

Aromatics Formation in the Oxidations of Trichloroethylene with Methane

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Experiments on oxidation of multi-chlorinated hydrocarbons, C_2HCl_3 , with hydrocarbon fuels, CH_4 , were performed in a laboratory scale flow reactor under fuel-rich and fuel-lean conditions. The major reaction products, C_2Cl_2 , C_2H_4 , CO, CO_2 and HCl, can be found in a lower temperature region under a higher oxygen containing environment. The aromatic compounds, including C_6H_6 , $C_6H_5CH_3$, C_6H_5Cl , $CH_3C_6H_4Cl$ and $C_6H_5Cl_2$ were detected. Trace intermediates including C_2H_2 , C_3H_6 , C_3H_4 , C_4H_8 , C_4H_6 , C_4H_4 , CH_3Cl , C_2H_3Cl , C_2HCl , trans- $CHClCHCl$, cis- $CHClCHCl$, $COCl_2$, C_2Cl_4 , and C_2Cl_6 were also found. The formation pathways for the detected aromatic species are discussed.

Keywords : trichloroethylene, aromatics formation, methane, combustion.

1. Introduction

Chlorocarbons are thought to be associated with the formation of aromatics, such as di-benzo-dioxins and di-benzo-furans in incinerators, and some are toxic and in some cases carcinogenic. Long-term exposure to even low levels of these compounds is not suggested because of health related effects (Junk and Ford, 1980; Oberg *et al.*, 1985; Qun and Senkan, 1994). Different technologies have been developed for the safe destruction of chlorocarbons. Thermal destruction of organic pollutants in an oxygen-rich atmosphere is the one most often used in the chemical waste disposal industry. It is reported that combustion of chlorinated hydrocarbons under severe conditions converts all carbon to CO_2 (Booty *et al.*, 1995).

Theoretically, incineration could result in the total conversion of hazardous organic compounds

to innocuous thermodynamic end-products, such as CO_2 and H_2O , and other simple compounds such as HCl, which could be quantitatively neutralized and collected with existing pollution control equipment. In practice, a total conversion to innocuous materials cannot be achieved without considerable cost, and for an incinerator of less than optimum design or operating conditions, most of the thermally stable components in the waste feed may not be totally decomposed (Ho *et al.*, 1995).

Commercialized incineration at high temperatures with an excess of oxygen has become the chosen method, and is available. For chlorinated hydrocarbons, this technique may destroy all the initial parent species, but reaction products are not all converted to CO_2 , as these combustion facilities are run in an oxygen-rich environment where there is no stable and desirable end adduct for chlorine. Chlorine oxide and Cl_2 are neither acceptable end products for discharge to the atmosphere, nor are they formed in a selective or quantitative manner for complete collection or neutralization. If an incinerator with an excess of oxygen operates under less than optimum

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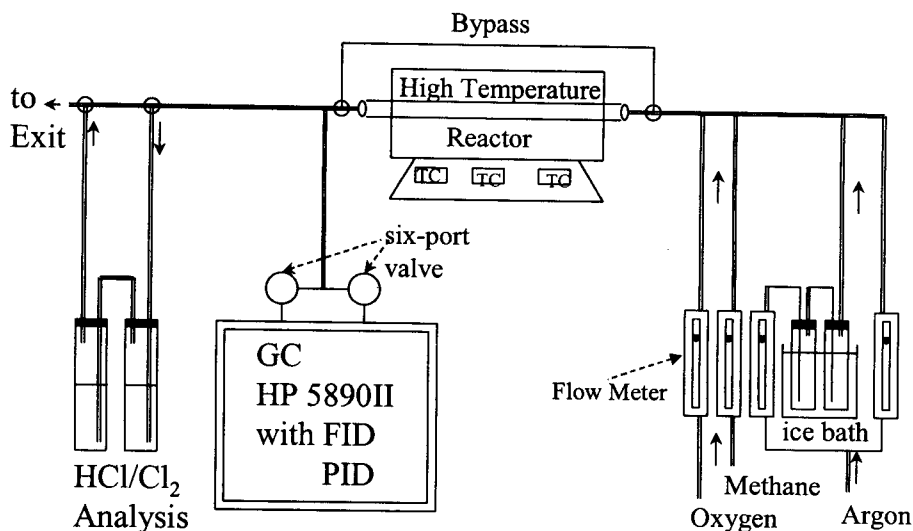


Figure 1. Schematic diagram of the experimental system for $C_2HCl_3/CH_4/O_2/Ar$. TC denotes a thermocouple and proportional controller pair providing temperature control for the high temperature reactor.

conditions, some chlorine-containing carbon products can usually be found as effluent, including partially decomposed and oxidized fragments of the initial chlorocarbons. These incomplete combustion products can and often do cause the formation of polyaromatic hydrocarbons (PAHs) and soot (Huang et al., 1997; Yildirim and Senkan, 1995).

