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# Kinetics of the Reaction of the $CCl_2$ Biradical with Molecular Chlorine

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The kinetics of the reaction of $CCl_2$ with molecular chlorine has been studied using the laser photolysis/photoionization mass spectrometry technique. Dichloromethylene biradicals were produced by the pulsed laser photolysis of carbon tetrachloride, and the kinetics of their decay due to reaction with $Cl_2$ were monitored in direct time-resolved experiments. Rate constants were determined as a function of temperature (300−750 K) and can be described by the Arrhenius expression $k_1 = (1.3 \pm 0.3) \times 10^{-11} \exp(-(281 \pm 96)\ \mathrm{K}/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Rate constants of reaction 1 are independent of the bath gas density within the experimental range [He] = $(3-12) \times 10^{16}$ atoms cm$^{-3}$. $CCl_3$ was observed as a primary product of the reaction.

## Introduction

Gas phase reactions of chlorinated hydrocarbons play important roles in such complex chemical processes as industrial chlorination, the chemistry of the Earth's atmosphere, and the combustion and incineration of chlorinated hydrocarbons (CHCs). Kinetic modeling of these processes is essential for understanding their mechanisms and for the use of these mechanisms as tools of prediction and control. The success of such modeling is currently limited by a lack of fundamental information on the rates and products of a large number of elementary reactions involving chlorinated hydrocarbon radicals.[1]

The singlet biradical $CCl_2$ is known to be among the intermediates of CHC pyrolysis and combustion. It is, for example, the major product of the thermal decomposition of $CHCl_3$.[2] Another source of formation of $CCl_2$ in the combustion of CHCs is the thermal decomposition of dichloroketene,[3] which has been shown to be an important intermediate in the combustion of trichloroethene.[4] However, very little is known about the kinetics and reactivity of $CCl_2$. The only two experimental studies of chemical reactions involving $CCl_2$ are those of Tiee et al.[5] and Kumaran et al.[2] Tiee et al. used laser induced fluorescence in combination with the photolytic production of $CCl_2$ to study the kinetics of its reactions with $O_2$, CO, NO, $F_2$, $C_2H_4$, and $C_3H_8$ at room temperature; only upper limits of the rate constants were obtained for the reactions with $O_2$ and $C_2H_4$. Kumaran et al. studied the thermal decomposition of chloroform in shock tube experiments. These authors observed the formation of $CCl_2$ as the only channel of $CHCl_3$ decomposition and determined the rates of $CCl_2$ decomposition and self-reaction at high temperatures. No other reactions of $CCl_2$ have been studied; clearly, more experimental and theoretical investigations of the reactivity of $CCl_2$ are needed to understand its role in CHC combustion.

Here we report the results of our experimental investigation of the reaction of the $CCl_2$ biradical with molecular chlorine

$$CCl_2 + Cl_2 \rightarrow CCl_3 + Cl \qquad \Delta H^\circ_{298} = -36.9 \pm 4.2\ \mathrm{kJ\ mol^{-1}}\ {}^{6-8} \quad (1)$$

Reaction 1 was studied over a 300−750 K temperature interval at low densities of helium bath gas ([He] = $(3-12) \times 10^{16}$ atoms cm$^{-3}$). The experimental study is described in the next section. A discussion of the results concludes the article.

## Experimental Study and Results

Dichloromethylene biradicals were produced by the pulsed, 193-nm laser photolysis of carbon tetrachloride:[5,9]

$$CCl_4 \xrightarrow{193\ \mathrm{nm}} CCl_2 + 2Cl\ (\text{or } Cl_2) \quad (2a)$$

$$\rightarrow CCl_3 + Cl \quad (2b)$$

$$\rightarrow \text{other products} \quad (2c)$$

The decay of $CCl_2$ was subsequently monitored in time-resolved experiments using photoionization mass spectrometry. Details of the experimental apparatus[10] and procedures[11] used have been described before and thus are only briefly reviewed here.

Pulsed unfocused 193-nm radiation (4 Hz) from a Lambda Physik EMG 201MSC excimer laser was directed along the axis of a heatable Pyrex reactor (1.05 cm i.d., coated with halocarbon wax or poly(dimethylsiloxane)[12]). Gas flowing through the tube at ≈4 m s$^{-1}$ contained $CCl_4$ (≤0.3%), molecular chlorine in varying concentrations, and an inert carrier gas (He) in large excess. The flowing gas was completely replaced between laser pulses.

