

REACTIONS OF $^1\text{CX}_2$ DURING CHLOROFLUOROCARBON PYROLYSIS

John J. DiFelice and Edward R. Ritter
Department of Chemical Engineering
Villanova University
Villanova, PA 19085

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INTRODUCTION

Singlet carbenes are reactive intermediates which behave in a fashion quite different from radicals. In hydrocarbon and hydrochlorocarbon systems, radicals and radical chemistry typically dominate. However, in chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) systems, formation of perhalogenated singlet carbenes ($^1\text{CX}_2$) has been observed (DiFelice and Ritter, 1993; Westmoreland, 1993). While radicals undergo abstraction reactions and addition to double bonds, singlet carbenes can insert into single bonds. Singlet carbenes are species which have two paired nonbonded electrons; since paired electrons have opposite spin, singlet carbenes can insert into single bonds (March, 1992). Triplet carbenes, in contrast, contain unpaired electrons and behave essentially like radicals. Formation of perhalogenated triplet carbenes ($^3\text{CX}_2$) is less favorable in CFC and HCFC systems since the $^1\text{CX}_2$ singlet state is as much as 56 kcal/mol lower in energy than the triplet state (Melius, 1993).

The insertion of $^1\text{CX}_2$ into single bonds makes CFC and HCFC pyrolytic chemistry unique and interesting. However, there have been few studies on the combustion and pyrolysis chemistry of these compounds. Most experimental studies of CFCs and HCFCs are at conditions relevant to stratospheric ozone depletion (NIST, 1991a). These conditions are typically at much lower pressure and temperature than those encountered during incineration or pyrolysis. Recent combustion studies by Naegli, et al. (1991) and Tokuhashi, et al. (1990) demonstrate the need for further research on the incinerability and pyrolysis chemistry of these species. These studies focused on CF_2Cl_2 (Freon-12) and CHF_2Cl (Freon-22). They demonstrated that these species can be broken down in an incineration environment, and that significant quantities of by-products (PICs) are formed. These by-products have been neither completely classified, nor quantified.

Previous work (Ritter, 1993 and DiFelice and Ritter, 1993) has focused on the thermal reactions of $\text{CF}_2\text{Cl-CFCl}_2$ (Freon-113) and CHF_2Cl under pyrolytic conditions in helium and helium/hydrogen mixtures. These studies have characterized the pyrolysis under inert and reducing conditions. Studies have shown that formation and reaction of perhalogenated singlet carbenes ($^1\text{CX}_2$) are important during CHF_2Cl pyrolysis, while they are of questionable importance during $\text{CF}_2\text{Cl-CFCl}_2$ pyrolysis. The significance of various carbene insertion reactions are important for the mechanistic modeling of CHF_2Cl pyrolysis. Determination of their significance would also give insight into the $\text{CF}_2\text{Cl-CFCl}_2$ pyrolytic system. The carbene insertion reactions investigated include insertion into carbon-hydrogen (C-H) bonds and carbon-halogen (C-X) bonds. Other CFCs studied during the investigation include CF_2Cl_2 (Freon-12), CF_3Cl (Freon-13), and $\text{C}_2\text{HF}_4\text{Cl}$ (Freon-124).

EXPERIMENTAL

The experimental flow tube reactor consists of a quartz or alumina flow tube which passes through a 6 zone electrically heated tube furnace (see Figure 1). Typical reaction times range from 0.05 to 2 seconds with temperatures from 773 - 1098 K. In atmospheric pressure flow tube reactors, there is always the concern for significant wall reactions. Ritter et al. (1990) observed significant differences between experimentally determined rate constants for chlorobenzene decomposition when carried out in 0.4 and 1.0 cm id reactor tubes. However, they observed little difference between decomposition rates in 1.0 and 1.6 cm id reactors. In these studies 1.6 and 2 cm i.d. reactors are used to reduce the importance of possible surface reactions. Quartz flow tubes can be used for lower temperatures (less than 775°C), however, alumina is required at higher temperatures due to the rapid degradation of quartz by fluorides. The reactor operates isobarically near 1 atm total pressure. Liquid reagents such as $\text{CF}_2\text{Cl-CFCl}_2$ or CHCl_3 (chloroform) are admitted to the reactor by sparging helium gas through the liquid held at 0°C in an ice point impinger. Gaseous CFCs enter directly through calibrated rotameters. Calibration of the reactor temperature is performed using a 1/8" diameter Type-K thermocouple probe. This probe is moved axially to obtain the temperature of the reactor.

Helium is allowed to flow through the reactor to minimize radiation error from the furnace wall by cooling the bare-bead junction to the temperature of the gas.

Samples are drawn through a cold surface water cooled sampling probe by use of a vacuum pump. Gas leaving the probe passes through a heated line to a six port gas sampling valve equipped with a 1 mL sample volume for on-line analysis using GC/FID. Reactant and stable products are quantified using a GOW MAC model 750 P GC with dual flame ionization detectors. Gas chromatographic separations are carried out using a packed column Graphpac 60/80 mesh with 5% Flurocol (Supelco) or Carbopac with 5% Krytox (Alltech) which give excellent separation for complex mixtures of hydrocarbons, fluorocarbons, and CFCs. Accurate calibration of FID responses for parent CFCs are obtained by using a reactor bypass. GC/MS analyses are performed off-line for product identification. After initial identification, product responses are calibrated using standards prepared from the pure materials which are obtained from PCR Chemicals Inc, Gainesville, Fl. Standards are prepared to determine GC response factors.

