obtained from MG Industries (He, >99.9999%; CF_4, >99.9%), Aldrich (C_2H_5Cl, >99.7%), SynQuest Laboratories, Inc. (CH_3CHCl_2, ≥99.6%), and Matheson (C_2H_6, ≥99.999%; Cl_2, 99.999%). The indicated purity values are nominal, as specified by the manufacturer. All gases except helium and CF_4 were purified by vacuum distillation prior to use. Helium was purified by passing through liquid nitrogen cooled traps. To verify that no potential impurities in the ethane or chlorinated ethanes could affect the measured rate constants, these gases were analyzed for potential contaminants by gas chromatography. After purification by vacuum distillation, the purity of all chloromethanes exceeded the specifications provided by the manufacturers. A discussion of impurities and their potential influence on the experimental results is given in the next subsection (II.3).

II.3. Results. Conditions and results of experiments to determine the values of the rate constants of reactions 1−3 are presented in Tables 1 and 2. The rate constants demonstrate no dependence on pressure, initial concentration of Cl atoms, bulk flow velocity, or concentration of the CF_4 spin−orbit quencher within the experimental ranges. The fact that the rate constants are independent of the initial Cl atom concentration indicates the absence of any influence of potential secondary reactions on the kinetics of Cl atoms, as can be expected due to the low

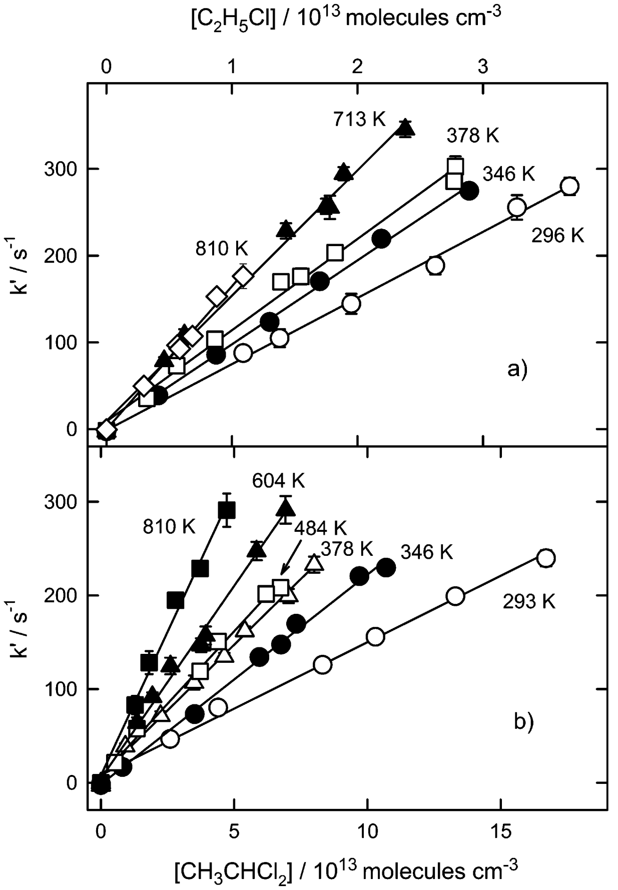

Figure 2. Examples of experimentally obtained k' vs [C_2H_5Cl] (a) and k' vs [CH_3CHCl_2] (b) dependences. Experimental temperatures are indicated on the plots.

values of $[Cl]_0$ used ($[Cl]_0 = (0.9-9) \times 10^{10}$ atoms cm^{-3}). Potential regeneration of Cl atoms through the secondary $R + Cl_2 \rightarrow RCl + Cl$ processes (rate constants 2×10^{-11} cm^3 molecule^{-1} s^{-1} or less[22,52−55]) are negligible due to the low Cl_2 concentrations ($<2 \times 10^{11}$ molecules cm^{-3}).

To ensure that the measured rates of Cl atom decay in the presence of $C_2H_{6-X}Cl_X$ represent the homogeneous reactions 1−3, experiments were conducted with reactors of different internal diameters (1.93−4.66 cm) possessing different surface-to-volume ratios. The experimentally obtained values of the rate constants were independent of the reactor used (Tables 1 and 2). This independence, as well as the linearity of the observed k' vs [$C_2H_{6-X}Cl_X$] dependences, indicates the absence of any significant effects of heterogeneous reactions on the values of the rate constants.

