

COMPUTER MODELING OF CHLORINE-CATALYZED INHIBITION REACTIONS IN C₂H₄/H₂/AIR/Cl₂ OXIDATION

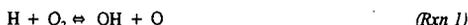
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Keywords: Chlorinated hydrocarbons, oxidation, chlorine inhibition

INTRODUCTION

This paper pertains to research currently underway in the area of chlorinated hydrocarbon combustion. The effects on combustion of chlorinated hydrocarbons or in the presence of chlorine is of practical importance, particularly as related to the incineration of hazardous wastes consisting of organic material containing chlorinated hydrocarbons. Overall, this effort has been undertaken in order to obtain a better understanding at the microscopic level of the oxidation process relating to free radical branching and inhibition of free radical branching. Additionally, this effort may provide insight for a better understanding of the conditions resulting in flame blow-out.

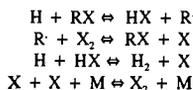
The effects on the concentration of free radicals such as H and OH in the presence of Cl have been previously studied by others. The principal reaction for the production of free radicals is given as



In the presence of chlorine, this reaction is generally considered to become inhibited by a reduced H atom concentration as a result of the formation of molecular hydrogen through the following net reaction,



The actual route through which H₂ is formed will vary depending on the temperature and concentration of species present. A generalized kinetic model for catalyzed recombination of H atoms (Westbrook, 1982) considers a cycle of reactions to result in the above net reaction. This cycle consists of the following reactions,



where X represents the halogen atom and R represents methyl, ethyl, or vinyl radicals.

This cycle of reactions will be of significance in recombining H atoms when the rates on each of the reactions are of the same relative order and particularly when no reaction significantly inhibits the ability of another reaction to proceed. For instance, if the first reaction of the cycle is limiting, the importance of following reactions dependent on the free radical R will be greatly reduced. Thus, the net recombination reaction must be rigorously analyzed by evaluation of each of the individual reactions involved in the cycle. These types of analyses are currently underway and preliminary findings are presented.

Additionally, conditions for blow-out are being assessed in order to establish the mechanism leading to this phenomena. The difficulty in assessing this is due primarily to the interdependency of temperature and the reaction mechanisms contributing to the rate of change of free radicals.

MODELING APPROACH

This study focuses on computer simulation predictions of the effects on ethylene oxidation by the introduction of chlorine in concentrations of less than 0.005 initial mole fraction, and under lean fuel conditions. Ethylene, being a hydrogen lean fuel, will produce a lower concentration of H atoms and changes in the concentration should therefore be more apparent.

The computational analysis was conducted using the Sandia CHEMKIN (Kee et al, 1989) and Perfectly-Stirred Reactor (PSR) (Glarborg et al, 1990) codes running on an IBM RISC 6000 computer. Calculations were performed adiabatically whereby inlet gas temperature and the mixture composition were specified.

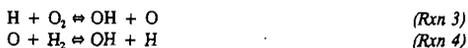
The thermochemical data were acquired primarily from a Sandia National Laboratories report (Kee et al., 1992), although some estimations were conducted based on group additivity theory (Benson, 1976). The detailed chemical kinetic reaction mechanism consisting of 189 reversible and 77 irreversible elementary reactions was used. These elementary reactions were compiled from three different sources and account for the chlorinated hydrocarbon chemistry of trichloroethane (Chang and Senkan, 1986), inclusion of HCl and Cl₂ inhibiting reaction mechanisms (Westbrook et al., 1977), and premixed CH₃Cl/CH₄/air flames employing enhanced third-body effectivities (Lee et al., 1993).

For the adiabatic configuration, the fuel equivalence ratio of ethylene was approximately 0.75. The inlet temperature was set at 1650 K and chlorine was introduced in the form of Cl₂. To minimize the deviations of the inlet mole fractions of fuel and air, an initial mole fraction for H₂ of approximately 0.02 was included, and as the inlet mole fraction of Cl₂ was increased, the H₂ mole fraction was correspondingly decreased. The Cl₂ mole fraction was varied from 0.000 to 0.020; however, the primary region of interest was below 0.005 mole fraction Cl₂. The residence time was varied throughout the region of no conversion of C₂H₄ at the initial time to a time where the conversion was greater than 0.90. The residence time was increased as specified and then reduced to a time less than the time required for blow-out to occur. At the blow-out time, sensitivity analysis were conducted for the purpose of evaluating the dominant reactions at this point.