This study was performed in a tubular flow reactor of 10 mm inside diameter to examine the high temperature oxidation of C_2HCl_3 with a methane argon bath. We characterize the reactant loss, intermediate and product formation as functions of time, temperature, and oxygen concentrations to describe the reaction process.

Experimental Method

A schematic diagram of the reactor system is shown in Figure 1. The high temperature tubular flow reactor was operated isothermally and isobarically in the range of 575 – 850 °C and at 1 atm total pressure, with average gas residence times in the range from 0.3 to 1.5 s.

Our experimental data was collected by maintaining a constant temperature and changing the flow rates of carrier and reactants (to maintain the constant reactant ratio), while varying the reaction time. A small computer code was used to calculate the needed flows for a selected reaction time and concentration ratio.

Argon was used as both a carrier and dilution gas. One part of the argon flow was passed through a two-stage saturation bubbler to pick up C_2HCl_3 (99.7%, Riedel-de Haen), which was held at 0°C using an ice bath. The other part of the argon flow was used to achieve the desired molar ratio between argon, methane, oxygen, and C_2HCl_3 . Cylinder methane (91.3% CH_4 , 8.3% C_2H_6 and 0.4% C_3H_8) and oxygen were added into the flow before it entered the reactor, and the flow was preheated to 180 °C at the reactor entrance. The quartz reactor tube, with 10 mm ID, was housed in a three-zone Carbolite TZF 12/65/550 electric tube furnace 40 cm in length. The actual temperature profile of gas in the radial direction of the tubular reactor was obtained using the type K thermocouple, which could be moved coaxially within the reactor.

