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American Chemical Society

2010


http://hdl.handle.net/10138/18719
http://dx.doi.org/10.1021/jp909419v

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Kinetics of the Reactions of CH₂Cl, CH₃CHCl, and CH₃CCl₂ Radicals with Cl₂ in the Temperature Range 191–363 K

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Received: September 30, 2009; Revised Manuscript Received: December 22, 2009

The kinetics of three chlorinated free radicals with Cl₂ have been studied in direct time-resolved measurements. Radicals were produced in low initial concentrations by pulsed laser photolysis at 193 nm, and the subsequent decays of the radical concentrations were measured under pseudo-first-order conditions using photoionization mass spectrometer (PIMS). The bimolecular rate coefficients of the CH₃CHCl + Cl₂ reaction obtained from the current measurements exhibit negative temperature dependence and can be expressed by the equation

\[ k(\text{CH}_3\text{CHCl} + \text{Cl}_2) = ((3.02 \pm 0.14) \times 10^{-12}) (T/300 \text{ K})^{-1.89 \pm 0.19} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \] (1.7–5.4 Torr, 191–363 K).

For the CH₃CCl₂ + Cl₂ reaction the current results could be fitted with the equation

\[ k(\text{CH}_3\text{CCl}_2 + \text{Cl}_2) = ((1.23 \pm 0.02) \times 10^{-11}) (T/300 \text{ K})^{-0.26 \pm 0.10} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \] (3.9–5.1 Torr, 240–363 K).

The measured rate coefficients for the CH₂Cl + Cl₂ reaction plotted as a function of temperature show a minimum at about \( T = 240 \text{ K} \); first decreasing with increasing temperature and then, above the limit, increasing with temperature. The determined reaction rate coefficients can be expressed as

\[ k(\text{CH}_2\text{Cl} + \text{Cl}_2) = ((2.11 \pm 1.29) \times 10^{-12}) \exp(773 \pm 183 \text{ K}/T) (T/300 \text{ K})^{2.26 \pm 0.67} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \] (4.0–5.6 Torr, 201–363 K).

The rate coefficients for the CH₃CCl₂ + Cl₂ and CH₂Cl + Cl₂ reactions can be combined with previous results to obtain:

\[ k_{\text{combined}}(\text{CH}_3\text{CCl}_2 + \text{Cl}_2) = ((4.72 \pm 1.66) \times 10^{-13}) \exp(971 \pm 106 \text{ K}/T) (T/300 \text{ K})^{3.07 \pm 0.23} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \] (3.1–7.4 Torr, 240–873 K) and

\[ k_{\text{combined}}(\text{CH}_2\text{Cl} + \text{Cl}_2) = ((5.18 \pm 1.06) \times 10^{-13}) \exp(525 \pm 63 \text{ K}/T) (T/300 \text{ K})^{2.52 \pm 0.13} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \] (1.8–5.6 Torr, 201–873 K).

All the uncertainties given refer only to the 1σ statistical uncertainties obtained from the fitting, and the estimated overall uncertainty in the determined bimolecular rate coefficients is about ±15%.

CH₂Cl + Cl₂ → products (1)

CH₃CHCl + Cl₂ → products (2)

CH₃CCl₂ + Cl₂ → products (3)

These reactions have all been studied previously, but the temperature range (\( T = 191–295 \text{ K} \)) measured in this work has not been an object of previous kinetic studies for the title reactions.

Johnston et al. and Bell et al. have studied the CH₂Cl + Cl₂ reaction by means of transition state theory (TST) and BEBO theory, respectively. Seetula et al. measured the CH₂Cl + Cl₂ reaction at (295–873 K, \( p = 1.8–5.3 \text{ Torr} \)) and CH₃CCl₂ + Cl₂ reaction rate coefficients, using similar LP-PIMS setup with a different temperature controlling system than is used in the present work, and also studied the reaction transition states with ab initio methods. This work was performed to extend the temperature ranges in which CH₂Cl + Cl₂ and CH₃CCl₂ + Cl₂ reactions have been measured to lower temperatures, which have not been previously attained.

