

# Thermal decomposition of dichloroketene and its reaction with H atoms

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## Abstract

The thermal unimolecular decomposition of dichloroketene  $\text{CCl}_2\text{CO} \rightarrow \text{CCl}_2 + \text{CO}$  (reaction 1) was studied experimentally and computationally. Dichloroketene was produced by the pulsed laser photolysis of hexachloroacetone, and the kinetics of its decay due to reaction 1 was monitored using photoionization mass spectrometry. Rate constants of reaction 1 were determined in direct time-resolved experiments as a function of temperature (740–870 K) and bath gas density ( $[\text{He}] = (3\text{--}25) \times 10^{16} \text{ atom cm}^{-3}$ ,  $[\text{N}_2] = 12 \times 10^{16} \text{ molecule cm}^{-3}$ ). Reaction 1 is in the falloff region under these conditions. The potential energy surface (PES) of reaction 1 was studied using quantum chemical methods. The experimental  $k_1(T, P)$  dependence was reproduced with an RRKM/master equation model based on quantum chemical calculations. Parameterized expressions for the rate constants of reaction 1 and the reverse reaction, that of  $\text{CCl}_2$  with  $\text{CO}$ , were obtained over wide ranges of temperatures and pressures. The enthalpy of formation of  $\text{CCl}_2\text{CO}$  was determined in quantum chemical calculations. The kinetics of the reaction of dichloroketene with hydrogen atoms (reaction 2), an important channel of destruction of  $\text{CCl}_2\text{CO}$  in flames, was studied computationally. The PES of reaction 2 was studied using quantum chemical methods. Temperature and pressure dependences of the rate constants of the four dominant reaction channels were obtained in transition state theory and master equation calculations; the technique of isodesmic reactions for transition states was applied to the channel of Cl atom abstraction. Analysis of the experimental data and the computational models of reactions 1 and 2 demonstrates that thermal decomposition is a major pathway of destruction for dichloroketene in combustion systems.

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## 1. Introduction

Kinetic modeling of processes such as the combustion and incineration of chlorinated hydrocarbons and industrial chlorination 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 species [1–3]. Dichloroketene ( $\text{CCl}_2\text{CO}$ ) has been demonstrated to be an important intermediate in the combustion of chlorinated hydrocarbons [4]. Werner and Cool [4] experimentally observed its formation in a  $\text{CH}_4/\text{C}_2\text{HCl}_3/\text{O}_2/\text{Ar}$

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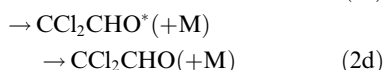
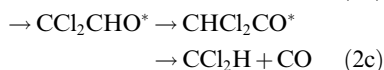
flame under low Cl/H ratio conditions. Kinetic modeling performed by these authors demonstrated the importance of elementary reactions involving the formation and destruction of chlorinated ketenes. One of several major pathways of the destruction of trichloroethylene under the conditions of [4] is an abstraction of Cl by an H atom leading to the formation of dichlorovinyl radical,  $\text{CHCCl}_2$ . Reaction of the latter with molecular oxygen produces dichloroketene. Successive dechlorination of  $\text{CCl}_2\text{CO}$  by H-addition/Cl-elimination displacement reactions leads to the formation of chloroketene and ketene [4]. Despite the importance of the elementary reactions of  $\text{CCl}_2\text{CO}$ , their kinetics remain completely unknown: no experimental or theoretical information on reactions of dichloroketene is currently available in the literature.

In the experimental part of this article, we report the results of our investigation of the thermal unimolecular decomposition of dichloroketene



In the computational part of this work, the potential energy surface (PES) of reaction 1 was studied using quantum chemical methods. An RRKM/master equation model of reaction 1 and the reverse reaction, that of  $\text{CCl}_2$  with CO, was created on the basis of the PES calculations and the experimental data. This model was used to provide parameterized expressions for the  $k(T, P)$  dependences. The enthalpy of formation of dichloroketene was determined in quantum chemical calculations.

