Low-Pressure Study of the Reaction of Cl Atoms with Isoprene

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The kinetics of the reaction of chlorine atoms with isoprene (1) has been studied using the discharge-flow mass-spectrometric method: $Cl + C_5H_8 (+M) \rightarrow C_5H_8Cl (+M)$ (1a); $Cl + C_5H_8 \rightarrow C_5H_7 + HCl$ (1b). As a result of direct and relative measurements, the overall rate constant $k_1 = (6.7 \pm 2.0) \times 10^{-11} \exp\{(485 \pm 85)/T\}$ cm^3 molecule^{-1} s^{-1} was obtained at a pressure of 1 Torr of helium over the temperature range 233−320 K. k_1 was found to be pressure-independent (within 10%) at $T = 298$ K in the pressure range 0.25−3 Torr. Both HCl and C_5H_8Cl adduct were detected as products of reaction 1. The measurements of the HCl yield as a function of temperature led to the branching fraction for the H-atom abstraction channel (1b): $k_{1b}/k_1 = (1.22 \pm 0.4) \exp\{-(595 \pm 90)/T\}$ ($P = 1$ Torr, $T = 233$−320 K); $k_{1b}/k_1 = 0.169 \pm 0.022$ at 298 K. The results are compared with those reported in a recent study[4] carried out at 298 K. In addition, the rate coefficient has been measured for the reaction $Cl + Br_2 \rightarrow BrCl + Br$ (2), which was used as the reference in the relative study of reaction 1. Combining the present results obtained in the range 233−320 K with those available from a previous study in the range 298−401 K,[10] the following Arrhenius expression is recommended: $k_2 = (2.3 \pm 0.4) \times 10^{-10} \exp\{(135 \pm 60)/T\}$ cm^3 molecule^{-1} s^{-1}.

Introduction

The reaction of Cl atoms with isoprene ($CH_2{=}C(CH_3){-}CH{=}CH_2$ or C_5H_8) is of potential atmospheric relevance as a possible oxidation process of isoprene in the marine atmosphere, where both Cl atoms and isoprene can be simultaneously present. Effectively, Cl-atom concentrations as high as 10^4−10^5 molecule cm^{-3} may exist in the marine boundary layer,[1,2] and isoprene has been shown to be emitted by phytoplankton in seawater.[3] The title reaction is also of special kinetic and mechanistic interest, since it proceeds through both addition and abstraction channels:

$$Cl + C_5H_8 (+M) \rightarrow C_5H_8Cl + (M) \qquad (1a)$$

$$\rightarrow C_5H_7 + HCl \qquad (1b)$$

The precise knowledge of the kinetics and mechanism of both channels requires a detailed study of the overall reaction as a function of temperature and pressure. One study of reaction 1 has been published so far,[4] where the overall rate constant has been measured at 298 K at 760 Torr and in the low-pressure range 0.16−5 Torr, using a continuous photolysis relative-rate method. The branching ratio of the abstraction channel (1b) has also been measured at 298 K. Measurements of k_1 have been made also recently at 298 K in the pressure range 15−60 Torr.[5] In the present paper we report complementary results on reaction 1, including low-pressure measurements of k_1 and k_{1b} as a function of temperature, in the range 233−320 K. Both absolute and relative measurements of k_1 were carried out. In the relative study the reference reaction was

$$Cl + Br_2 \rightarrow BrCl + Br \qquad (2)$$

The temperature dependence of k_2 was determined in order to complement the literature data.

Experimental Section

The discharge-flow mass spectrometric method has been used to study the kinetics and mechanism of reaction 1. The modulated molecular-beam mass spectrometer has been described in detail earlier.[6] The reactor consisted of a Pyrex tube (45 cm in length and 2.4 cm i.d.) with a jacket for the circulation of the thermostated liquid (ethanol). The configuration of the fixed inlet and the movable double injector for the introduction of the reactants into the reactor is shown in Figure 1. To reduce the wall loss of Cl atoms, the inner surfaces of the reactor and the injector were coated with halocarbon wax. Two methods of Cl-atom generation were used: microwave discharge of Cl_2 diluted in He, which was used as the carrier gas in all the experiments, and reaction of hydrogen atoms with Cl_2

$$H + Cl_2 \rightarrow Cl + HCl \qquad (3)$$

$$k_3 = 3.17 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 7)}$$

(All the rate constants are given at 298 K unless specified.) H atoms were produced by flowing a H_2/He mixture through a microwave discharge. Cl atoms were detected as BrCl at $m/e = 116$, after scavenging by Br_2 at the end of the reactor (5 cm upstream of the sampling cone) through the fast reaction

$$Cl + Br_2 \rightarrow BrCl + Br \qquad (2)$$

$$k_2 = (2.3 \pm 0.4) \times 10^{-10} \exp\{-(135 \pm 60)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (this work)}$$

This method of Cl detection was preferred to the direct detection at peaks $m/e = 35$ or 37 (Cl^+), since complications may arise from the contribution at these peaks of Cl_2 (precursor of Cl atoms) and products of reaction 1 (C_5H_8Cl adduct and HCl). The fragmentation of these chlorinated species in the ion source

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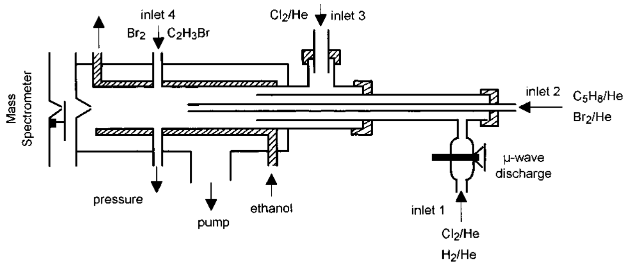

Figure 1. Diagram of the apparatus used.

of the mass spectrometer (operating at ca. 30 eV) could effectively be significant and is not precisely quantifiable for C_5H_8Cl. All the other relevant species were detected at their parent peaks: $m/e = 36$ (HCl^+), 62 ($C_2H_3Cl^+$), 68 ($C_5H_8^+$), 70 (Cl_2^+), 106 ($C_2H_3Br^+$), 160 (Br_2^+).