Gas was sampled through a hole (0.04 cm diameter) in the side of the reactor and formed into a beam by a conical skimmer before the gas entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion was photoionized and mass selected. A hydrogen resonance lamp (10.2 eV, $MgF_2$ window) was used to ionize all species detected in the current study. Temporal ion signal profiles were recorded on a multichannel scaler from a short time before each laser pulse up to 35 ms following the pulse. Typically, data from 5000 to 45 000 repetitions of the experiment were accumulated before the data were analyzed.

Experiments were conducted under pseudo-first-order conditions with $Cl_2$ in large excess over $CCl_2$ ([$Cl_2$] = $4.6 \times 10^{12}$−$7.6 \times 10^{13}$ molecules cm$^{-3}$). The observed exponential decay

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**TABLE 1: Conditions and Results of Experiments To Determine the Rate Constants $k_1$ of the Reaction of $CCl_2$ with $Cl_2$**

| *T*/K | [M][a] | [$CCl_4$][b] | [$Cl_2$][c] | $[R]_0$[d] | I[e] | $k_3$/s$^{-1}$ | $k_1$[f] |
|---|---|---|---|---|---|---|---|
| 300 | 12.4 | 7.20 | 9.5−76.0 | 1.5 | 9.3 | 0.9[g] | 4.50 ± 0.66 |
| 301 | 6.1 | 6.63 | 7.1−38.3 | 2.0 | 13 | 30.7[g] | 5.22 ± 1.08 |
| 301 | 11.7 | 11.50 | 10.0−49.0 | 1.3 | 4.8 | 2.2[g] | 4.32 ± 0.87 |
| 301 | 12.0 | 26.60 | 5.1−25.0 | 2.3 | 3.7 | 104.4 | 5.12 ± 0.69 |
| 302 | 3.0 | 6.84 | 8.1−42.2 | 2.4 | 15 | 12.1[g] | 5.52 ± 1.52 |
| 353 | 11.9 | 2.29 | 6.2−37.0 | 2.0 | 22 | 33.2 | 7.47 ± 1.34 |
| 383 | 12.1 | 1.68 | 5.5−23.0 | 0.8 | 11 | 19.2[g] | 7.91 ± 1.41 |
| 440 | 11.9 | 2.00 | 6.9−33.0 | 2.1 | 22 | 49.8 | 6.89 ± 1.11 |
| 550 | 12.2 | 2.02 | 4.6−26.0 | 2.3 | 19 | 82.1 | 7.93 ± 2.83 |
| 650 | 12.0 | 2.08 | 11.0−21.0 | 2.3 | 13 | 99.9 | 7.60 ± 3.21 |
| 700 | 12.1 | 0.54 | 6.3−20.0 | 1.6 | 28 | 122.2 | 8.83 ± 3.19 |
| 750 | 12.2 | 0.79 | 4.9−30.0 | 1.9 | 22 | 71.0 | 8.99 ± 1.76 |

[a] Concentration of the bath gas (helium) in units of $10^{16}$ atoms cm$^{-3}$. [b] In units of $10^{13}$ molecules cm$^{-3}$. [c] In units of $10^{12}$ molecules cm$^{-3}$. [d] Estimated concentration of the polyatomic radical products of $CCl_4$ photolysis (see text). In units of $10^{11}$ molecules cm$^{-3}$. [e] Estimated photolyzing laser intensity in mJ pulse$^{-1}$ cm$^{-2}$. [f] In units of $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Error limits represent a sum of $2\sigma$ statistical uncertainty and estimated systematic uncertainty. [g] Pyrex reactor coated with halocarbon wax was used. Pyrex reactor coated with poly(dimethylsiloxane) was used in all other experiments.