RESULTS

Results for exit mole fraction versus residence time are plotted in Figures 1 through 4 for varying inlet concentrations of Cl₂. These results agree with general expectations in that as the Cl₂ concentration is increased from 0.0025 to 0.01 mole fraction, the ignition and blow-out residence times increase. Below a value of 0.0025, the results from computer modelling indicate that ignition will not occur. This prediction also agrees with expectations since the more reactive Cl₂ possesses a greater tendency than H₂ to interact with other species in the reactor, particularly at lower temperatures.

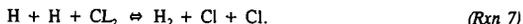
At the point just prior to blow-out, sensitivity analyses were conducted. Species evaluated included H, OH, O and H₂. The most significant reactions were the free radical chain branching reactions



Since the concentrations of the free radicals decreased as the Cl₂ concentration increased, this result is evidence that Cl₂ plays a role in the removal of OH and H radicals. In conjunction with Westbrook's findings, one mode of chlorine-catalyzed recombination consistent with the results obtained in this analysis would include the following reactions,



where the net reaction would yield,



Reactions 5 and 6 were among the more significant reactions as indicated from the sensitivity analysis. Preliminary assessment of the possibility of this pathway has included the evaluation of the forward and reverse rate constants and rates. Continued investigations will include in-depth analysis kinetics of this particular pathway as well as investigation into other possible pathways. Other such pathways under investigation include the set of reactions



and



where the net reaction results in H atom recombination. The rates for these sets of reactions are being evaluated at various temperatures and species concentrations to determine their relative order and role in H atom recombination.

ACKNOWLEDGEMENT

This work is supported by the National Science Foundation National Young Investigation Program (Grant Number CTS-9258149)

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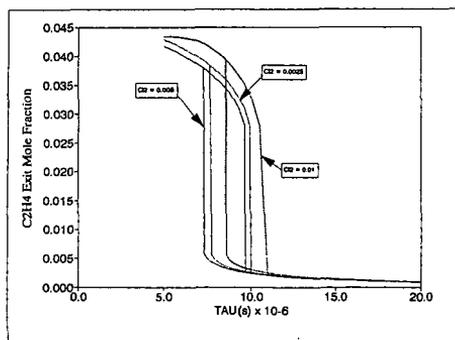


Figure 1. Ethylene Oxidation: Exit mole fraction of ethylene in a perfectly-stirred reactor for initial Cl_2 inlet mole fractions of 0.0025, 0.005, and 0.01.

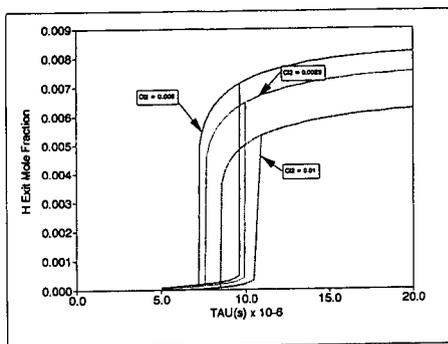


Figure 2. Ethylene Oxidation: Exit mole fraction of H in a perfectly-stirred reactor for initial Cl_2 inlet mole fractions of 0.0025, 0.005, and 0.01.

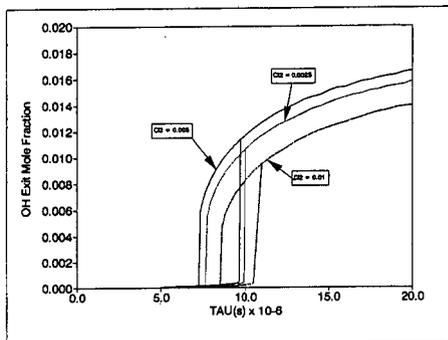


Figure 3. Ethylene Oxidation: Exit mole fraction of OH in a perfectly-stirred reactor for initial Cl_2 inlet mole fractions of 0.0025, 0.005, and 0.01.

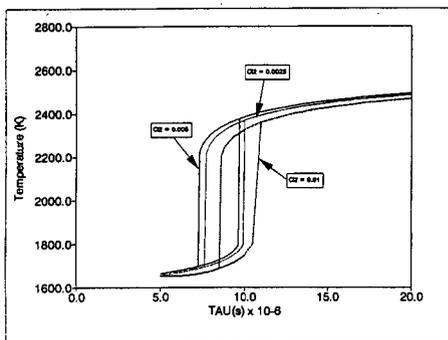


Figure 4. Ethylene Oxidation: Temperature profile in a perfectly-stirred reactor for initial Cl_2 inlet mole fractions of 0.0025, 0.005, and 0.01.