Kinetics of the CH₃CHCl + Cl₂ reaction at 298 K has been measured directly by Knyazev et al. using LP-PIMS at low pressures (2–11 Torr). Kaiser et al. have studied the CH₃CHCl + Cl₂ reaction with respect to the CH₃CHCl + O₂ reaction using relative rate method and initiating the reactions using 351 nm photolysis of Cl₂ in a reaction cell (\( T = 298 \text{ K}, 700 \text{ Torr of N}_2 \)) and employing absorption spectroscopy for product analysis. Dobis and Benson measured the kinetics of...
Experimental Section

Details of the experimental apparatus and the procedures used to measure the bimolecular reaction rate coefficients of the studied radicals—molecule reactions have been described previously,21 and only an overview is given here. The reactions were studied in a temperature-controlled stainless steel flow tube reactor (8 mm i.d., coated with Halocarbon Wax, Supelco) coupled to a photoionization mass spectrometer. Reactions were initiated by producing the radicals homogeneously along the reactor with unfocused exciplex laser (ASX-750) photolysis of suitable precursors at 193 nm. The gas flow velocity inside the reactor was about 5 m s⁻¹ which ensured that the repetitive photolysis at 5 Hz always photolyzed a fresh gas mixture. In every measurement the molecular reactant was in large excess over initial radical concentration ([Cl₂] ≫ [R]₀) resulting in pseudo-first-order decay kinetics with respect to radical concentration.

The change in the radical concentration as a function of time was continuously measured by taking a portion of the gas mixture through a small hole in the wall of the reactor. The sampled gas was formed into a beam by a conical skimmer and ionized with a radiation from a resonance gas lamp (Cl₂ with CaF₂ windows, 8.9–9.1 eV). The ion of the radical was mass selected in a quadrupole mass filter (Exretl, C-50/150-QC/19 mm rods) and detected with an electron multiplier. The resulting single ion counts were recorded with a multichannel scaler (EG&G Ortec MCS plus). Typically 1500–20000 laser pulses were needed for averaging before an exponential function ([R] = [R]₀ exp(−kt)) was fit to the measured radical signal to obtain the pseudo-first-order decay rate coefficient (k') as the initial radical concentration ([R]₀) decreases to concentration [R], at time t.

Exciplex laser photolysis at 193 nm was used to produce the radicals for the kinetic measurements. The chloromethyl radicals were produced in the photolysis of CH₂ClBr

\[
\text{CH}_2\text{ClBr} + h\nu(193 \text{ nm}) \rightarrow \text{CH}_2\text{Cl} + \text{Br} \quad (4)
\]

→ other products

The 1-chloroethyl radicals were generated in the photolysis of 1,1-dichloroethane. The primary dissociation channel is the C–Cl bond fission

\[
\text{CH}_2\text{CHCl}_2 + h\nu(193 \text{ nm}) \rightarrow \text{CH}_2\text{CHCl} + \text{Cl} \quad (5)
\]

→ other products

The dichloroethyl radicals were produced from methyl chloroform

\[
\text{CH}_2\text{CCl}_3 + h\nu(193 \text{ nm}) \rightarrow \text{CH}_2\text{CCl}_2 + \text{Cl} \quad (6)
\]

→ other products

Initial radical concentrations in the measurements were calculated with the known absorption cross section (CH₂ClBr and CH₂ClCl)² laser fluence, and the concentration of the precursor, or it was estimated²¹ from the precursor decomposition signal (CH₂(CHCl₃). Calculated initial radical concentrations were between 0.5 and 6 \times 10^{11} \text{ molecules cm}^{-3} in all measurements. Mostly it was close to 1 \times 10^{11} \text{ molecules cm}^{-3} to avoid interference from second-order radical reactions. No dependencies of the rate coefficients on initial radical concentrations were observed in these experiments.

At the beginning (and in the end) of measurements the decay rate of the produced radical concentration was measured without added reactant. The radical loss rate obtained this way corresponds to all the other losses of the radical in the system, except for the loss in the reaction under study, and was termed as the wall rate coefficient (k₊). After this the reactant gas (C₁₃) was introduced to the carrier gas flow in different concentrations, which were determined by measuring the pressure change in a known volume, and the respective pseudo-first-order rate coefficients of the radical loss were measured. When the measured first-order radical decay rate coefficients (k') were plotted as a function of used reactant concentration [Cl₂], the bimolecular reaction rate coefficient k(R + Cl₂) could be obtained from the slope of the plot according to the k' = k₊ + k(R + Cl₂)[Cl₂] equation. An example of this procedure is shown in Figure 1 for the CH₃Cl + Cl₂ reaction with the measured radical decay and product formation signals in the insets.