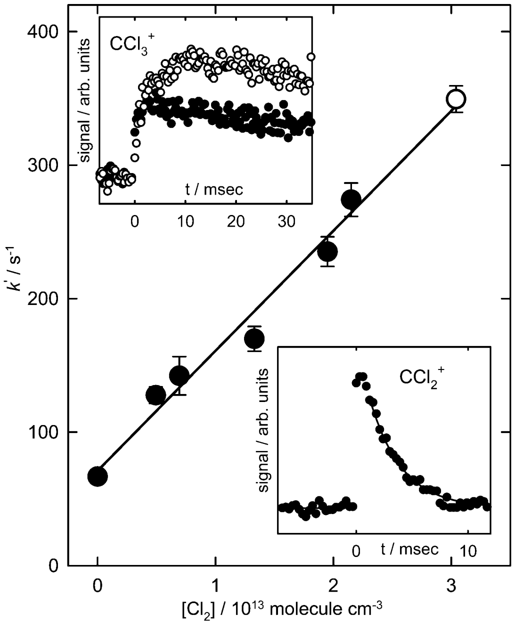

**Figure 1.** Pseudo-first-order $CCl_2$ decay rate $k'$ vs [$Cl_2$]. The intercept at [$Cl_2$] = 0 corresponds to the rate of heterogeneous decay of $CCl_2$. $T = 750$ K, [He] = $1.2 \times 10^{17}$ molecules cm$^{-3}$, $[CCl_2]_0 \leq 1.9 \times 10^{11}$ molecules cm$^{-3}$, and [$CCl_4$] = $7.9 \times 10^{12}$ molecules cm$^{-3}$. The lower right inset shows the recorded $CCl_2$ decay profile for the conditions of the open circle: [$Cl_2$] = $3.04 \times 10^{13}$ molecules cm$^{-3}$; $k' = 349$ s$^{-1}$. The upper left inset shows the profiles of $CCl_3$ in the absence (filled circles) and in the presence (open circles) of the $Cl_2$ reactant for the same experimental conditions.

of the $CCl_2$ radical was attributed to reaction 1 and heterogeneous loss:

$$CCl_2 \rightarrow \text{heterogeneous loss} \tag{3}$$

The $CCl_2$ ion signal profiles were fit to an exponential function ($[CCl_2]_t = [CCl_2]_0 \exp(-k't)$; $k' = k_1[Cl_2] + k_3$) by using a nonlinear least squares procedure. In a typical experiment to determine $k_1$, the kinetics of the decay of $CCl_2$ radicals was recorded as a function of concentration of molecular chlorine. Values of $k_3$ were determined in the absence of $Cl_2$. Values of $k_1$ were obtained from the slopes of linear plots of $k'$ vs [$Cl_2$] (Figure 1).

The 193-nm photolysis of carbon tetrachloride is known to produce $CCl_3$, $CCl_2$, and CCl radicals among its products.[5,9] Collisional quenching of the electronically excited states of $CCl_2$ has been studied for a large number of inorganic and organic collider gases (e.g., refs 13−18); rate constants comparable with the gas kinetic collision rate have been obtained in all measurements. In particular, rate constants larger than $2 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ have been reported for quenching by $CCl_4$.[15] In the current study, large concentrations of helium bath gas, $CCl_4$, and $Cl_2$ were used (Table 1); under these conditions, collisional quenching of the $CCl_2$ excited states should occur on time scales much shorter than those of the $CCl_2$ decay due to reaction 1 ($k' < 350$ s$^{-1}$). Therefore, the observed kinetics of $CCl_2$ is that of the singlet species in the ground state.

Concentrations of the polyatomic radical products of the $CCl_4$ photolysis were kept low ($[R]_0 \leq 2.4 \times 10^{11}$ molecules cm$^{-3}$) to ensure that radical−radical reactions had negligible rates in comparison with the rate of reaction 1. The photolytic depletion of the $CCl_4$ precursor was small (0.1−3%) and could not be measured directly due to the low sensitivity of the detection system to $CCl_4$. Instead, the degree of photolytic depletion of $CCl_4$ was estimated by comparing the ion signals of $CCl_3$ obtained in the 193-nm photolysis of $CCl_4$ and $(CCl_3)_2CO$ and measuring the fraction of $(CCl_3)_2CO$ decomposed due to photolysis. It was assumed that $CCl_3$ production is the dominant process in reaction 2 and in the photolysis of perchloroacetone (ion signals of $CCl_3$ produced were more intense than those of $CCl_2$ by approximately a factor of 5). The values of $[R]_0$ given in Table 1 were obtained by multiplying the concentration of $CCl_4$ by its estimated relative photolytic depletion; the concentration of $CCl_2$ is a fraction of $[R]_0$. It should be noted that, under the pseudo-first-order conditions employed in this study, exact knowledge of $[CCl_2]_0$ is not necessary for the data analysis.