Absolute concentration of Cl atoms was measured from the titration reaction 2 using an excess of Br_2. In this case, $[Cl] = \Delta[Br_2] = [ClBr]$. [Cl] was determined also from the measurements of the dissociated fraction of a known Cl_2 concentration passing through the microwave discharge ($[Cl] = 2\Delta[Cl_2]$). The concentrations of the stable species in the reactor were calculated from their flow rates obtained from the measurements of the pressure drop of mixtures of the species with helium in calibrated volume flasks.

The purities of the gases were as follows: He > 99.9995% (Alphagaz) was passed through liquid-nitrogen traps; Cl_2 > 99% (Ucar); Br_2 > 99.99% (Aldrich); C_2H_3Br > 99.5% (Ucar); H_2 > 99.998% (Alphagaz); HCl, 5% mixture in He (Praxair).

Results

Rate Constant for the Cl + Isoprene Reaction 1: Temperature Dependence. *Direct Measurements of k_1.* To measure the overall rate constant of reaction 1, k_1, Cl atom decay kinetics were monitored in the presence of excess of isoprene. Cl atoms were produced by microwave discharge of a Cl_2/He mixture that was introduced into the reactor through inlet 1 of the injector, whereas C_5H_8 was flowed through the central tube (inlet 2). Experiments were carried out at a total pressure of 1 Torr and at two temperatures, $T = 298$ and 320 K. The initial concentration of Cl atoms, $[Cl]_0$, was $(1.0-1.5) \times 10^{11}$ molecule cm^{-3}, and the initial concentration of isoprene, $[C_5H_8]_0$, was varied in the range $(1.6-22.8) \times 10^{11}$ molecule cm^{-3}. The excess of isoprene was limited by the mass spectrometric detection sensitivity of Cl atoms ($[Cl] \approx 10^{10}$ molecule cm^{-3} at $S/N = 1$) and the high value of k_1 (near collision frequency). The flow velocity in the reactor was (1700−1900) cm s^{-1}. The concentrations of isoprene and Cl atoms were simultaneously measured as a function of reaction time. A consumption of C_5H_8 was also observed as a result of the use of insufficient excess of C_5H_8 over Cl. In most cases, this consumption was less then 10%, and it reached 30% in a few kinetic runs. For the rate-constant calculations, we used the mean values of $[C_5H_8]$ over the reaction time of the Cl kinetics.

Heterogeneous complications appeared when isoprene was flowed into the reactor. A slow decrease with time of the Cl signal intensity at fixed reaction distance was observed. This was probably due to a heterogeneous reaction of Cl with adsorbed isoprene at the reactor wall. For this reason, C_5H_8 was introduced through the central tube of the movable injector (Figure 1) in order to exclude continuous contact of C_5H_8 with the surface of the reactor upstream of the reactor end. The process leading to wall modification having been observed to be quite slow, it was possible to measure rapidly two or three points of Cl decay kinetics under conditions where the surface of the reactor could be considered chemically stable.

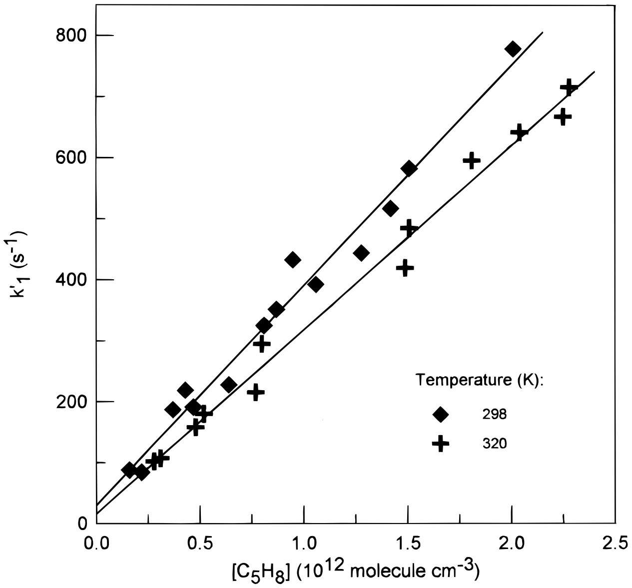

Figure 2. Pseudo-first-order plot of Cl consumption in the reaction Cl + C_5H_8 (1).

The obtained results are presented in Figure 2 as pseudo-first-order plots. The pseudo-first-order rate constant values were corrected to take into account the axial diffusion of Cl atoms. The diffusion coefficient of Cl in He, D_{Cl-He}, was calculated from D_{Ar-He}:[8] $D_{Cl-He} = 608$ and 684 $cm^2\ s^{-1}$ at $P = 1$ Torr and $T = 298$ and 320 K, respectively. Corrections were less than 12%. The slopes of the straight lines in Figure 2 give the values of k_1 at $T = 298$ and 320 K:

$$k_1 = (3.6 \pm 0.5) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}\ (298\ K)$$

$$k_1 = (3.0 \pm 0.4) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}\ (320\ K)$$

The quoted uncertainties represent one standard deviation with addition of 10% for systematic errors. The intercepts in Figure 2, 30 ± 16 (298 K) and 16 ± 15 s^{-1} (320 K), are in fair agreement with the Cl wall-loss rate 10 ± 5 s^{-1} measured in the absence of isoprene. This indicates that the heterogeneous reaction of Cl with isoprene observed for high contact time was negligible in the kinetic experiments.

As noted above, Cl atoms were scavenged by Br_2 at the end of the reactor to be detected as BrCl molecules. This led to a simultaneous production of Br atoms, which probably reacted with isoprene, although the rate constant is about 1 order of magnitude lower than that of Cl atoms (preliminary data from this work). The important point is that Br-atom reactions could not affect BrCl concentration through formation or consumption reactions, and therefore, they had no impact on the registrated kinetics of Cl. In addition the Br + isoprene reaction had a negligible effect on isoprene, considering the estimated rate constant of this reaction and the contact time of Br and isoprene species ($t \approx 3 \times 10^{-3}$ s).

