

MECHANISM OF ACCELERATION AND INHIBITION IN HYDROCARBON COMBUSTION
BY CHLOROCARBONS OR HCl

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ABSTRACT

The thermal decomposition of dichloromethane in hydrogen/oxygen mixtures and argon bath gas was carried out at 1 atmosphere pressure in tubular flow reactors. A detailed kinetics reaction mechanism based upon fundamental thermochemical principles and Transition State Theory was developed and used to model results obtained from our experiments. Sensitivity analysis is used to indicate the primary reactions which inhibit CO oxidation (burnout) and the overall hydrocarbon combustion process. An opposite effect, reaction enhancement or acceleration, is observed in the presence of chlorocarbons under fuel rich or pyrolytic conditions at initiation.

INTRODUCTION

Chlorinated hydrocarbons (ClHC) have been used on a large scale by industry as raw materials for products and as solvents. In both cases, large amounts of wastes chlorocarbons are often generated. Reasonable methods for effective destruction of these ClHCs include: conversion to HCl and CO₂ (oxidation/incineration), and conversion to HCl and hydrocarbons (pyrolysis in a hydrogen or methane rich atmosphere). There is, therefore, a significant need to develop quantitative insights into the mechanisms of these pyrolysis and oxidation processes in order to better understand and ultimately to optimize these reaction processes and the conversion of chlorocarbons. In this paper, we present results from an experimental study on dichloromethane (CH₂Cl₂) reactions in H₂/O₂ atmospheres in a tubular flow reactor. We also present a detailed kinetic model based upon fundamental thermochemical principles for the reagent and product concentration profiles versus time and temperature. Sensitivity results clearly illustrate the reactions which cause acceleration in fuel rich pyrolysis regimes and inhibition of CO burnout in the later stages. This study provides a better understanding of the fundamental combustion processes which occur during the incineration of CH₂Cl₂ or similar chlorinated methanes.

EXPERIMENTAL The thermal decomposition of CH₂Cl₂ in H₂/O₂ mixtures with argon bath gas was carried out at 1 atmosphere total pressure in tubular flow reactors of different surface to volume (S/V) ratios. Varying the S/V ratio helps verify that homogeneous reactions dominate our observations, and allows us to decouple the apparent wall and bulk phase decomposition rates¹. The reactions were analyzed systematically over temperature ranges from 600 to 820 °C, with

average residence times in range of 0.1 to 2.0 seconds.

The high temperature quartz tubular flow reactors were heated in a three zone Lindberg electric tube furnace. Temperature profiles were obtained using a type K thermocouple probe moved axially within the reactor under representative flow conditions. Tight temperature control resulted in the reactor being isothermal to within $\pm 5^\circ\text{C}$ over the central 80% of the furnace length for all temperatures studied. Argon carrier gas was passed through one set (two in series) of saturation bubblers kept at 0°C using an ice bath in order to pick up CH_2Cl_2 . A second supply of argon (after the bubblers) was brought in as make-up to adjust the initial CH_2Cl_2 ratio. Feed O_2 and H_2 were added into the flow stream as required. Complete mixing occurred in an 18 cm section of the flow tube, upstream of the furnace. The reactor effluent was monitored by an on-line Gas Chromatograph (GC) equipped with Flame Ionization and Thermal Conductivity Detectors. The inlet vapor mixture is transferred directly from the saturator to the GC sampling inlet via a reactor by-pass line to determine the GC peak area which corresponded to the initial concentrations. The reactor effluent gas passed through a heated (80°C) transfer line to the GC gas sample valve and exhaust.

Product identification was confirmed by GC/Mass Spectrometry (Finnigan 4030, 50 m x 0.22 mm I.D. methyl silicon stationary phase column) on batch samples of gas drawn from the reactor exit into evacuated 25 ml stainless steel or Pyrex sample cylinders.

Quantitative analysis of the HCl product was performed for all reactions. Samples for HCl analysis were collected independent from GC sampling. In this analysis, the effluent was passed through a two stage bubbler containing 0.01M NaOH before exhausting to the hood. The HCl produced by reaction was then calculated based upon titration of the bubbler solution with 0.01 M HCl to its phenolphthalein end point.