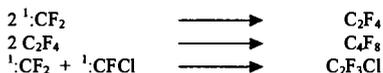
HCl and HF produced are quantified by diverting the total reactor effluent through a 2 stage impinger containing standardized NaOH solution and an appropriate indicator dye. Cl⁻ and F⁻ concentrations are measured directly using ion selective electrodes (Fisher Scientific). The electrodes are calibrated using standardized Cl⁻ and F⁻ solutions prepared at pH similar to the samples. All standards and samples contain the total ionic strength adjuster appropriate to the halide which is being measured. These measurements give total F⁻ and Cl⁻ only and do not speciate between halogen and hydrogen halide gases. They are used to check material balance on halogens.

RESULTS AND DISCUSSION

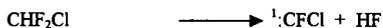
Results from CHF₂Cl pyrolysis in helium at 2 seconds reaction time suggest that CHF₂Cl conversion primarily follows first order kinetics at low temperatures (773 - 898K) via unimolecular HCl elimination:



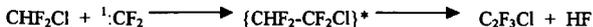
The major products of the pyrolysis in helium include perfluoroethylene (C₂F₄, the most abundant product), perfluoropropene (C₃F₆), octafluorocyclobutane (C₄F₈), and chlorotrifluoroethylene (C₂F₃Cl). Perfluoroethylene is formed by ¹CF₂ combination, C₄F₈ by dimerization of C₂F₄, and C₂F₃Cl by recombination of ¹CF₂ and ¹CFCl.



The product C₂F₃Cl is observed at temperatures only above 898K, suggesting either some degree of HF elimination from CHF₂Cl occurs at higher temperatures



or that ¹CF₂ inserts into CHF₂Cl followed by α, β HF elimination from the adduct:



Perfluoropropene (C₃F₆) most likely results from reaction of ¹CF₂ and C₂F₄. Although carbenes are believed to add to double bonds to form cyclopropanes (March, 1992), perfluorocyclopropane (cyC₃F₆) is not observed. This suggests that rapid isomerization to the perfluoropropene occurs, or some other mechanism is responsible for the production of this species.

The elimination of HCl from CHF₂Cl represents the lowest dissociation channel. However, at higher temperatures (above 898K) it becomes apparent that conversion of CHF₂Cl moves away from first order kinetics. When a first order assumption is applied over the entire temperature range (773 - 1023K), an Arrhenius plot yields an activation energy of 43 kcal/mol. This energy barrier, however, is lower than the Δ H of the reaction based upon the H_r of ¹CF₂ used by Paulino and Squire (1991). This suggests that there is a shift in reaction mechanism at higher temperatures.

923K. Results obtained at 973K, however, show a noticeable increase in CF_2Cl_2 conversion. This result suggests that $^1\text{CF}_2$ plays a role in CF_2Cl_2 conversion, under these conditions. This system is currently being investigated in more detail.

CONCLUSION

Insertion of $^1\text{CF}_2$ into C-H bonds appears to be important during the pyrolysis of CHF_2Cl and mixtures of CHF_2Cl and $\text{C}_2\text{HF}_4\text{Cl}$ at temperatures greater than 898K. Addition of H_2 to the CHF_2Cl pyrolytic system inhibits conversion by scavenging $^1\text{CF}_2$ by reaction with H_2 . Dichlorocarbene insertion into C-X appears to be an unfavorable reaction based upon experiments involving CHCl_3 and CF_3Cl . Similar reactions involving CF_2Cl_2 are currently being.

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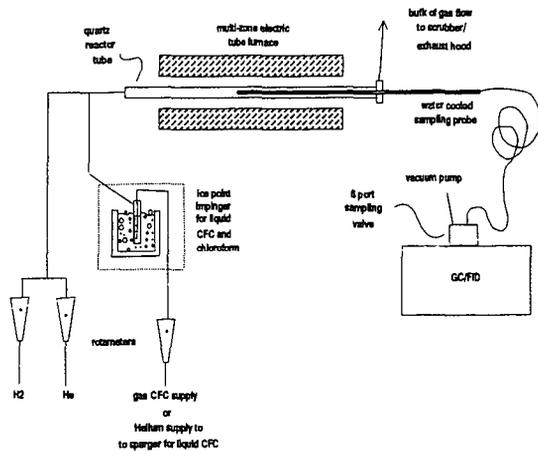


Figure 1. EXPERIMENTAL APPARATUS

C/Co vs. T(K); t=2 sec

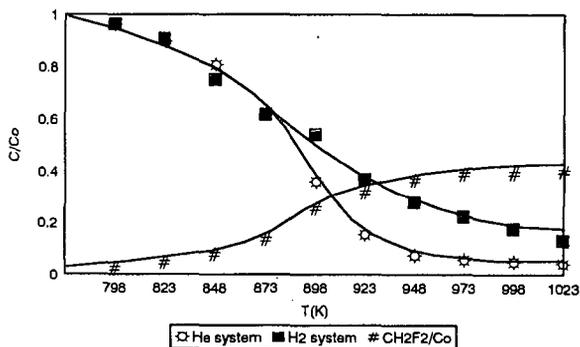


Figure 2. CHF₂Cl PYROLYSIS IN HE AND H₂

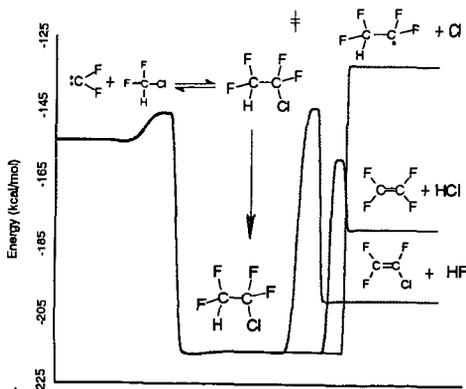


Figure 3. ¹³C:CF₂ INSERTION INTO CHF₂Cl