Experiments were performed to establish that the decay constants did not depend on the initial radical concentration, the concentration of the $CCl_4$ precursor, or the photolyzing laser intensity. Two types of reactor wall coatings were used to reduce the wall loss of $CCl_2$: halocarbon wax and poly(dimethylsiloxane).[12] Experiments were performed in the 300−383 K temperature range to demonstrate that the experimental rates of reaction 1 did not depend on the type of wall coating.

Rate constants of reaction 1 were determined at $T = 300$−750 K and [He] = $(3-12) \times 10^{16}$ atoms cm$^{-3}$. The upper temperature limit of the experiments was determined by the thermal instability of the poly(dimethylsiloxane) wall coating. An example of a $k'$ vs [$Cl_2$] plot is shown in Figure 1. The intercept at [$Cl_2$] = 0 corresponds to the rate of heterogeneous decay of $CCl_2$ radicals, $k_3$. The conditions and results of the experiments are presented in Table 1.

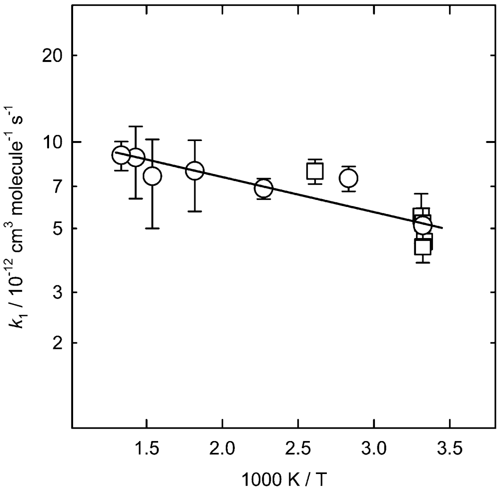

**Figure 2.** Temperature dependence of the rate constant of reaction 1. Symbols: experimental results. Squares represent data obtained using the reactor coated with halocarbon wax; circles represent data obtained with the poly(dimethylsiloxane) coating. Error limits of individual points are 2$\sigma$ statistical uncertainties. Line: Arrhenius fit (expression I).

The sources of error in the measured experimental parameters were subdivided into statistical and systematic and propagated to the final values of the rate constants using different mathematical procedures for propagating systematic and statistical uncertainties.[19] The error limits of the experimentally obtained rate constant values reported in this work represent a sum of 2$\sigma$ statistical uncertainty and estimated systematic uncertainty.

The values of the bimolecular rate constant $k_1$ determined in this study are presented on an Arrhenius plot in Figure 2. The results yield the Arrhenius expression

$$k_1(T) = (1.3 \pm 0.3) \times 10^{-11} \exp(-(281 \pm 96)\ \mathrm{K}/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad \text{(I)}$$

The rate constants demonstrate no dependence on pressure within the experimental range. Error limits in expression I are 2$\sigma$ and represent statistical uncertainties of the fit only. Systematic uncertainties are, on average, 8% of the experimental rate constant values.

Formation of $CCl_3$ was observed in reaction 1 (Figure 1). Although $CCl_3$ is also formed as a product of the photolysis of $CCl_4$, in the absence of $Cl_2$ its kinetics is that of pure exponential decay due to heterogeneous wall losses. In the presence of $Cl_2$, the temporal profiles of $CCl_3$ had an additional component which exhibited a rise following the laser pulse (with the characteristic rise time in agreement with the decay time of the $CCl_2$ signal) and then a decay due to wall loss. This additional component was attributed to the formation of $CCl_3$ in reaction 1.

Gases used in the experiments were obtained from Aldrich (carbon tetrachloride, >99.9%), Matheson (chlorine, 99.999%), and MG Industries (helium, >99.999%, <1.5 ppm of $O_2$). $CCl_4$ and $Cl_2$ were purified by vacuum distillation prior to use. Helium was used without further purification.