RESULTS AND DISCUSSION It was found that complete decay (99 %) of the CH_2Cl_2 at a 1 second residence time occurs at about 820°C for all the reactant ratio sets studied. The major products of CH_2Cl_2 decomposition were CH_3Cl , CH_4 , CO , and HCl. The quantity of chlorinated products decreased with increasing temperature and residence time. Oxygen had almost no effect on the decay of CH_2Cl_2 when conversion was below 50 % (less than 750°C) and/or the initial O_2 concentration was below 5 %. Formation of CH_3Cl as one of the major products increased to a maximum at an 80% CH_2Cl_2 conversion level. This was observed for all reactants ratio sets. The CH_3Cl concentration dropped quickly with increasing temperature and/or increased O_2 . The higher the ratio of O_2 to H_2 , the lower the temperature needed to observe the formation of CO and CO_2 . The major products observed for CH_2Cl_2 conversion levels in excess of 90% are HCl and non-chlorinated hydrocarbons: CH_4 , C_2H_2 , C_2H_4 , CO , and CO_2 . Minor intermediate products whose concentrations were also monitored include: $\text{C}_2\text{H}_3\text{Cl}$, 1,2- $\text{C}_2\text{H}_2\text{Cl}_2$, and 1,1- CH_2CCl_2 .

A detailed kinetic reaction mechanism was developed and used to model

results obtained from the experimental reaction systems. The kinetic reaction mechanism includes 144 elementary reaction steps involving 67 stable compound and free radical species. The addition, beta scission and recombination type reactions were all analyzed by Quantum Rice-Ramsperger-Kassel (QRRK) theory^{2,3}. Species thermodynamic properties were developed with Thera⁴. All rate constants involving chlorocarbon species were evaluated and generated in this laboratory.

Experimental data are compared with model predictions in Figure 1 for reagent decomposition and product distribution between 600°C and 800°C. The calculated mole fractions for CH₂Cl₂ are in very good agreement with those determined experimentally. For CO, CH₄, and CH₃Cl, model predictions also are in reasonable accord with the experimental data. The model predicts the mole fraction levels of CO₂ versus time and temperature reasonably well. It slightly over-predicts CO₂ at higher temperature, and slightly under-predicts chlorinated C₂ products.

Sensitivity analysis under CO burnout conditions indicates that the reaction $\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$ is a major sink for OH. This decrease in OH effectively stops the CO conversion by $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$. The reaction of $\text{CO} + \text{HO}_2 \rightarrow \text{CO}_2 + \text{OH}$ becomes the primary mechanism for CO conversion to CO₂. The OH reaction with HCl will occur in preference to CO conversion because of its higher rate constant, provided chlorocarbons which lead to HCl levels comparable to that of CO are present. The inhibition effect is dominant in the CO burnout regime where significant levels of HCl can dramatically effect conversion.

A synergistic effect now occurs. The reaction of $\text{Cl} + \text{HO}_2$, part of which goes to $\text{HCl} + \text{O}_2$ (termination), now becomes an important part of the inhibition process. Decreased CO burnout results in lower temperature and makes the HO₂ radical more important since its unimolecular decomposition is slowed.

The model tells us one more interesting component relating to the effects of chlorocarbon inhibition. The addition of limited quantities of high temperature H₂O to the oxidation system, where Cl or O atoms are present, shifts the reactions $\text{OH} + \text{HCl} \rightleftharpoons \text{H}_2\text{O} + \text{Cl}$ and $\text{OH} + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{O}$ to left, thereby increasing the OH concentrations and improving CO conversion.

We also observe that chlorocarbons initiate reactions in fuel rich regions of ClC/HC/O₂ mixtures at rates higher than those which occur during normal oxidation of hydrocarbons (HC). This results in pyrolysis or molecular weight growth reactions in the fuel rich zones and increased possibility of soot formation. The reason for the increased HC reactions is again the presence of chlorine. Carbon-chlorine bonds are known to be weaker than carbon-hydrogen, carbon-carbon or carbon-oxygen bonds. The C-Cl bond will break at lower temperatures resulting in chain branching.

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Fig. 1 model prediction