The rate constants of reactions 1−3 exhibit positive temperature dependences (Figures 3−5). The experimental $k_1(T)$ dependence obtained can be represented with the modified Arrhenius expression

$$k_1 = (4.91 \times 10^{-12})T^{0.47} \exp(-82\ \mathrm{K}/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (299-1002\ \mathrm{K}) \quad \mathrm{(III)}$$

In reactions 2 and 3, different temperature dependences were obtained in the low-temperature (293−378 K) and the high-temperature (484−810 K) regions. The differences are due to the regeneration of Cl atoms at higher temperatures as a consequence of the fast thermal decomposition of the radical products with a Cl atom in the β position.[56] At low temperatures, where thermal decomposition of these radical products (CH_2CH_2Cl and CH_2CHCl_2) is negligible, the experimentally determined rate constants represent sums of the rates of Cl atom attack on both the α and the β H atoms of the C_2H_5Cl and the CH_3CHCl_2 molecules. Thus, the Arrhenius expressions obtained in the low-temperature region

$$k_2 = (3.42 \pm 0.95) \times 10^{-11} \exp(-447 \pm 84\ \mathrm{K}/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (296-378\ \mathrm{K}) \quad \mathrm{(IV)}$$

$$k_3 = (3.7 \pm 2.3) \times 10^{-11} \exp(-1001 \pm 161\ \mathrm{K}/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (293-378\ \mathrm{K}) \quad \mathrm{(V)}$$

correspond to the total rates of reactions 2 and 3, $k_2 = k_{2a} + k_{2b}$ and $k_3 = k_{3a} + k_{3b}$.

At temperatures above 373 K, rates of decomposition of CH_2CH_2Cl and CH_2CHCl_2 (products of reaction channels 2b and 3b, respectively) increase sharply with an increase in temperature.[56] Decomposition of these radicals results in regeneration of Cl atoms, which, when the decomposition rates are comparable with the rates of $Cl + C_2H_{6-X}Cl_X$, should result in nonexponential Cl decay profiles. Fortunately, temperature dependences of the radical decomposition rates are rather sharp; at $T \geq 480$ K CH_2CH_2Cl and CH_2CHCl_2 should decompose virtually instantaneously on the time scale of the current experiments (characteristic time is less than 0.7 ms for CH_2CH_2Cl[56]). Therefore, at sufficiently high temperatures, reaction channels 2b and 3b result in regeneration of Cl atoms and cannot be observed in experiments where determination of rate constants is based on detection of Cl.

Thus, at temperatures above 480 K, the experimental rate constants correspond to abstraction of H atoms in the α positions only (channels 2a and 3a). These results can be represented by the expressions

$$k_{2a} = (3.28 \pm 0.82) \times 10^{-11} \exp(-560 \pm 130\ \mathrm{K}/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (484-810\ \mathrm{K}) \quad \mathrm{(VI)}$$

$$k_{3a} = (1.87 \pm 0.41) \times 10^{-11} \exp(-905 \pm 119\ \mathrm{K}/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (484-810\ \mathrm{K}) \quad \mathrm{(VII)}$$

The temperature interval between 378 and 484 K, where decomposition of the CH_2CH_2Cl and the CH_2CHCl_2 radical products is expected to occur on the time scales roughly similar to those of the Cl decay due to reactions 2 and 3, was avoided in the experiments because interference from Cl regeneration cannot be quantitatively factored out in an easy and reliable way. Here, evaluation of the expected rates of decomposition of CH_2CH_2Cl and CH_2CHCl_2 was based on the results of ref 56.

In principle, for each of the reactions 2 and 3, it is possible to describe the experimental temperature dependence of the rate constants with a single modified Arrhenius expression covering the whole experimental temperature range. Deviations of individual data points from such expressions will be less than 12% for reaction 2 and less than 20% for reaction 3. However, it is known[56] that decomposition of the radical products of the β-abstraction channels occurs at temperatures above 378 K. Therefore, such a simple representation of the $k_2(T)$ and $k_3(T)$ dependences would not be physically meaningful; instead, the analysis described above is appropriate.

The error limits of the experimentally obtained values reported in this work (Tables 1 and 2) represent 2σ statistical (random) uncertainty. The maximum estimated systematic uncertainty is

TABLE 2: Conditions and Results of Experiments To Measure Rate Constants of the Reactions of Cl Atoms with 1,1-Dichloroethane (Reaction 3)