Products of the studied reactions were sought by applying different ionization energies by changing the light-emitting gas and the window material of the resonance gas lamp. Lamps and windows employed to ionize and detect radicals and products were: a Cl lamp with CaF₂ windows (8.9–9.1 eV) for CH₃Cl, CH₃CHCl, and CH₃CCl₂; a H lamp with MgF₂ windows (10.2 eV) for CHCl, CH₂Cl, CHCl₂, CCl₂, CH₂Cl₂, CH₂CCl, CH₂CHCl₂, CH₂CCl₂; and a Ne lamp with a CHS (collimated hole structure) plate (16.7 and 16.9 eV) for Cl, HCl, Cl₂, CCl₂, CH₃Cl, CH₃CHCl, CH₃CCl₂, CH₃CCl, and CH₃CCl₂. All the experiments to study the kinetics of the reactions were performed using a chlorine lamp for ionization. However, some radical signals were measured with a hydrogen laser
Results and Discussion

The results of the performed measurements and the corresponding experimental conditions are presented in Table 1. The determined bimolecular $R + Cl_2$ reaction rate coefficients together with the results from previous studies are shown as a function of temperature on a double-logarithmic plot in Figure 2. For the current results of the $CH_3CHCl + Cl_2$ and $CH_3CCl_2 + Cl_2$ reactions, the rate coefficients’ dependence on temperature can be expressed by the equation: $k = k_{300K}(T/300 \text{ K})^n$, where $T$ is temperature in K, $k_{300K}$ is the room temperature ($T = 300$ K) rate coefficient, and $n$ is the coefficient describing temperature dependence. The rate coefficients measured for the $CH_2Cl + Cl_2$ reaction and for the $CH_3CCl_2$ reaction with $Cl_2$ combined with previous data,$^{15,16}$ show a discernible curvature in their double-logarithmic plots and a temperature-dependent pre-exponential factor had to be used for a better fit. Three parameter fits of the modified Arrhenius equation $k = \hat{A} \exp(B/T)(3730 \text{ K})^n$, where $T$ is temperature in K, and $\hat{A}$, $B$, and $m$ are fitting parameters, are given separately for the current data and also for the whole data including previously measured values by Seetula et al.$^{15,16}$ These obtained expression for the rate coefficients can be found in Table 1. The preferred fits, i.e., the fits with widest experimental range, have been included in Figure 2.

The only product observed for the reactions studied was $CH_2Cl$ (m/z = 88) in $CH_2Cl + Cl_2$ reaction in agreement with the previous work by Seetula et al.$^{15,16}$ The measured signal is shown in the inset of Figure 1 together with the corresponding $CH_2Cl$ radical decay profile. The exponential fits to the signals

<table>
<thead>
<tr>
<th>$R$ = $CH_2Cl$, ($CH_2Cl + Cl_2$ $\rightarrow$ products)</th>
<th>$R$ = $CH_3CHCl$, ($CH_3CHCl + Cl_2$ $\rightarrow$ products)</th>
<th>$R$ = $CH_3CCl_2$, ($CH_3CCl_2 + Cl_2$ $\rightarrow$ products)</th>
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<td>$k = ((2.11 \pm 1.29) \times 10^{-14}) \exp((773 \pm 183) K/T)(T/300 \text{ K})^{2.69 \pm 0.67} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$</td>
<td>$k = (1.0 \pm 0.03) \times 10^{-13} \exp((736 \pm 63) K/T)(T/300 \text{ K})^{1.89 \pm 0.19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$</td>
<td>$k = ((1.23 \pm 0.02) \times 10^{-13})(T/300 \text{ K})^{-0.26 \pm 0.10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$</td>
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Range of precursor concentrations used: (0.77–3.0) $\times 10^{11}$ molecules cm$^{-3}$ for $CH_3ClBr$, (1.87–6.95) $\times 10^{12}$ molecules cm$^{-3}$ for $CH_3CHCl$ and (0.07–1.42) $\times 10^{13}$ molecules cm$^{-3}$ for $CH_3CCl_2$. $^a$Statistical uncertainties shown are 1σ. Estimated overall uncertainty in the measured bimolecular rate coefficients is about ±15%.
correspond to the pseudo-first-order decay \((k'_s(CH_3Cl) = 113 \pm 7\ s^{-1})\) and formation \((k'_s(CH_2Cl_2) = 107 \pm 6\ s^{-1})\) rate coefficients and their similar values within the statistical uncertainties of the fits are taken as an indication that the signals are formed in the same reaction.