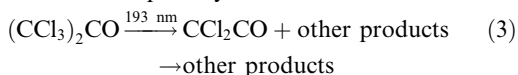
The experimental and modeling results of the current study demonstrate that thermal decomposition is a major channel of destruction of dichloroketene in flames, which hitherto has not been accounted for in kinetic models of combustion and pyrolysis of chlorinated hydrocarbons. Kinetic modeling performed in [4] demonstrated the importance of another channel of destruction of dichloroketene in flames, its reaction with H atoms. The computational part of the current work was extended to include four main channels of the reaction of  $\text{CCl}_2\text{CO}$  with H (reaction 2)



as well as other channels, which were shown to be less important. The PES of reaction 2 was studied using quantum chemical methods, and rate constants were calculated using transition state theory, RRKM/master equation technique, and, for channel 2a, the technique of isodesmic reactions for transition states (IRTS) [5,6].

## 2. Experimental study and results

Dichloroketene was produced by the pulsed, 193-nm laser photolysis of hexachloroacetone



The decay of  $\text{CCl}_2\text{CO}$  was subsequently monitored in time-resolved experiments using photoionization mass spectrometry. Details of the experimental apparatus [7] and procedures [8–11] used have been described before. Thus, only experimental details specific to the current study are presented here.

An uncoated quartz reactor (1.05-cm i.d.) was used. A hydrogen resonance lamp (10.2 eV,  $\text{MgF}_2$  window) was used to ionize  $\text{CCl}_2\text{CO}$ . Temporal ion signal profiles were recorded on a multichannel scaler from a short time before each laser pulse up to 25 ms following the pulse. Typically, data from 2000 to 10,000 repetitions of the experiment were accumulated before the data were analyzed.

The  $\text{CCl}_2\text{CO}$  ion signal profiles were fit to an exponential function ( $[\text{CCl}_2\text{CO}]_t = [\text{CCl}_2\text{CO}]_0 e^{-k't}$ ) using a non-linear least squares procedure. Unimolecular decay of  $\text{CCl}_2\text{CO}$  was observed only above 650 K. Below this temperature, the concentration of  $\text{CCl}_2\text{CO}$  did not change with time, which was experimentally verified. Nevertheless, experimental profiles of  $\text{CCl}_2\text{CO}$  obtained below 650 K were fitted with exponential decay functions, and formal decay rate constants ( $k_0$ ) were obtained, with associated uncertainty limits, to account for any potential minor distortion of the signal profile due to imperfections of the relative alignment of the reactor and the photolyzing laser beam. The values of  $k_0$  (very close to zero, in the range of  $-0.1$  to  $1.7 \text{ s}^{-1}$ ) were subtracted from those of  $k'$  to obtain the rate constants of reaction 1 ( $k_1 = k' - k_0$ ); the experimental uncertainties of both  $k'$  and  $k_0$  were combined to yield the uncertainties of  $k_1$ .

Reaction 1 was studied in the 740–870 K temperature interval. The highest temperature used was determined by the appearance at higher temperatures of a large background at the mass of dichloroketene ( $m/e = 110$ ) due to photofragmentation of the ion of the photolytic precursor, hexachloroacetone, in the ion source. Since the concentration of hexachloroacetone dropped as a result of photolysis, the background signal at mass 110 also exhibited a sharp drop following the photolyzing laser pulse. This change in the background signal complicated the analysis of exponential decays of the  $\text{CCl}_2\text{CO}$  signal, and thus prevented experiments at temperatures above 870 K. The lower limit of the experimental temperature range was determined by the criterion  $k_1 > 10 \text{ s}^{-1}$ , which limited the effects of the uncertainty in  $k_0$  on the values of  $k_1$ . A typical  $\text{CCl}_2\text{CO}$  signal decay profile is shown in Fig. 1.

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