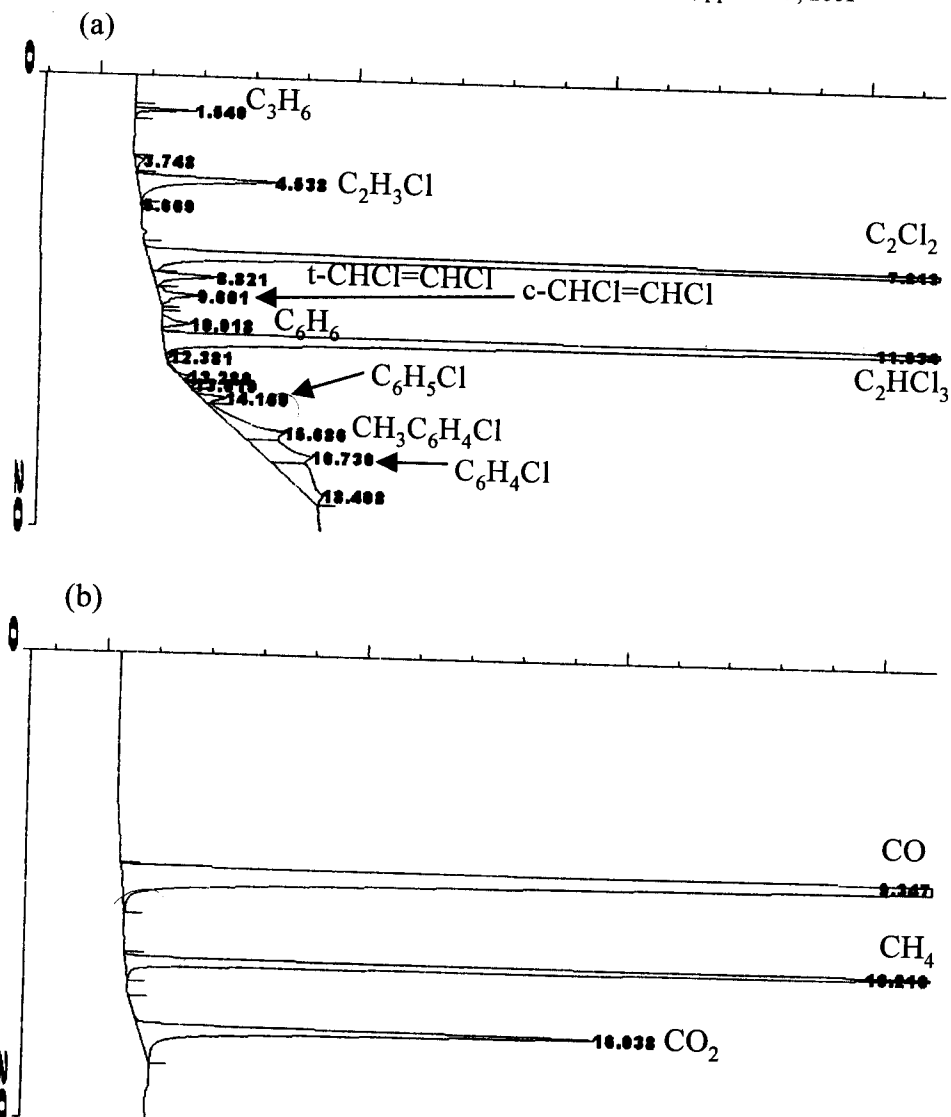


Figure 2. Sample chromatograms. Temperature program: 40°C (3 min), 15°C/min to 220°C (final, 5 min). Carrier Gas: Helium. (a) Detector (PID): 220°C. Column: 3.175 mm × 3 m length stainless steel, with 25% SE30 on Chromosorb PAW 80/100. Reaction condition: C_2HCl_3 : CH_4 : O_2 =1:3:10 (fuel-lean), 0.7 s under 750°C. (b) Detector (FID): 200°C. Column: 3.175 mm × 4.6 m length Carboxen 1000 connected to a CO/ CO_2 converter (300°C). Reaction condition: C_2HCl_3 : CH_4 : O_2 =1:3:5 (fuel-rich), 0.7 s under 775°C.

The temperature measurements were performed with a steady flow of argon gas through the reactor. The reactor effluent was monitored using an on line gas chromatograph (HP 5890 GC, Hewlett-Packard 5890 series II) with a flame ionization detector (FID) and a photoionization detector (PID). The outlet lines between the reactor and GC analysis were heated to 110°C to limit condensation. Two six-port gas-sampling valves (Valco Co.), each with a 1.0 ml volume loop, were used to inject the sample and both

were maintained at 170°C. A 3.175 mm × 3 m length stainless steel packed column packed with 25% SE30 on Chromosorb PAW 80/100 mesh (Hewlett-Packard) was connected to the PID. A 3.175 mm × 4.6 m length Carboxen 1000 stainless steel packed column (SUPELCO) was connected to a CO/ CO_2 converter and then to the FID. The CO/ CO_2 converter is a catalyzed column packed with 5% Ruthenium Alumina (Aldrich) which operated at 300 °C to convert CO and CO_2 to CH_4 by using H_2 as a reductant.

Representative chromatographs are shown in Figure 2 with compounds of interest labeled.

Positive identification of all reactor effluent species except CO and CO₂ was made by GC/MS applied to batch samples drawn from the reactor exit into previously evacuated 25ml Pyrex glass sample cylinders. A Finnigan TSQ 700 GC/MS, with a 1.0 μm, 0.32 mm × 50 m DB-1 column (J & W Scientific) was used.

The reactor outlet gases were passed through heated transfer lines, with a loosely packed plug of glass wool to trap any solid such as carbon soot, then to the GC samplers and the exhaust. The bulk of the outlet gases, however, was passed through a sodium-bicarbonate flask to neutralize the HCl, and then released to the atmosphere via a fume hood.

Quantitative analysis of HCl and Cl₂ were performed for each run. The sample for HCl/Cl₂ analyses was independently collected from the GC sampling as illustrated in Figure 1. In the HCl analysis, the effluent from the reactor was diverted through a two-stage bubbler containing 0.01M aqueous NaOH before being exhausted to a fume hood. The concentration of HCl in the effluent was then calculated after titrating a solution with 0.01M HCl to its phenolphthalein end point. For the Cl₂ analysis, the effluent was passed through the two-stage bubbler containing the solution of 3,3-dimethylbenzidine to absorb the Cl₂ produced by the reaction. The concentration of Cl₂ was then determined by the spectrophotometric measurement of the absorbance of the resulting solution at 435 nm wavelength.

Results and Discussion

Ten temperatures ranging from 575 to 800 °C were studied in the tubular flow reactor, and for each temperature it had a minimum of 4 gas-phase residence time points from 0.3 to 1.5 s

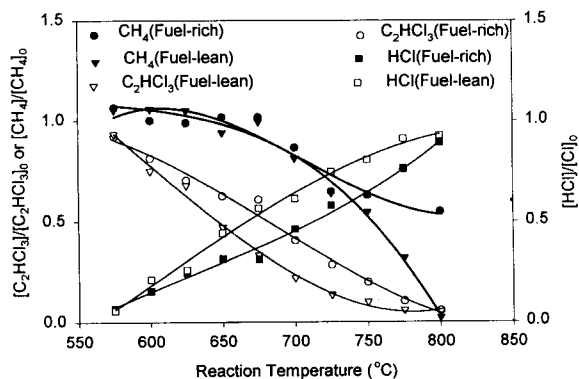
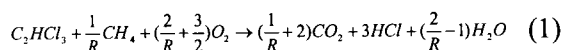


Figure 3. Normalized concentration (C/C_0) profiles of C_2HCl_3 and CH_4 as a function of temperature under fuel-rich ($\phi=1.25$) and fuel-lean ($\phi=0.75$) conditions.