no.[a]	T/K	P[b]/Torr	$[C_2H_4Cl_2]$[c] range/10^{13}	$[CF_4]$[c]/10^{14}	k_0[d]/s^{-1}	V[e]/m s^{-1}	$[Cl]_0$[c]/10^{10}	$((k' - k'_{OBS})/k'_{OBS}))_{max}$[f]	k_3[g,i]/10^{-12}	k_3[h,i]/10^{-12} (corrected)
1	293	2.28	2.60−16.7	11.3	8.2 ± 8.7	21.4	1.2	0.032	1.42 ± 0.09	1.33 ± 0.09
2	297	3.52	2.16−18.1	9.5	7.3 ± 9.3	32.2	3.9	0.036	1.35 ± 0.08	1.26 ± 0.08
3	320	2.86	1.98−11.1	7.8	4.8 ± 6.2	24.2	2.2	0.022	1.54 ± 0.10	1.45 ± 0.10
4	320	2.84	1.30−9.63	20.0	7.7 ± 8.4	22.6	3.0	0.021	1.65 ± 0.15	1.56 ± 0.15
5	346	3.63	0.81−10.7	4.7	−1.8 ± 7.0	35.9	8.0	0.027	2.24 ± 0.10	2.15 ± 0.10
6	378	3.94	0.918−8.0	8.6	6.9 ± 6.2	37.3	4.5	0.026	2.81 ± 0.13	2.72 ± 0.13
7	378	3.97	2.47−12.7	10.2	13 ± 14	37.3	2.1	0.037	2.61 ± 0.20	2.52 ± 0.20
8*	378*	4.03	0.664−3.99	15.2	1.0 ± 5.4	7.3	2.2	0.099	2.78 ± 0.21	2.69 ± 0.21
9	484	7.15	0.527−6.74	7.4	6.9 ± 9.0	27.9	3.6	0.028	3.10 ± 0.22	3.01 ± 0.22
10	523	5.89	0.422−9.62	7.5	13.5 ± 8.6	44.1	2.0	0.032	3.21 ± 0.17	3.12 ± 0.17
11	556	4.37	0.637−4.92	11.9	13 ± 11	31.7	2.1	0.018	3.93 ± 0.37	3.84 ± 0.37
12	604	5.97	1.36−6.93	8.7	5 ± 12	34.9	1.3	0.026	4.11 ± 0.31	4.02 ± 0.31
13	713	7.55	1.03−6.79	12.4	4 ± 12	50.1	4.4	0.029	5.55 ± 0.32	5.46 ± 0.32
14*	758*	4.08	0.77−2.94	5.4	−1.0 ± 6.5	14.5	2.4	0.074	5.84 ± 0.37	5.75 ± 0.37
15	810	7.24	1.29−4.72	9.7	8 ± 16	39.4	1.5	0.021	6.13 ± 0.58	6.04 ± 0.58

[a] Experiment number. A Pyrex reactor with i.d. = 4.66 cm was used in experiments marked with an asterisk, and a quartz reactor with i.d. = 1.93 cm was used in unmarked experiments. [b] Reactor pressure. [c] Units of concentrations are molecules cm^{-3}. [d] Zero-abscissa intercept on the k' vs $[C_2H_4Cl_2]$ dependence. [e] Average flow velocity. [f] Maximum relative value of the diffusion correction. [g] Values of k_3 before correction for the effects of $C_2H_2Cl_2$ impurity. [h] Values of k_3 corrected for the effects of $C_2H_2Cl_2$ impurity (see the text). [i] Units of rate constants are cm^3 molecule^{-1} s^{-1}. Error limits represent statistical uncertainties and are reported as 2σ. Maximum estimated systematic uncertainties are 8% of the rate constant value (see the text).

8% of the rate constant value. The error limits in expressions IV−VII are given as 2σ and represent only the statistical uncertainties of the fit.

To evaluate potential effects of impurities in the chlorinated ethanes on the measured rate constants, these gases were analyzed for contaminants by gas chromatography. A Shimadzu GC-9A gas chromatograph and a Hewlett-Packard 5890 II Plus/5989B GC/MS instrument were used in these analyses. It was found that, after purification by vacuum distillation, the purity of both chloroethanes (C_2H_5Cl, >99.98%; CH_3CHCl_2, 99.72%) exceeded the specifications provided by the manufacturers. The CH_3CHCl_2 sample obtained from SynQuest Laboratories, Inc. was stabilized with 0.1% nitromethane. The GC/MS analysis confirmed the 0.1% impurity of CH_3NO_2 and revealed the presence of impurities of two isomers of dichloroethylene (*cis*-1,2-$C_2H_2Cl_2$, 0.075%; *trans*-1,2-$C_2H_2Cl_2$, 0.020%) as well as 1,2-$C_2H_4Cl_2$ (0.055%), 1,1,1-$C_2H_3Cl_3$ (0.026%), and 1,1,2-$C_2H_3Cl_3$ (0.007%). Reactions of a Cl atom with CH_3NO_2, 1,2-$C_2H_4Cl_2$, 1,1,1-$C_2H_3Cl_3$, and 1,1,2-$C_2H_3Cl_3$ are too slow[35,57−60] to affect the results of the current experimental study. However, corrections for the reactions of Cl with dichloroethylenes had to be applied to the values of k_3. The temperature-independent value of the rate constant of the reaction

$$\mathrm{Cl} + 1,2\text{-}\mathrm{C_2H_2Cl_2} \rightarrow \text{products} \tag{4}$$

($k_4 = 9.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}[61]) was used. The corrections are 7% at the lowest temperature used and smaller at higher temperatures. The corrected values of k_3 are presented in Table 2.