## Discussion

The results of the current study provide the first experimental determination of the rate constant of reaction 1 as a function of temperature. The observed absence of a pressure dependence is in agreement with the expected mechanism of this reaction being that of a simple abstraction. However, a more complex reaction mechanism consisting of an initial formation of the $CCl_4$ adduct followed by its chemically activated decomposition into $CCl_3 + Cl$ is also possible. Although the chemically activated mechanism should result in a pressure dependence of the rate constant, variation of the pressure by a factor of 4 as used in the current experimental study may not be sufficient to reveal such a dependence if the reaction is close to the low-pressure limit. Therefore, the experimental data cannot provide decisive support for either mechanism. The rate of reaction 1 is relatively large ($4.9 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at room temperature) and exhibits only a weak positive temperature dependence. Thus, the reaction of $CCl_2$ with $Cl_2$ is significantly faster than the reactions of chlorinated methyl radicals with molecular chlorine (room temperature rate constants in the range $2 \times 10^{-16}$–$3 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [20,21]), indicating a higher reactivity of the biradical species. Reaction 1 is exothermic: $\Delta H°_{298}(1) = -36.9 \pm 4.2$ kJ mol$^{-1}$ is obtained if the values of $\Delta H_f°_0(CCl_2) = 229.3 \pm 1.7$ kJ mol$^{-1}$ [6] and $\Delta H_f°_{298}(CCl_3) = 71.1 \pm 2.5$ kJ mol$^{-1}$ [7] are used; this exothermicity is in agreement with the large reaction rate. The weakness of the temperature dependence indicates that reaction 1 is likely to be barrierless.

The potential energy surface (PES) of the abstraction pathway of reaction 1 was studied in the current work using quantum chemical methods with the purpose of verifying the above suggestion of the absence of an energy barrier. Molecular structures were optimized using the BH&HLYP//6-311+G(d) method.[22,23] A version of the BH&HLYP functional implemented in the Gaussian 98 program[24] was used. Single point energy values were calculated at the stationary points of the PES using other methods, as described below. The Gaussian 98 program was used in all calculations.[24] Spin-unrestricted Hartree–Fock wave functions were used because the use of restricted methods resulted in unstable wave functions. A transition state (PES saddle point) for reaction 1 was found at the BH&HLYP/6-311+G(d) level; however, the energy of this transition state was below that of the reactants by 12.5 kJ mol$^{-1}$ (8.1 kJ mol$^{-1}$ with zero point energy (ZPE) included). Single point energy calculations at the QCISD(T)/6-311+G(d)[25] level also resulted in the transition state energy being below that of the reactants by 19.5 kJ mol$^{-1}$ (by 15.1 kJ mol$^{-1}$ with ZPE included). These levels of quantum chemistry calculations, however, resulted in incorrect values of the reaction enthalpy: $\Delta H°_0(1)$ values of $-97.7$ and $-85.7$ kJ mol$^{-1}$ were obtained in the BH&HLYP and the QCISD(T) calculations, respectively. These large errors in $\Delta H°_0(1)$ are, most likely, caused by the underestimation of the $Cl_2$ bond strength due to the insufficient size of the basis set used (a 0 K $Cl_2$ bond strength of 162.7 and 172.0 kJ mol$^{-1}$ was obtained in the BH&HLYP and the QCISD(T) calculations, respectively, as compared to the experimental value[8] of 238.7 kJ mol$^{-1}$). This significant overestimation of the $Cl_2$ energy could have affected the position of the transition state relative to the reactants ($CCl_2 + Cl_2$). To approximately compensate for the effects of the small basis set, the QCISD(T)/6-311+G(3df) energies were estimated via the formula QCISD(T)/6-311+G(3df) ≈ QCISD(T)/6-311+G(d) + [PMP2/6-311+G(3df) − PMP2/6-311+G(d)], where PMP2 is the spin-projected[26] MP2 method.[27] The thus calculated $Cl_2$ 0 K bond strength (226.2 kJ mol$^{-1}$) is closer to the experimental value and the resultant 0 K enthalpy of reaction 1 ($-47.7$ kJ mol$^{-1}$ with ZPE included) is significantly closer to the above value of $\Delta H°_{298}(1) = -36.9 \pm 4.2$ kJ mol$^{-1}$. At this level of calculations, the energy of the transition state is still below that of the reactants by 23.1 kJ mol$^{-1}$ (ZPE included).

The results of the quantum chemical study are in agreement with the suggestion introduced above on the basis of the experimentally observed weak $k_1(T)$ dependence that reaction 1 does not have an energy barrier.Detailed information on the properties of the PES stationary points obtained in quantum chemical calculations are provided in the Supporting Information.

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**Supporting Information Available:** Table 1S including the results of the quantum chemical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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