Secondary reactions of Cl atoms with primary products of reaction 1, C_3H_7 and C_5H_8Cl, could be also considered as negligible, taking into account the very high value of the rate constant of the primary reaction, k_1, and the sufficient excess of isoprene over Cl atoms used in most experiments.

The heterogeneous effects discussed above were more pronounced at low temperatures. Consequently, the direct

TABLE 1: Experimental Conditions and Results for the Study of the Cl + Br_2 Reaction (2)

no. of expts	T (K)	$[Br_2]^a$	k_2^b
7	320	0.3−4.5	1.40 ± 0.12
17	298	0.45−4.65	1.42 ± 0.06
6	273	0.2−3.7	1.41 ± 0.08
6	248	0.35−4.45	1.37 ± 0.14
6	233	0.5−4.5	1.28 ± 0.04

[a] Units of 10^{12} molecule cm^{-3}. [b] Units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Errors are 2σ.

measurements of k_1 have been limited to 298 and 320 K. The study at lower temperature was carried out using the relative-rate method. In the relative measurements of k_1, the competition between reactions 1 and 2 was studied:

$$Cl + C_5H_8 \rightarrow \text{products} \qquad (1)$$

$$Cl + Br_2 \rightarrow BrCl + Br \qquad (2)$$

The kinetics of the reference reaction 2 has been investigated in separate experiments.

Kinetics of the Cl + Br_2 Reaction. Reaction 2 has been studied under pseudo-first-order conditions using an excess of Br_2 over Cl atoms. Cl atoms produced in a microwave discharge of Cl_2/He mixtures were introduced into the reactor through inlet 1, and Br_2 through inlet 2 of the movable injector. Vinyl bromide, C_2H_3Br, was added at the downstream end of the reactor (inlet 4) in order to titrate Cl atoms that were indirectly detected at $m/e = 62$ ($C_2H_3Cl^+$).

$$Cl + C_2H_3Br \rightarrow C_2H_3Cl + Br \qquad (4)$$

$$k_4 = 1.43 \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}\ (\text{ref } 9)$$

This procedure, as described above for the Br_2 titration reaction 2, is more reliable than the direct detection of Cl atoms at their parent peaks (m/e =35/37). Experiments were carried out at 1 Torr pressure in the temperature range 233−320 K. The initial concentration of Cl atoms was (1−1.5) × 10^{11} molecule cm^{-3}, and the Br_2 concentration range was (0.3−4.65) × 10^{12} molecule cm^{-3} (see Table 1). Flow velocities in the reactor were 1280−1790 cm s^{-1}. The consumption of Br_2 in the presence of Cl was negligible (less than 5%) for most experiments, and it was significantly higher (up to 25%) in only a few kinetic runs. In all cases, the mean Br_2 concentration over the whole reaction time was used in the calculation of k_4.

An example of a pseudo-first-order plot obtained at T = 298 K is shown in Figure 3. All the pseudo-first-order rate constants, k'_2, were corrected for axial diffusion. The maximal correction was about 13%. It can be seen in Figure 3 that the pseudo-first-order plots obtained from Br_2 decay kinetics in excess of Cl atoms (square symbols) are in excellent agreement with those derived from Cl kinetics. The slope of the linear least-squares fit to the experimental data of Figure 3 yields the value

$$k_2 = (1.42 \pm 0.06) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1} \qquad (T = 298\ K)$$

The error is two standard deviations. All the results obtained for k_2 at the different temperatures of the study are reported in Table 1.

The results from the present work are shown also in Figure 4 together with the data obtained in previous studies.[10−13] It can be seen that our results and those from the other k_2 temperature-dependence study (using laser flash-photolysis resonance-fluorescence technique)[10] are in excellent agreement. The straight line in Figure 4, resulting from the least-squares analysis of our data and those from ref 10, provides the following Arrhenius expression:

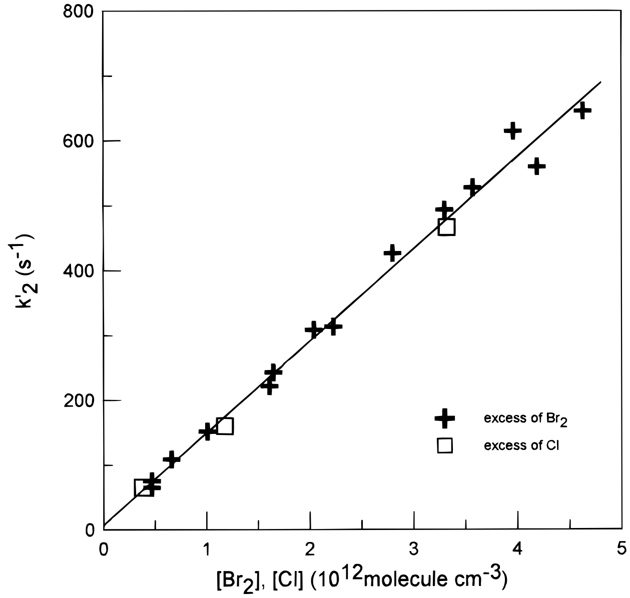

Figure 3. Pseudo-first-order plot of Cl or Br_2 consumption in reaction Cl + Br_2 (2) at T = 298 K.