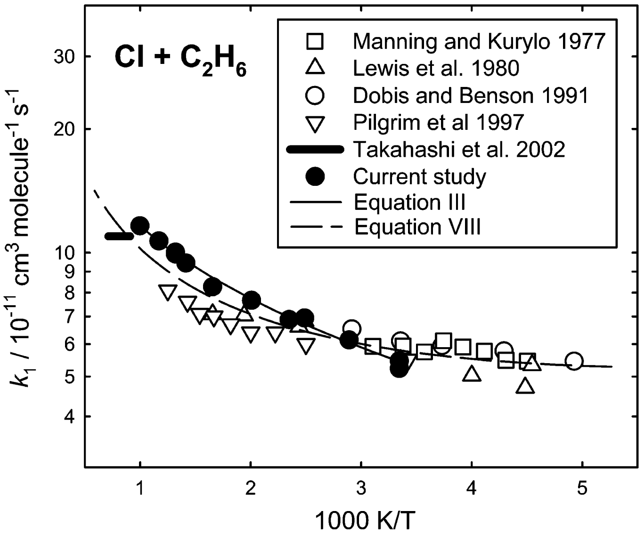

Figure 3. Temperature dependence of the rate constant of reaction 1. Results of direct studies where temperature dependences were obtained are displayed: Manning and Kurylo,[19] Lewis et al.,[20] Dobis and Benson,[21] Pilgrim et al.,[24] Takahashi et al.,[26] and the current study. Solid and dotted lines represent the modified Arrhenius fits to the results of the current study (eq III) and to the combined data set shown in this plot (eq VIII), respectively.

III. Discussion

III.1. Experimental Rate Constant Values. Reaction 1 has been studied previously, with the results of direct and indirect studies being in general agreement with each other (see, for example, refs 19−26). Reviews of data published prior to 1997 ($T \leq 604$ K) can be found in refs 28 and 27. The rate constants obtained in the current study agree with these earlier lower temperature measurements (Figure 3; direct studies that reported temperature dependences are displayed). Three direct studies[24−26] of reaction 1 appeared since the publication of the reviews of refs 27 and 28. In the room-temperature study of Tyndall et al.,[25] a value of $k_1 = 5.75 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was reported, in agreement with the results of the current and earlier investigations. The experiments of Pilgrim et al.[24] were performed in the 292−800 K temperature range using the 193 nm laser photolysis of CF_2Cl_2 to produce Cl atoms and long-path infrared absorption to detect the HCl formed in reaction 1. The results of ref 24 are somewhat lower than those obtained in the current study, with the difference reaching ~20% at $T \geq 700$ K. These differences fall within the combined experimental uncertainties of the two studies. The recent study of Takahashi et al.[26] was conducted under shock tube conditions ($T = 1100−1400$ K) using atomic resonance spectroscopy for Cl atom detection. The authors report a temperature-independent value of $k_1 = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, in agreement with the results of the current and the earlier studies.

If the temperature dependence of k_1 obtained in the current work is combined with the values reported in the studies included in Figure 3,[19−21,24,26] the resultant combined set of data can be represented with the following modified Arrhenius expression:

$$k_1 = (7.23 \times 10^{-13})T^{0.70} \exp(+117\ \mathrm{K}/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}\ (203{-}1400\ \mathrm{K}) \quad \text{(VIII)}$$

Only two direct determinations of the rate constant of reaction 2 are available in the literature.[22,35] Wine and Semmes[35] used laser photolysis of Cl_2 and resonance fluorescence to detect Cl atoms in the 258−419 K temperature interval; reactions 2 and 3, as well as several other reactions of Cl atoms with chlorinated ethanes, were studied. Kaiser et al.[22] used laser photolysis of Cl_2 and time-resolved infrared spectroscopy to detect HCl formed in reaction 2 at 298 K. The results of the current study are in agreement with these two earlier investigations (Figure 4).

Tschuikow-Roux et al.[31,33] and Niedzielski et al.[29,30] studied reaction 2 in the 280−368 K temperature interval using the relative-rate technique with photolytic production of Cl atoms and gas chromatographic analysis of final products. The results of these studies agree with each other. Reference 29 presents the most comprehensive set of data, which is displayed in Figure 4 along with the $k_2(T)$ values of refs 22 and 35 and those of the current work. The room-temperature relative-rate study of ref 34 results in a k_2 value (8.1×10^{-12} cm^3 molecule^{-1} s^{-1}; eq III was used for the rate constant of the Cl + C_2H_6 reference reaction) that is in agreement with the results of direct studies; it is not included in Figure 4 to avoid plot congestion.

As was discussed in subsection II.3, different $k_2(T)$ temperature dependences were obtained in the low-temperature (296−378 K) and the high-temperature (484−810 K) regions. At low temperatures, the experimentally determined rate constants represent sums of the rates of Cl atom attack on both the α and the β H atoms of C_2H_5Cl ($k_2 = k_{2a} + k_{2b}$). At high temperatures, fast thermal decomposition of the CH_2CH_2Cl radical[56]

$$CH_2CH_2Cl \rightarrow Cl + C_2H_4 \qquad (5)$$

results in the regeneration of Cl, and thus, reaction channel 2b is not observed. Under these conditions, $k_2 = k_{2a}$. Reaction 5 has been studied experimentally in ref 56 under conditions (temperatures and pressures) similar to those used in the current study; theoretical modeling performed in ref 56 provided a convenient means for calculating the values of k_5 and evaluating the temperature range where the effect of reaction 5 changes from negligible to complete regeneration of Cl atoms. This intermediate temperature interval between 378 and 484 K, where decomposition of CH_2CH_2Cl is expected to occur on time scales roughly comparable to those of the Cl decay due to reaction 2, was avoided in the experiments because of the difficulty in quantitative interpretation of the nonexponential Cl decays.