The CH3Cl + Cl2 reaction has been studied before by Johnston et al.\(^{13}\) using transition state theory and Bell et al.\(^{14}\) using the BEBO method. These early theoretical studies give rate coefficients that differ orders of magnitude from the current results \((k_{300K} = 3.5 \times 10^{-15}\ cm^3\ molecule^{-1}\ s^{-1}\) with TST\(^{13}\) and \(k_{300K} = 5.9 \times 10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}\) with BEBO\(^{14}\) respectively) and will not be considered here afterward. Direct, more recent studies have been performed by Seetula et al.\(^{15,16}\) (\(T = 295-873\ K, p = 1.8-5.3\ Torr\)) with essentially similar LP-PIMS setup as was used in the present study. The agreement between these values and the bimolecular rate coefficients obtained in this work is excellent as can be seen in Figure 2. The rate coefficients measured by Seetula et al.\(^{15,16}\) are presented with hollow squares, and the results from the current work are indicated with filled squares. Considering only the current results, the rate coefficients of the CH3Cl + Cl2 reaction can be expressed as a function of temperature with equation \(k(CH_3Cl + Cl_2) = ((2.11 \pm 1.29) \times 10^{-14}) \exp(773 \pm 183\ K/T)(T/7300\ K)^{1.26+0.67}\ cm^3\ molecule^{-1}\ s^{-1}\). Taking the previous results into account, the expression becomes: \(k_{combined}(CH_3Cl + Cl_2) = ((5.18 \pm 1.06) \times 10^{-14}) \exp(525 \pm 63\ K/T)(T/7300\ K)^{2.52+0.13}\ cm^3\ molecule^{-1}\ s^{-1}\). Seetula et al.\(^{15}\) also studied the reaction transition states by ab initio calculations and found that as the electron density of the radical center decreases the transition state of the R + Cl2 reaction becomes tighter.

The room temperature rate coefficient of the CH3CHCl + Cl2 reaction has been measured by Knyazev et al.\(^{17}\) by Kaiser et al.\(^{18,19}\) and by Dobis and Benson.\(^{20}\) Knyazev et al.\(^{17}\) measured it at low pressures (2–11 Torr) with a similar method as in the present work and obtained \(k_{300K}(CH(CHCl + Cl_2) = (4.37 \pm 0.70) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}\) in reasonably good agreement with the current value \(k_{300K}(CH(CHCl + Cl_2) = (3.02 \pm 0.45) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}\). Kaiser et al.\(^{18,19}\) measured reaction 2 indirectly in a relative rate determination using 351 nm light to photolyze Cl2 in order to initiate the reactions in a reaction cell \((T = 298\ K\ and\ 700\ Torr\ N_2\)) using absorption spectroscopy for analysis method and CH3CHCl + O2 as a reference reaction. They obtained 0.42 as a ratio of the CH3CHCl + Cl2 and CH3CHCl + O2 reaction rate coefficients. Dobis and Benson\(^{20}\) studied the CH3CHCl + Cl2 reaction with a VLPR technique in the millitorr pressure range and obtained \(k_{300K}(CH_3CHCl + Cl_2) = (1.7 \pm 1.0) \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}\) in a gross disagreement with the current result.

The CH3CCL2 + Cl2 reaction has been studied by Seetula et al.\(^{15}\) both experimentally to measure the kinetics of the reaction and also using an ab initio calculation to locate the reaction transition states and energies. The rate coefficients measured by Seetula et al.\(^{15}\) \((T = 414-873\ K, p = 3.1-7.4\ Torr)\) are presented with hollow triangles in Figure 2, together with the current results (filled triangles). The agreement between the two set of results is good. The expression: \(k(CH_2CCl_2 + Cl_2) = ((1.23 \pm 0.02) \times 10^{-13})(T/300\ K)^{-0.26\pm0.10}\ cm^3\ molecule^{-1}\ s^{-1}\) fits well to the data measured in this work. When previous values\(^{15}\) are taken into account, a two-parameter fit cannot give an adequate description of the temperature dependence and a three-parameter fit is used instead: \(k_{combined}(CH_2CCl_2 + Cl_2) = ((4.72 \pm 1.66) \times 10^{-15}) \exp(971 \pm 106\ K/T)(T/300\ K)^{3.07+0.23}\ cm^3\ molecule^{-1}\ s^{-1}\).