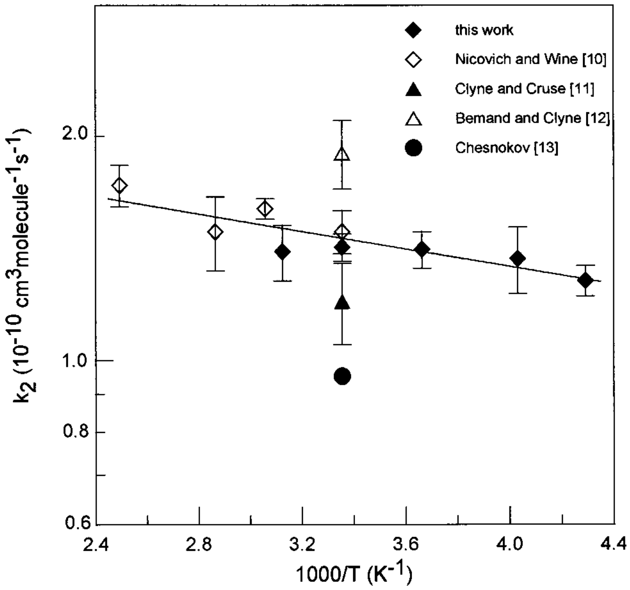

Figure 4. Arrhenius plot of the rate constant of the reaction Cl + Br_2 (2).

$$k_2 = (2.3 \pm 0.4) \times 10^{-10} \exp\{-(135 \pm 60)/T\}\ cm^3\ molecule^{-1}\ s^{-1},\ T = 233{-}401\ K$$

where the quoted uncertainties represent 2σ. This expression is very close to that obtained in ref 10, $k_2 = (2.4 \pm 1.25) \times 10^{-10} \exp\{-(144 \pm 176)/T\}$ cm^3 $molecule^{-1}$ s^{-1}, but with a reduced uncertainty and extended temperature range 233−401 K. The above expression of k_2, combining the data from this work and ref 10, have been used in the relative study of reaction 1 described below.

Kinetics of the Cl + C_5H_8 Reaction: Relative Measurements. In the relative study of reaction 1 using reference reaction 2, the fast titration of the initial concentration of Cl atoms, $[Cl]_0$, by a mixture of excess isoprene and Br_2 was realized and the yield of BrCl as a function of the $[C_5H_8]/[Br_2]$ ratio was measured. The concentration of BrCl formed was defined by the fraction of $[Cl]_0$ reacting with Br_2:

$$[\mathrm{BrCl}] = \frac{k_2[\mathrm{Br}]}{k_2[\mathrm{Br}_2] + k_1[\mathrm{C_5H_8}]}[\mathrm{Cl}]_0 \qquad \text{(I)}$$

Considering the derived expression

$$\frac{[\mathrm{Cl}]_0}{[\mathrm{BrCl}]} - 1 = \frac{k_1}{k_2}\frac{[\mathrm{C_5H_8}]}{[\mathrm{Br}_2]} \qquad \text{(II)}$$

k_1/k_2, and hence k_1, could be obtained by plotting $([Cl]_0/[BrCl] - 1)$ as a function of the $[C_5H_8]/[Br_2]$ ratio. This method is free of heterogeneous complications due to rapid consumption of Cl atoms in the gas phase when sufficiently high concentrations of Br_2 and C_5H_8 are used.

In the experiments carried out at fixed $[Cl]_0$ and $[C_5H_8]$, $[Br_2]$ was varied and corresponding concentrations of BrCl were measured. Cl atoms were produced in a microwave discharge of a Cl_2/He mixture introduced through inlet 1 of the movable injector. Both Br_2 and C_5H_8 were introduced through the central tube of the injector (inlet 2).

It is noted that this method did not need absolute calibration of the mass-spectrometric signal of Cl atoms and BrCl because the initial concentration of Cl could be expressed in the units of the BrCl signal in the absence of isoprene, Cl being titrated by excess of Br_2. Thus, in the experiments, only the BrCl signal was detected, first in the C_5H_8-free system, corresponding to $[Cl]_0$, and second in the Br_2 and C_5H_8-containing system, corresponding to the fraction of $[Cl]_0$ reacted with Br_2. Reaction 2 led to simultaneous production of Br atoms together with BrCl. The key point for the treatment of the results described here is that the secondary chemistry induced by Br atoms could not lead to either formation or consumption of BrCl.

The initial concentration of Cl atoms was in the range $2-5 \times 10^{12}$ molecule cm^{-3}. The concentration ranges of C_5H_8 and Br_2 were $(4.4-9.9) \times 10^{12}$ and $(1.6-77) \times 10^{12}$ molecule cm^{-3}, respectively. The reaction time was typically 5×10^{-3} s. All the experimental data obtained at the different temperatures of the study are presented in Figure 5. According to expression II, the slopes of the linear dependences in Figure 5 give the k_1/k_2 ratio at each temperature. All the results obtained in this way are presented in Table 2. Table 2 also reports the calculated values of k_1, derived from the values of k_2 given by the Arrhenius expression (see above) with addition of a conservative 10% uncertainty, considering the deviation of all experimental points from the straight line of Figure 4, which did not exceed 7%.

The values of k_1 obtained at $T = 298$ and 320 K are in excellent agreement with those directly obtained (within 6% for central values). The temperature dependence of k_1 combining the absolute and relative measurements is presented in Figure 6. The following Arrhenius expression is derived:

$$k_1 = (6.7 \pm 2.0) \times 10^{-11} \exp[(485 \pm 85)/T] \quad \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

Quoted uncertainties are 2σ. A negative temperature dependence of k_1 is observed, as expected for a reaction that proceeds predominantly through an addition mechanism.

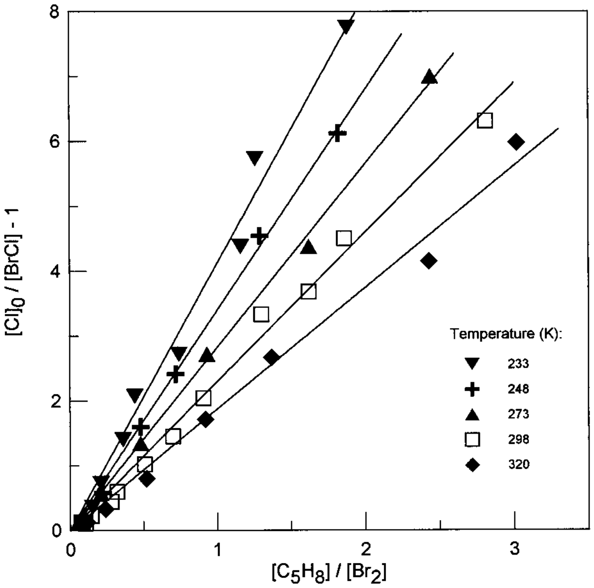

Figure 5. Experimental BrCl yield of Cl atom titration by $Br_2 + C_5H_8$ mixtures at $P = 1$ Torr and different temperatures (see expression II of the text).