The current study presents the first direct determination of the rate constant of reaction channel 2a. This information, combined with the results of the relative-rate study of Niedzielski et al.,[29] is used to derive the channel-specific $k_{2a}(T)$ and $k_{2b}(T)$ rate constant dependences (vide infra).

Reaction 3 has been studied before at low temperatures (≤412 K) in direct laser photolysis/resonance fluorescence experiments of Wine and Semmes[35] and in the relative-rate investigation of Tschuikow-Roux et al.[32] The results of these two studies and of the current work are displayed in Figure 5. As can be seen from the plot, the k_3 values of Tschuikow-Roux et al. are in agreement with those of the current study, although the activation energy of ref 32 is somewhat lower than that of the current work. The results of Wine and Semmes agree with the room-temperature k_3 value of the current study but are somewhat lower at higher temperatures (30% difference at 378 K). In this experimental investigation[35] of reactions 2 and 3 and several other reactions of Cl with chlorinated ethanes, the kinetics of Cl decay was affected by the regeneration of chlorine atoms, as reported by the authors. The following reactions of the Cl-containing radical products were suggested in ref 35 as the cause of this Cl regeneration: thermal decomposition, reaction with Cl_2, and reaction with the chlorinated ethane substrates (Cl

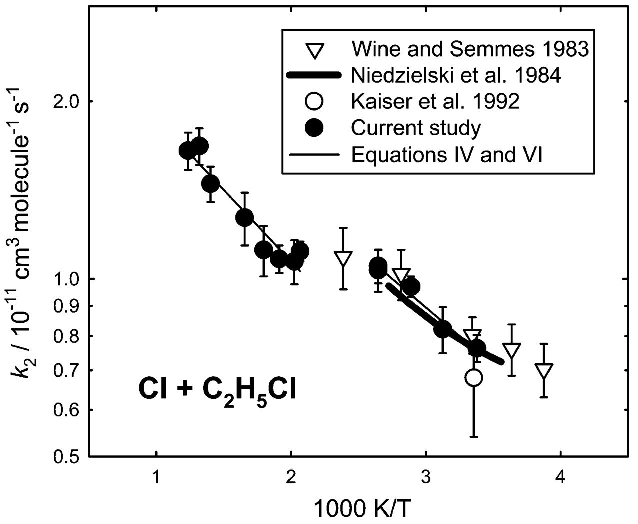

Figure 4. Temperature dependence of the rate constant of reaction 2. Results of direct studies and indirect studies where temperature dependences were reported are displayed: Wine and Semmes,[35] Niedzielski et al.,[29] Kaiser et al.,[22] and the current study. Here, the relative rate data of ref 29 were converted to the values of k_2 using the experimental temperature dependence of the Cl + CH_4 reference reaction reported by Bryukov et al.[18] Thin solid lines represent the Arrhenius fits of eqs IV and VI in the low- and the high-temperature regions.

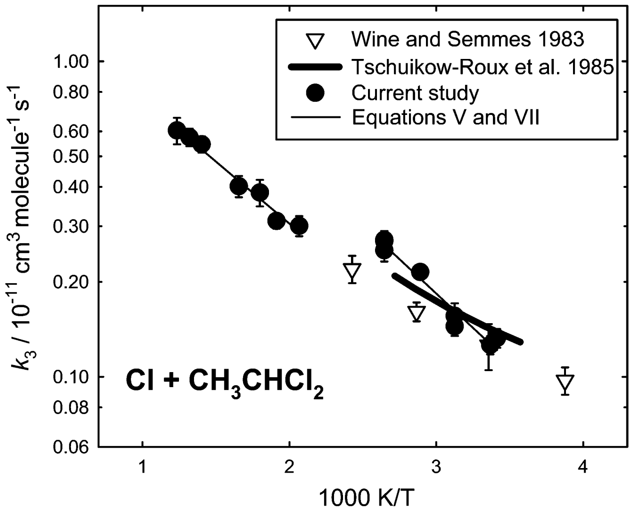

Figure 5. Temperature dependence of the rate constant of reaction 3. Results of direct studies and indirect studies where temperature dependences were reported are displayed: Wine and Semmes,[35] Tschuikow-Roux et al.,[32] and the current study. Here, the relative-rate data of ref 32 were converted to the values of k_3 using the experimental temperature dependence of the Cl + CH_4 reference reaction reported by Bryukov et al.[18] Thin solid lines represent the Arrhenius fits of eqs V and VII in the low- and the high-temperature regions.

substitution). To suppress this regeneration, the authors added large amounts of O_2 to convert radical products such as $C_2H_3Cl_2$ into relatively unreactive peroxy radicals. At temperatures above 400 K in the absence of added O_2, Wine and Semmes observed nonexponential Cl atom decays, which did not depend on Cl_2 concentration; addition of O_2 resulted in the disappearance of the nonexponentiality. However, Cl decay rates were slower than was expected from kinetic modeling using the above secondary reactions. The authors of ref 35 concluded that kinetic observations at $T > 400$ K cannot be explained using the kinetic scheme employed. This conclusion has negative implication for the rate constants obtained at these temperatures; it may rationalize the differences between the results of the current experimental study and those of Wine and Semmes at $T \approx 400$ K.