The rate coefficients of the CH3CHCl radical reaction with Cl2 exhibit a negative temperature dependence, which is notably different from the other two title reactions. The CH3CHCl radical is also significantly more reactive toward Cl2 than the other radicals studied in this work; at room temperature, it is about 10 times more reactive than CH3Cl and about 20 times more than CH3CCl2. It should, however, be pointed out that the rate coefficients of CH2Cl + Cl2 and CH2CCl2 + Cl2 reactions also possess negative temperature dependences below a certain temperature. For the CH3CCl2 radical the changing temperature is about \(T = 340\ K\) and for the CH2Cl radical about \(T = 240\ K\) as seen in Figure 2. An intriguing question is whether the higher reactivity of CH3CHCl radicals, than the other radicals studied in this work, is connected to its strong negative temperature dependence. Interesting information would be the value of \(k(CH_3CHCl + Cl_2)\) at temperatures 600–800 K. Unfortunately, we are not currently able to reach those temperatures.

The temperature dependence of the CH3CHCl + Cl2 reaction rate coefficients shows a slight deviation from linearity on a logarithmic scale. Nevertheless, the aforementioned equation \((k = k_{300K}(T/300\ K)^{q})\) can still be used to properly describe the temperature dependence.

It seems obvious that CH3CCL2 radical has lower reactivity toward Cl2 than CH3CHCl. The same can be expected for CH3Cl, although the reasons for the behavior in reactivity can be different. In the CH3CCL2 case, the radical site is hardest to attack because of the sterical hindrance of the two relatively large Cl atoms and a methyl group attached to it; this could make the reactivity lower compared to CH3Cl. Because of the electron-withdrawing inductive effect of the halogen atoms in the CH3CCL2 radical, the radical site is more electron deficient than in CH3Cl and CH3CHCl. This can cause the lower reactivity compared to CH3CHCl and CH3Cl radicals. In the CH3CHCl
radical, the electron density of the radical site should be higher than that in the CH₂Cl radical due to the methyl group’s ability to serve as an electron donor. Therefore the reactivity of CH₂CHCl should be even higher than the reactivity of CH₂Cl, and the 10-fold difference in the room temperature reaction rate coefficient is noteworthy to be pointed out.

The reactivity differences among radical–molecule reactions toward a common reactant have been related to readily obtainable radical properties by making correlations of the observed rate coefficients against a chosen molecular property, to gain understanding about the underlying reasons for different reactivity. Linear correlations have been sought by making free energy plots for the reactions under study. The logarithm of the room temperature rate coefficient is usually taken as a measure of the free energy of activation in similar types of reactions and is plotted against different radical properties. One example of such a procedure is to plot the logarithm of the room temperature rate coefficient (log(k₉₀₀K)) of the radical–molecule reaction against the electron affinity of the molecular reagent (EA(reactant)) subtracted from the ionization potential of the radical (IP(R)); [log(k₉₀₀K) vs (IP(R) − EA(reactant))]. Paltenghi et al. observed that this expression provides a good simultaneous correlation for oxygen and ozone reactions with alkyl radicals, instead of just correlating the logarithm of reaction rate coefficients with the ionization potential of the alkyl radicals (IP(R)) in one set of reactions. Another such example is to plot the log(k₉₀₀K) for the radical–molecule reaction against ΔElectronegativity of the reactive radical, which is given in an arbitrary scale based on the simple sum of Pauling electronegativities of the substituent atoms/groups. ΔElectronegativity of the radical is used for estimating the electron-withdrawing inductive effects of the substituents in the radical center. This scale was first introduced by Thomas and transported to gas kinetics by Gutman and co-workers who found it to be useful in explaining the observed differences in the rate coefficients of the methyl and halogenated methyl radical reactions with H₂. The similar linear relationship was observed to hold for larger alkyl radicals when a group electronegativity value of 1.82 was assigned to the methyl group as a substituent. It was also shown to correlate linearly with the rate coefficients of the R + Cl₂ and R + Br₂ reactions.