TABLE 2: Temperature Dependence of the Ratio k_1/k_2: Experimental Conditions and Results for Cl + C_5H_8 → Products (k_1) and Cl + Br_2 → BrCl + Br (k_2)

no. of expts	T (K)	$[C_5H_8]^a$	$[Br_2]^a$	$[C_5H_8]/[Br_2]$	$k_1/k_2{}^b$	$k_1{}^c$
7	320	7.7−8.6	2.6−75.2	0.11−3.0	1.87 ± 0.18	2.82 ± 0.55
12	298	4.4−7.9	1.6−77.0	0.1−2.8	2.37 ± 0.12	3.46 ± 0.53
6	273	5.5−5.8	2.3−72.2	0.1−2.4	2.83 ± 0.12	3.96 ± 0.56
6	248	6.4	3.5−69.5	0.1−1.8	3.40 ± 0.14	4.52 ± 0.66
8	233	9.3−9.9	5.1−65.7	0.15−1.9	4.12 ± 0.41	5.31 ± 1.06

[a] Units of 10^{12} molecule cm^{-3}. [b] Errors are 2σ. [c] Units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}.

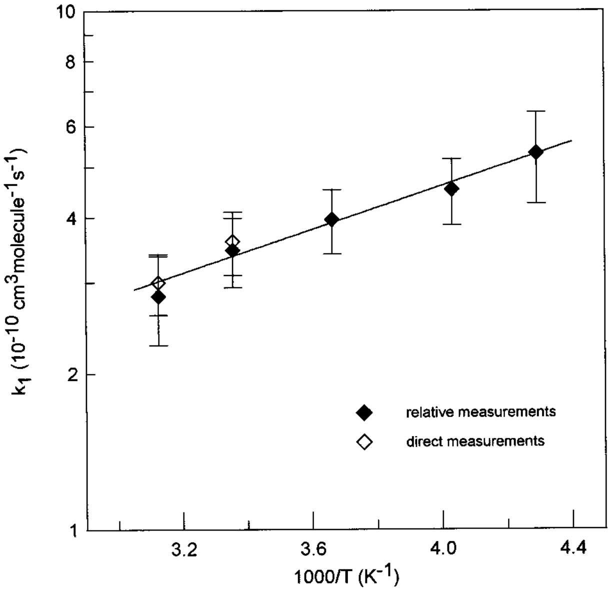

Figure 6. Temperature dependence of the overall rate constant of the reaction Cl + C_5H_8 → products (1).

Rate Constant for the Cl + Isoprene Reaction 1: Pressure Dependence. The pressure dependence of k_1 was measured using the relative-rate method described above, which was considered to be more precise than the absolute one, at least for the measurements of the variation of k_1 with pressure. Experiments were carried out at $T = 298$ K, the pressure being changed between 0.25 and 3 Torr. Experimental conditions were about the same as in the previous section. The obtained

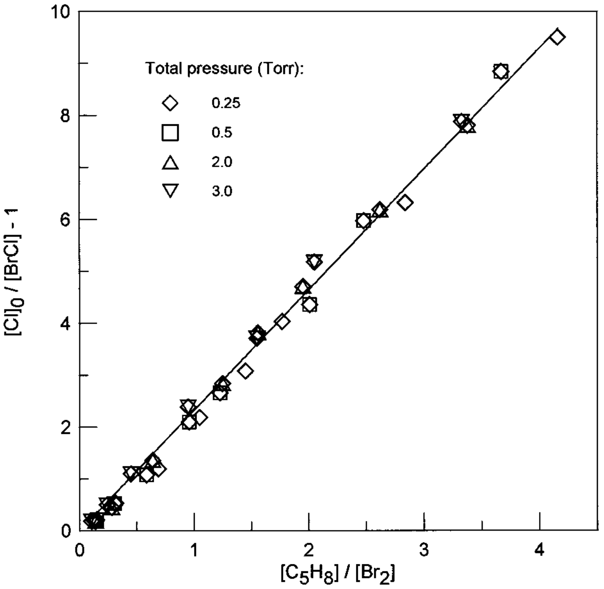

Figure 7. Experimental BrCl yield of Cl-atom titration by $Br_2 + C_5H_8$ mixtures at $T = 298$ K and different pressures (see expression II of the text).

TABLE 3: Pressure Dependence of the Ratio k_1/k_2: Experimental Conditions and Results for $Cl + C_5H_8 \rightarrow$ Products (k_1) and $Cl + Br_2 \rightarrow BrCl + Br$ (k_2)

no. of expts	P (Torr)	$[C_5H_8]^a$	$[Br_2]^a$	$[C_5H_8]/[Br_2]$	k_1/k_2 ^{b}	k_1 ^{c}
8	0.25	5.25−5.5	1.3−42.5	0.13−4.2	2.24 ± 0.11	3.27 ± 0.50
8	0.5	5.85−6.35	1.6−42.9	0.15−3.7	2.34 ± 0.12	3.42 ± 0.53
12	1.0	4.4−7.9	1.6−77.0	0.1−2.8	2.37 ± 0.12	3.46 ± 0.53
8	2.0	5.25−5.5	1.8−48.4	0.14−3.4	2.34 ± 0.09	3.42 ± 0.58
7	3.0	5.2−5.45	1.6−51.7	0.1−3.3	2.41 ± 0.10	3.52 ± 0.51

[a] Units of 10^{12} molecule cm^{-3}. [b] Errors are 2σ. [c] Units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}.