The temperature dependence of the kinetics of reaction 3 is similar to that of reaction 2. At low temperatures (296−378 K), the observed Cl atom decays represent sums of the rates of Cl atom attack on both the α and the β H atoms of CH_3CHCl_2 ($k_3 = k_{3a} + k_{3b}$). At high temperatures (484−810 K), fast thermal decomposition of the CH_2CHCl_2 radical results in the regeneration of Cl, and thus, reaction channel 3b is not observed. Under these conditions, $k_3 = k_{3a}$. The intermediate temperature interval between 378 and 484 K, where decomposition of CH_2CHCl_2 is expected to occur on time scales roughly comparable to those of the Cl decay due to reaction 3, was avoided. It was assumed that the temperature and pressure dependence of the rate constant of thermal decomposition of CH_2CHCl_2 is similar to that of CH_2CH_2Cl.[56]

III.2. Site-Specific Abstraction Rate Constants. The ratio of the rates of abstraction of a hydrogen atom in the α and β positions in reaction 2 was studied by two groups using relative-rate techniques.[29−31,33,34] The room-temperature values of the k_{2a}/k_{2b} ratio obtained in different studies are in agreement with each other. The temperature dependence of this ratio was studied by Tschuikow-Roux et al.[31,33] and Niedzielski et al.[29,30] over the 280−368 K temperature interval; these studies used the same experimental method (photolytic production of Cl atoms and gas chromatographic analysis of final products), and their results coincide. The most comprehensive set of data was presented in ref 29 (281−367 K), which reported the

$$k_{2a}/k_{2b} = 1.1\ \exp(429\ \mathrm{K}/T) \qquad \mathrm{(IX)}$$

temperature dependence. The α- and β-abstraction rates for reaction 3 were studied by Tschuikow-Roux et al.[32] relative to those of the Cl + CH_4 reaction. These authors found a

$$k_{3a}/k_{3b} = 0.873\ \exp(765\ \mathrm{K}/T) \qquad \mathrm{(X)}$$

temperature dependence of the α-to-β-abstraction ratio (T = 280−368 K), in agreement with the earlier study of Cillien et al.[37]

The results of these relative-rate studies can be combined with those of the current determination of the overall rate constants to derive information on the site-specific rates of hydrogen abstraction. Here, the rate constants of reactions 2 and 3 obtained in the current work in the low-temperature region (where the observed rate constants represent the sums of both the α- and the β-abstraction channels) were converted into the values of site-specific rate constants using eqs IX and X. The resultant values of the α-abstraction rate constants, combined with the k_2 and k_3 dependences obtained in the current work in the high-temperature regions (where only the α-abstraction reaction is observed due to the regeneration of Cl atoms via thermal decomposition of the radical products of the β-abstraction channels), provide the $k_{2a}(T)$ and $k_{3a}(T)$ dependences over the 296−810 and 293−810 K temperature ranges, respectively. The values of the β-abstraction channel rate constants are obtained only in the low-temperature range, $T \leq 378$ K. The resultant temperature dependences of the site-specific rate constants are displayed in Figures 6 and 7. They can be reproduced with the following Arrhenius equations:

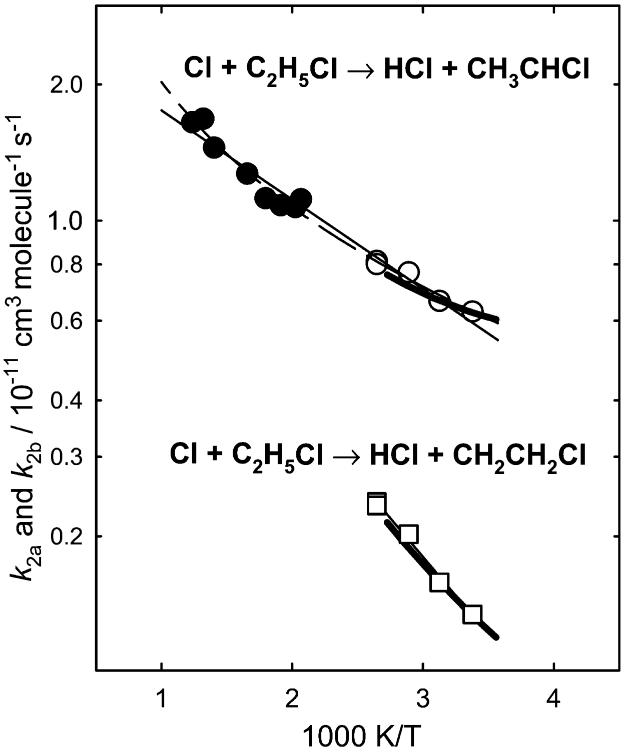

Figure 6. Temperature dependences of the rate constants of reactions 2a and 2b, α- and β-abstraction of hydrogen from C_2H_5Cl by a Cl atom: filled circles, experimental k_{2a} values obtained in the current study in the high-temperature region; open circles and squares, values of k_{2a} and k_{2b}, respectively, calculated from the experimental k_2 values determined in the low-temperature region and the α-to-β ratio of the site-specific rate constants reported by Niedzielski et al.,[29] eq IX; wide solid lines, results of the relative-rate study of Niedzielski et al.[29] converted to the values of k_{2a} and k_{2b} using the experimental temperature dependence of the reference reaction (Cl + CH_4) reported in ref 18; thin solid lines, Arrhenius fits of eqs XI and XII; dashed line, $k_{2a}(T)$ dependence of eq XV.

$$k_{2a}(T) = (2.76 \pm 0.28) \times 10^{-11}\ \exp(-455 \times 44\ \mathrm{K}/T) \qquad (296-810\ \mathrm{K})\ \ \mathrm{(XI)}$$

$$k_{2b}(T) = (1.92 \pm 0.47) \times 10^{-11}\ \exp(-789 \pm 84\ \mathrm{K}/T) \qquad (296-378\ \mathrm{K})\ \ \mathrm{(XII)}$$

$$k_{3a}(T) = (1.46 \pm 0.21) \times 10^{-11}\ \exp(-733 \pm 58\ \mathrm{K}/T) \qquad (293-810\ \mathrm{K})\ \ \mathrm{(XIII)}$$

$$k_{3b}(T) = (2.98 \pm 1.42) \times 10^{-11}\ \exp(-1686 \pm 160\ \mathrm{K}/T) \qquad (293-378\ \mathrm{K})\ \ \mathrm{(XIV)}$$

(rate constant units are cm^3 molecule^{-1} s^{-1}). The error limits in expressions XI−XIV are given as 2σ and represent only the statistical uncertainties of the fit. The $k_{2a}(T)$ dependence suggests some curvature; however, the existence of this curvature cannot be unequivocally asserted because of the scatter of the data points. An alternative modified Arrhenius expression

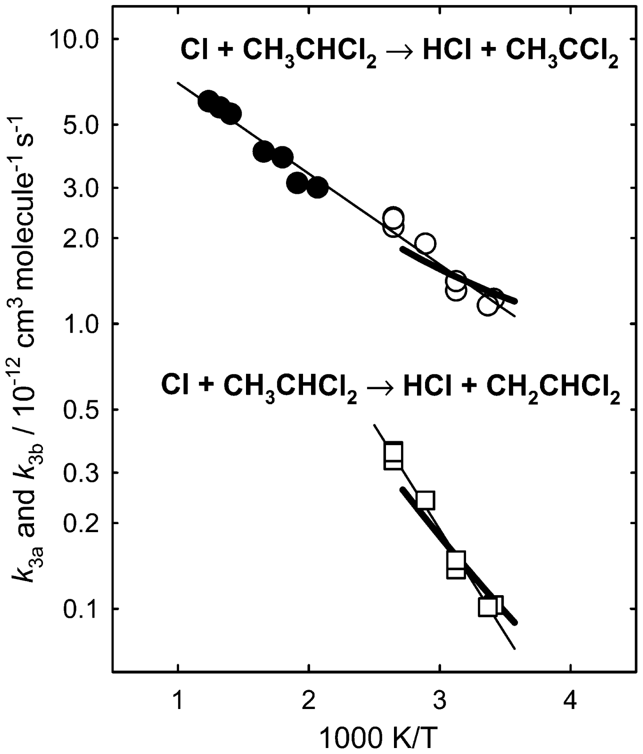

Figure 7. Temperature dependences of the rate constants of reactions 3a and 3b, α- and *β*-abstraction of hydrogen from CH_3CHCl_2 by a Cl atom: filled circles, experimental k_{3a} values obtained in the current study in the high-temperature region; open circles and squares, values of k_{3a} and k_{3b}, respectively, calculated from the experimental k_3 values determined in the low-temperature region and the α-to-*β* ratio of the site-specific rate constants reported by Tschuikow-Roux et al.,[32] eq X; wide solid lines, results of the relative-rate study of Tschuikow-Roux et al.[32] converted to the values of k_{3a} and k_{3b} using the experimental temperature dependence of the reference reaction ($Cl + CH_4$) reported in ref 18; thin solid lines, Arrhenius fits of eqs XIII and XIV.

accounting for the curvature can be used:

$$k_{2a}(T) = (8.12 \times 10^{-14})T^{0.81} \exp(-77\ \mathrm{K}/T)\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}\ (296-810\ \mathrm{K}) \quad \mathrm{(XV)}$$