Figure 3. (a) ΔElectronegativity of the radical (R) plotted against the room temperature (RT = 298 ± 3 K) rate coefficient in current and selected R + Cl₂ reactions. Electronegativities were taken from Pauling and an electronegativity value of 1.82 was assigned to the methyl group in accordance with ref 27. Fluorinated radicals have been included to the correlation by assigning an effective electronegativity value of 2.8 to a fluorine atom as a substituent, as was briefly noted in the text and discussed in ref 16. The rate coefficients for the selected R + Cl₂ reactions were taken from CH₃, CF₃, CCl₃, CHBrCl and CHCl₃, CH₃Br and CH₃Cl, CF₂Cl and CFC₁₂, C₂H₅, n-C₂H₅, and n-C₃H₇. The line in the picture is an unweighted, linear least-squares fit to the data. The current results are indicated by star symbols. (b) Electron affinity of the radical (R) plotted against the room temperature (RT = 298 ± 3 K) rate coefficient in current and selected R + Cl₂ reactions. Electron affinities were taken from ref 29 except for CH₃Br and CHBrCl. The case of substituted ethyl radicals, the EA of the radical was unavailable and was estimated with the help of ref 40, e.g., for CH₂Cl₂: EA(CH₂Cl₂) = EA(CH₂Cl)+ (EA(CHCl₂) − EA(CH₂)). The rate coefficients for the selected R + Cl₂ reactions were taken from: CH₃, C₂H₅, CCl₃, CHBrCl and CHCl₃, CH₃Br and CH₃Cl, CF₂Cl and CFC₁₂, C₂H₅, and n-C₃H₇. The line in the picture is an unweighted, linear least-squares fit to the data. The current results are indicated by star symbols.

As seen in Figure 3a, the rate of R + Cl₂ reactions are affected by the electron densities in the radical centers; the rate of the reaction decreases together with decreasing electron density. For example a Cl atom, or halogen atoms in general, when substituted in the radical center withdraw electrons from the center and decrease the electron density. Chlorine molecule has a large electron affinity (EA(Cl₂) ≈ 2.40 eV) and consequently when electron density is higher in the radical center, as it is for alkyl substituted radicals, the rates of R + Cl₂ reactions are enhanced (Figure 3a). This could also suggest that the more loosely the electron is bound to the radical (lower the ionization energy of the radical) the faster the reaction rate should be, i.e., rate coefficients of these reactions should correlate with IE(R). However, this correlation was not observed.
The rates increase with the electron density in the radical site, but not with the looseness of the weakest bound electron (i.e., lower IE(R)).

The room temperature rate coefficients of the R + Cl₂ reactions also correlate fairly well with the electron affinity of the radical (R) (Figure 3b). The increasing electron affinity reduces the radical reactivity toward Cl₂. This may be understood in the following way. The higher the electron affinity of the radical, the more the radical holds the electron and does not share it with Cl₂, which also has high EA. Consequently, the formation of the bond between the radical center and Cl₂ in the reaction can be hindered by the higher electron affinity of the radical.

By inspection of the results presented in parts a and b of Figure 3, some general conclusions can be drawn. (i) Replacing hydrogen atoms with halogen atoms in an alkyl radical decreases the R + Cl₂ reaction rate coefficients. (ii) Lengthening the carbon chain at α-position to the radical center increases the R + Cl₂ rate coefficients. (iii) Branching at the α-position seems to have a stronger rate enhancing influence than just the carbon chain length but more studies with the isomeric radicals are needed to further clarify this issue.

As has been discussed above, Seetula et al.15 studied the CH₂Cl + Cl₂ and CH₃Cl + Cl₂ reaction transition states by ab initio calculations, together with other alkyl and halogenated alkyl radical reactions with Cl₂ and found that as the electron density of the radical center decreases, the transition state of the R + Cl₂ reaction becomes tighter. Compared to the other radicals in this study, the CH₃CHCl radical has higher electron density in the radical center due to the methyl group substitution and it would be interesting to have an ab initio calculation of the potential energy surface for the reaction path with the transition state.

Conclusion

Three chlorinated alkyl radical reactions with Cl₂ have been studied in direct time-resolved measurements. The measured rate coefficients for two of the reactions studied (CH₂Cl + Cl₂ and CH₃CCl₂ + Cl₂) show an interesting behavior as temperature is varied: a negative temperature dependence below a specific limiting temperature and a positive dependence on temperature above it. The CH₃CHCl + Cl₂ reaction behaves differently at these temperatures and has steep negative temperature dependence over the whole experimental range covered. Linear correlations of the determined rate coefficients against radical properties have been sought in order to gain understanding about the factors affecting radical reactivity in R + Cl₂ reactions. CH₂Cl₂, from the CH₂Cl + Cl₂ reaction, was the only observed product in the studied reactions.

Acknowledgment. R.S.T. and M.P.R. acknowledge the support from the CoE of the Academy of Finland.

References and Notes