data are presented in Figure 7 and Table 3. Figure 7 shows no pressure dependence of the ratio k_1/k_2 within the experimental uncertainty. Yet the separate treatment of the experimental results at the different pressures shows a slight decrease of k_1/k_2 with decreasing pressure (see Table 3). There are two ways to obtain the values of k_1 at different pressures: first, using the absolute value of k_1 measured above at 1 Torr pressure (see above) in combination with the pressure dependence obtained from the k_1/k_2 ratios; second, from k_1/k_2 ratios and the rate-constant value of the reference reaction, k_2. The values of k_1, derived from the two methods, differed only by 4%. Considering this good agreement, the given values for k_1 are those from the relative method reported in Table 3, which were obtained using the pressure-independent value: $k_2 = (1.46 \pm 0.15) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. This value is derived from the Arrhenius expression of k_2, including a 10% uncertainty. The present determination of k_1 can be considered as pressure-independent in the pressure range investigated, and the following mean value is proposed:

$$k_1 = (3.4 \pm 0.5) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1},\qquad P = 0.25{-}3.0\ \text{Torr}$$

Branching-Ratio Measurements of the Cl + Isoprene Reaction 1. Both HCl ($m/e = 36, 38$) and signals at $m/e = 103, 105$, which correspond to the parent peaks of the adduct C_5H_8Cl, were detected as products of reaction 1:

$$Cl + C_5H_8\ (+M) \rightarrow C_5H_8Cl + (M) \tag{1a}$$

$$Cl + C_5H_8 \rightarrow C_5H_7 + HCl \tag{1b}$$

Quantitative measurements of the concentration were made only for HCl. The procedure of the branching-fraction measurements, k_{1b}/k_1, consisted of rapid titration of Cl atoms with an excess of isoprene, with subsequent measurement of the concentration of HCl formed: $k_{1b}/k_1 = [HCl]/[Cl]_0$. Cl atoms were produced in a microwave discharge of a Cl_2/He mixture introduced into the reactor through inlet 1 of the movable injector. First, in absence of isoprene, $[Cl]_0$ (as BrCl signal at $m/e = 116$) was measured, Br_2 being added into the reactor through the central tube of the injector (inlet 2). The residual signal at $m/e = 36$ was also measured. Then Br_2 was replaced by C_5H_8 and HCl formed in reaction 1 was measured at $m/e = 36$. To ensure that the residual signal at $m/e = 36$ was not changed when isoprene was replaced by Br_2 and vice versa, some experiments were carried out without a change of the chemical composition in the reactor, but with a change of the position of Br_2 introduction. First, Br_2 was added with C_5H_8 (in high excess over C_5H_8) so that $[Cl]_0 = [BrCl]$, and the residual signal at $m/e = 36$ was registrated. Then Br_2 was introduced through inlet 4 at the end of the reactor, and HCl produced as a result of Cl titration by isoprene was detected. Results obtained for k_{1b}/k_1 by these two methods were the same.

To measure the concentrations of HCl and BrCl, the "relative" calibration method was employed, based on the sequence of the two reactions:

$$H + Cl_2 \rightarrow HCl + Cl \tag{3}$$

$$Cl + Br_2 \rightarrow BrCl + Br \tag{2}$$

H atoms, formed in a microwave discharge of an H_2/He mixture (inlet 1), were rapidly consumed in the reactor by an excess of Cl_2 molecules introduced through inlet 3. Consequently, Cl atoms formed in reaction 3 were titrated by excess Br_2 (introduced through inlet 2), forming BrCl. In this case, $\Delta[Cl_2] = \Delta[Br_2] = [HCl] = [BrCl]$ so that mass-spectrometric signals of HCl and BrCl, corresponding to the same concentration, could be relatively calibrated. It was observed that $\Delta[Cl_2] = \Delta[Br_2]$ within 10%. Besides, absolute calibration of the HCl signal by flowing a known HCl concentration into the reactor and BrCl calibration using Br titration,

$$Br + ClNO \rightarrow BrCl + NO \tag{5}$$

$$k_5 = 1.5 \times 10^{-11} \exp(-52/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{(ref 14)}$$

were in good agreement (within 10%) with the relative calibration through reactions 2 and 3.

The branching-ratio experiments were carried out at $P = 1$ Torr in the temperature range 233−320 K. Reaction time was about 5×10^{-3} s. Concentrations of the C_5H_8 and Br_2 were in the range $(2{-}5) \times 10^{13}$ and $(2{-}8) \times 10^{14}$ molecule cm^{-3}, respectively.

Results obtained at five temperatures are presented in Figure 8 as a dependence of HCl concentration produced in reaction 1 versus initial concentration of Cl atoms. The ratio k_{1b}/k_1 was derived from the slopes of the straight lines in Figure 8 (which represent the linear least-squares fit to the experimental points): $k_{1b}/k_1 = [HCl]/[Cl]_0$. The results are reported in Table 4. The possible impact of the secondary reactions on the obtained results was negligible. First, secondary reactions of Cl atoms with the products of reaction 1, C_5H_7 and C_5H_8Cl, can be considered of minor importance because of the very rapid

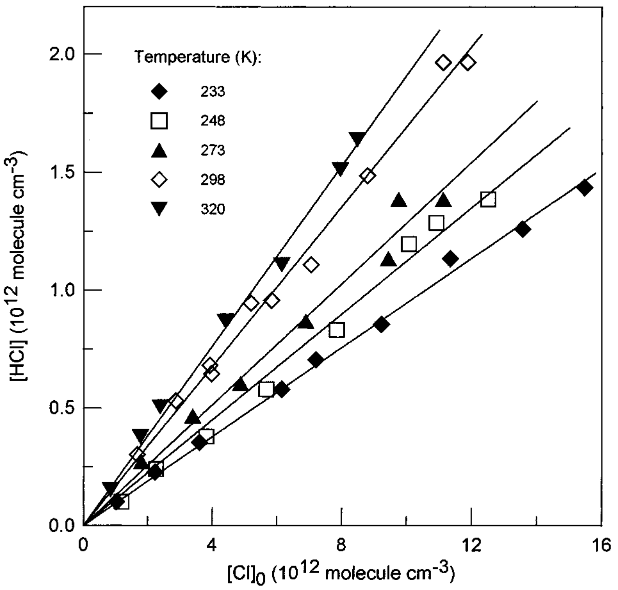

Figure 8. Experimental plots for HCl concentration formed in reaction Cl + C_5H_8 (1) versus initial Cl-atom concentration ([HCl] measured after completion of the reaction and C_5H_8 being used in excess over Cl).