The $k(T)$ dependences resulting from the relative-rate studies of Niedzielski et al.[29] and Tschuikow-Roux et al.[32] are also displayed in Figures 6 and 7. Here, the temperature dependence of the rate constants of the reference reaction ($Cl + CH_4$) used in these studies was taken from our recent experimental study[18] (eq X of ref 18). As one can see from the plots, the results of the current study are in general agreement with those of Niedzielski et al.[29] and Tschuikow-Roux et al.;[32] this is not unexpected because these earlier relative-rate studies were used here to derive the site-specific rate data. The activation energies of the $k_{3a}(T)$ and the $k_{3b}(T)$ dependences of Tschuikow-Roux et al. are somewhat lower than that those of eqs XIII and XIV, which reflects the differences between the results of the current study and those of ref 32 observed in Figure 5 (the overall $k_3(T)$ dependences).

An attempt at using transition-state theory to reproduce the temperature dependences of the α-abstraction rate constants (k_{2a} and k_{3a}) was performed. The properties (rotational constants and vibrational frequencies) of the reactants and the initial approximation to the properties of the transition state of reactions 2a and 2b were obtained in quantum chemical calculations performed at the BH&HLYP/6-311G(d,p) level.[62−64] The Gaussian 98[64] program was used in the calculations. The reaction energy barriers and the lowest vibrational frequencies of the transition states were adjusted to achieve approximate agreement of the calculated rate constants with the experimental data. However, the reaction models resulted in curvatures of the ln(k) vs T^{-1} dependences that are much larger than the experimental ones; thus, the transition-state-theory approach failed. A similar problem was observed in our recent study of the reaction of a Cl atom with chloromethane:[18] the calculated curvature of the Arrhenius plot significantly exceeded the experimental one. It was suggested[18] that variational effects and the effects of the dependence of the zero-point vibrational energy on the reaction coordinate[65,66] may be responsible for the failure of nonvariational transition-state theory.

It is interesting to note that the optimized energies of the transition states for reactions 2a and 3a obtained in the above computational exercise were approximately 2 kJ mol^{-1} below the energy of the reactants. Nevertheless, the calculated temperature dependences of the rate constants are positive despite the negative barriers because of the increase with temperature of the ratio of the partition functions of the transition state and the reactants. This strong temperature dependence of the partition function ratio is due to the presence in the transition states of low-frequency vibrational modes (Cl···H···R bends in the 90−154 cm^{-1} range), which are very close to the classical limit at all experimental temperatures.

The results of the current study confirm the qualitative observations of the previous studies:[32,35] that Cl substitution, in both the α and the *β* positions, increases the experimental activation energies for the abstraction of hydrogen by a chlorine atom. However, one should be very cautious in attempts to interpret these observations in terms of the effects of Cl substitution on the C−H bond energies and on the abstraction energy barriers. The above description of the failed attempt to model reactions 2a and 3a with transition-state theory demonstrates the differences between the observed positive activation energies and underlying negative values of the energy barriers. The decrease of the rate constants in the sequence of ethane, chloroethane, and dichloroethane can be rationalized on the basis of the transition-state theory expression for the rate constant. The ratio of the rotational partition function of the transition state to that of the reactants decreases in this sequence, which qualitatively explains the observed reactivity trend. The most likely mechanism of the α-abstraction reactions 2a and 3a, in view of the slightly negative barriers, is the formation of a loosely bound intermediate complex followed by a transition state, the energy of which is below the energy of the reactants (refs 67−69 provide examples of other reactions where similar mechanisms have been observed or invoked to explain experimental behavior).

IV. Conclusions

Reactions of Cl atoms with ethane, chloroethane, and 1,1-dichloroethane have been studied experimentally with the discharge flow/resonance fluorescence technique over wide ranges of temperatures and at pressures between 2.3 and 9.2 Torr. The resultant rate constants can be represented with the modified Arrhenius expressions III−VII.

The rate constants k_1 of the reaction of Cl atoms with ethane obtained in the current study agree with the results of earlier low-temperature measurements. Combination of the temperature dependence of k_1 obtained in the current work at temperatures ranging from ambient to 1002 K with the literature data results in the $k_1(T)$ dependence described by eq VIII.

Reactivity with respect to Cl atom attack decreases in the sequence of ethane, chloroethane, and dichloroethane. This trend can be qualitatively inferred from the decrease (in this series) in the ratio of the rotational partition function of the transition state to that of the reactant. Rate constants of the reactions of Cl with chloroethane and 1,1-dichloroethane demonstrate different temperature dependences in the low-temperature (room temperature to 378 K) and the high-temperature (484−810 K) regions. The differences are due to the regeneration of Cl atoms at higher temperatures as a consequence of the fast thermal decompositions of radical products with a chlorine atom in the β position. This information enables quantitative differentiation between the site-specific reaction channels. The results of the current study, combined with those of earlier relative-rate experiments,[29,32] were used to derive expressions for the temperature dependences of the rates of the site-specific abstraction channels (eqs XI−XV).

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