TABLE 4: Branching Ratio for H-Atom Abstraction Channel (1b) of Reaction Cl + C_5H_8 (1): Experimental Conditions and Results for Cl + C_5H_8 → C_5H_7 + HCl (k_{1b})

no. of expts	*T* (K)	$[Cl]_0$ [a]	k_{1b}/k_1 [b]
7	320	0.84−8.5	0.191 ± 0.024
11	298	1.7−11.9	0.169 ± 0.022
7	273	1.8−9.8	0.129 ± 0.021
8	248	1.2−12.5	0.113 ± 0.015
9	233	1.0−19.5	0.095 ± 0.011

[a] Units of 10^{12} molecule cm^{-3}. [b] Errors are 1σ + 10%.

titration of Cl atoms in the primary reaction with isoprene. The absence of visible changes in the concentration of the rapidly formed HCl with increasing reaction time allows us to exclude also the possible impact of the reactions of C_5H_7 and the adduct−radical C_5H_8Cl with Cl_2, reproducing Cl atoms (Cl_2 was present in reactor at about the same concentrations as Cl).

Another method was also used to measure k_{1b}/k_1 at 298 K. In this case, Cl atoms were produced in reaction 3, H atoms being formed in microwave discharge of the H_2/He mixture and introduced through inlet 1 and Cl_2 through inlet 3 of the reactor. Cl atoms were rapidly titrated by an excess of isoprene ($[C_5H_8] = (3-5) \times 10^{13}$ molecule cm^{-3}) flowed through inlet 2 ($[Cl]_0$ was varied in the range 5.3×10^{11} to 1.7×10^{13} molecule cm^{-3}). HCl formed was measured and corresponded to the increase of the signal intensity at $m/e = 36$. This method did not need any measurements of the absolute concentrations of the products or reactants. Only the relative mass-spectrometric signal intensity of HCl was required because the HCl signal produced by reaction 3, in the absence of isoprene, corresponded to $[Cl]_0$. The increase of HCl signal intensity by adding isoprene corresponded to the fraction of $[Cl]_0$ forming HCl in reaction 1. The stoichiometric conversion of initial Cl atoms into HCl by reaction 3 ($[Cl]_0 = [HCl]_0$) was verified as described above.

The obtained results are presented in Figure 9. The slope of the straight line gives $k_{1b}/k_1 = 0.177 \pm 0.020$, where the quoted uncertainty represents one standard deviation with an addition of 10% for systematic error. As one can see, this result is in excellent agreement with that obtained above, 0.169 ± 0.022.

The temperature dependence of the rate-constant ratio, k_{1b}/k_1, derived from the data of Table 4 is shown in Figure 10. All the data could be fitted by the following expression:

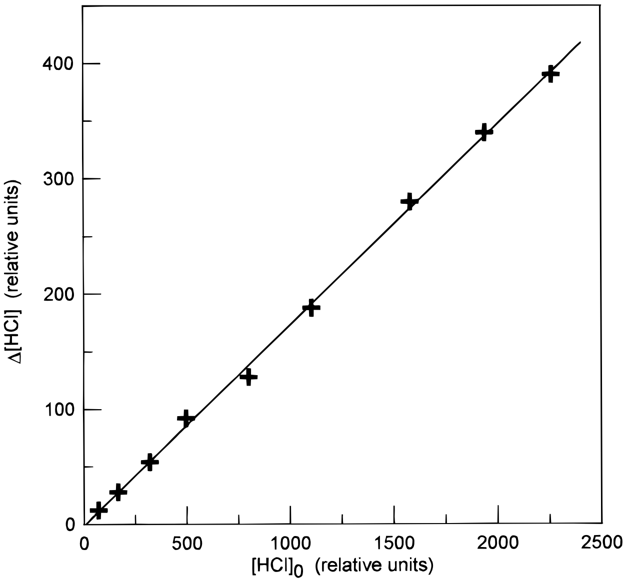

Figure 9. Dependence of the concentration of HCl formed in reaction Cl + C_5H_8 (1) versus consumed Cl concentration: $[HCl]_0 = [Cl]_0$ (see text).

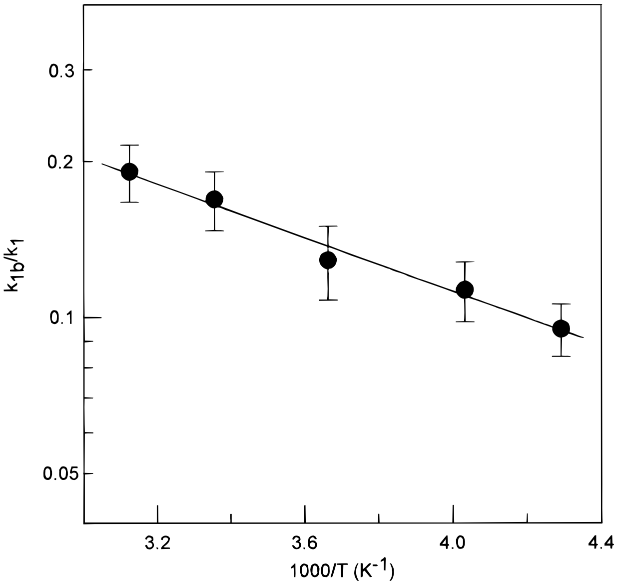

Figure 10. Temperature dependence of the branching ratio for the H-atom abstraction channel (1b) of reaction Cl + C_5H_8 (1).

$$k_{1b}/k_1 = (1.22 \pm 0.4) \exp\{-(595 \pm 90)/T\}$$

The uncertainties are 2σ. By use of this expression and that for the total rate constant k_1 obtained in this work, the rate constant of the H-atom abstraction channel of reaction 1 could be expressed in the following Arrhenius form:

$$k_{1b} = (8.2 \pm 5.1) \times 10^{-11} \exp\{-(110 \pm 175)/T\} \quad \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

with

$$k_{1b} = (5.7 \pm 1.6) \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K}$$

The observed low activation energy is not surprising considering the relatively high value of k_{1b}.

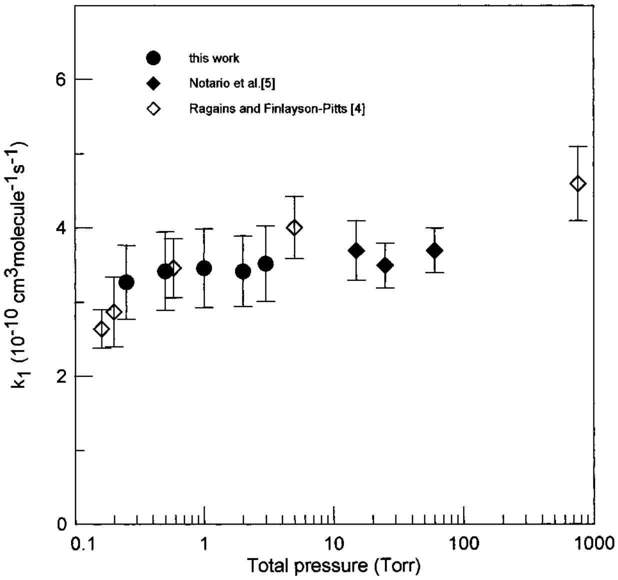

Figure 11. Pressure dependence of the rate constant of the reaction $Cl + C_5H_8$ (1) at $T = 298$ K.

Discussion

This paper reports the first temperature study of reaction 1. At room temperature, only one kinetic and mechanistic study of reaction 1 has been published so far,[4] while a kinetic study from our laboratory has been submitted for publication.[5] Figure 11 shows the pressure dependence of the overall rate constant k_1 on the basis of the data from our work and those of refs 4 and 5. As one can see, our pressure-independent value of k_1 (in the range 0.25−3.0 Torr) agrees well with the data from our laboratory obtained at $P = 15-60$ Torr, using the laser flash-photolysis resonance-fluorescence technique.[5] In contrast, a slight increase of k_1 with pressure is observed in the whole range (0.16−760 Torr) of study,[4] where a continuous photolysis relative method was used. The data from the three studies are, however, consistent within the given experimental uncertainty ranges.

Our data indicate that the high-pressure regime of reaction 1 extends at least to $P = 0.25$ Torr. Such low pressure is not inconsistent with the size and complexity of the Cl−isoprene adduct formed. Assuming that the rate constant of the H-atom abstraction channel does not depend on pressure in the pressure range of our work, the high-pressure limit of k_{1a} can be derived:

$$k_{1a}^{\infty} = k_1 - k_{1b} = (2.8 \pm 0.7) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

The high value of k_{1a}^{∞}, close to the gas kinetic limit, is comparable to those obtained recently for similar reactions of Cl atoms with ethylene (3.2×10^{-10} [15]) and propene (2.7×10^{-10} cm^3 molecule^{-1} s^{-1} [16]).

The branching ratio for the H-atom abstraction channel, reported in ref 1, $k_{1b}/k_1 = 0.15 \pm 0.04$ at 298 K and 760 Torr, agrees well with our room-temperature value, $k_{1b}/k_1 = 0.169 \pm 0.022$ at 1 Torr. The room-temperature value $k_{1b} \approx 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, obtained in the present work, is significantly higher than the rate constant for H-atom abstraction from a CH_3 group in alkanes ($k(CH_3) \approx 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}). Two possible explanations for this difference can be given. First, this difference may be due to the existence of an addition−elimination channel forming HCl in addition to the direct H-atom transfer channel that occurs in Cl + alkane reactions. Such an addition−elimination process has been suggested for the reaction Cl + propene, where an increase of the partial rate constant of the HCl-forming channel by 50% was observed with decreasing pressure from 100 to 10 Torr.[16] Besides, an addition followed by a pressure-dependent HCl elimination is proposed in ref 4 to explain the pressure dependence of k_1 observed. Such a process was suggested to occur at 760 Torr but not at the lowest pressures (Torr range) of their study. As already mentioned,[4] a second explanation of the high value of k_{1b} compared to $k(CH_3)$ in alkanes is that the allylic H abstraction can be faster than H abstraction in alkanes, the C−H bond for allylic hydrogens being lower (80−85 kcal mol^{-1}) compared with 100 kcal mol^{-1} for alkane C−H bond. This explanation seems to be more likely than that of the occurrence of an addition−elimination reaction, although the present data for reaction 1 do not allow us to distinguish between H-atom direct abstraction and addition−elimination mechanisms, since k_{1b} was not measured as a function of pressure. Let us note that in a recent laser-photolysis study[17] of the Cl + propene reaction where the HCl formed was measured by infrared long-path absorption, the data were not inconsistent with addition−elimination formation of HCl, but they also fit with an abstraction mechanism of an allylic H atom.

Concerning the atmospheric application of the present work, the obtained data, which are consistent with those of ref 4, support the conclusions of this study. The atmospheric lifetime of isoprene toward its reaction with Cl atoms, derived from our value of k_1, is $\tau = 1/(k_1[Cl]) = 6$ h, with $[Cl] = 10^5$ molecule cm^{-3}. This lifetime can be compared with the lifetime of isoprene toward its reactions with OH and NO_3 radicals, which are, respectively, $\tau \approx 6$ and 8 h for $[OH] = 5 \times 10^5$ and $[NO_3] = 5 \times 10^7$ molecule cm^{-3}, which are realistic concentrations in the marine atmosphere.

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