(evaluated at studied temperature and approximately 1 bar). The molar ratios for reactants are listed in Table 1. For a premixed C_2HCl_3 , CH_4 , O_2 and Ar mixture, the overall stoichiometry can be expressed as



where R is the molar ratio of C_2HCl_3 to CH_4 in the mixture. The equivalence ratio, ϕ , is given by

$$\phi = \frac{\left(\frac{2}{R} + \frac{3}{2}\right)}{\text{actual } O_2 \text{ in mixture}} \quad (2)$$

In this study, we have considered C_2HCl_3 and CH_4 together as fuel. Constant concentrations of 1% and 3% for C_2HCl_3 and CH_4 , respectively, were maintained throughout the experiments. Thus, the molar ratio (R) of C_2HCl_3 to CH_4 was 1/3 and the Cl/H was 0.231. O_2 of 5% and 10% in the influent gases were specified as fuel-rich ($\phi=1.25$) and fuel-lean ($\phi=0.75$), respectively.

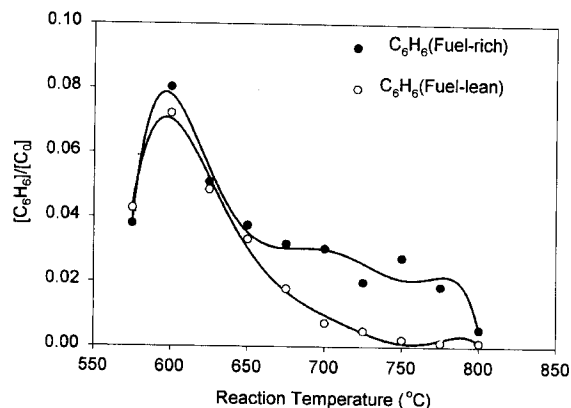
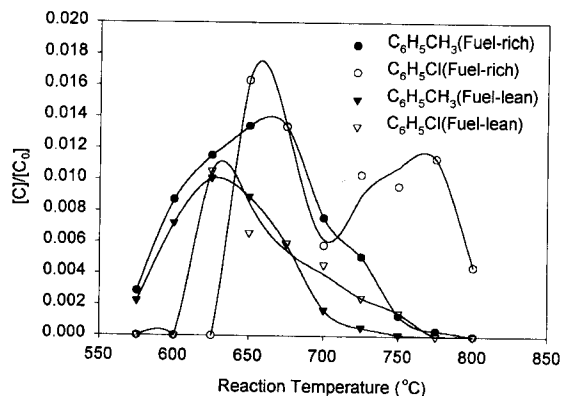
Experimental results for the decomposition of C_2HCl_3 and CH_4 are shown in Figure 3, which shows normalized concentration (C/C_0) as a function of temperature at an average residence time of 0.7 s. Since the residence times for reaction temperature above 700°C were from 0.3

Table 1. Reactant features.

	Mole percent				Equiv.	
	C ₂ HCl ₃	CH ₄	O ₂	Ar	Ratio, ϕ	Cl/H Ratio
Fuel-rich	1.0	3.0	5.0	91.0	1.25	0.231
Fuel-lean	1.0	3.0	10.0	86.0	0.75	0.231

to 1.0 s, 0.7 s was chosen for comparison in this study. C₂HCl₃ concentration consistently decreased with increasing temperature in both reaction environments. CH₄ concentration stayed in peak levels for the low-medium temperature range for both reaction systems, and then decreased with increasing temperature as those in fuel-lean system gave faster decay as expected. Major products for both reaction systems included C₂Cl₂, C₂H₄, CO, CO₂ and HCl. Figure 3 also presents the formation profiles of HCl for the fuel-rich and fuel-lean systems. Cl₀ denotes the total molar concentration of Cl from the inlet. HCl concentrations increased for both systems since the chlorinated reactant-- C₂HCl₃-- decomposed with increasing temperature and showed slower formation in fuel-rich cases since C₂HCl₃ had a slower decay. Aromatic compounds, including benzene (C₆H₆), toluene (C₆H₅CH₃), chlorobenzene (C₆H₅Cl), chlorotoluene (CH₃C₆H₄Cl, isomers included) and dichlorobenzene (C₆H₅Cl₂, isomers included) were detected. In addition to the aromatic products, trace intermediates including C₂H₂, C₃H₆, C₃H₄, C₄H₈, C₄H₆, C₄H₄, CH₃Cl, C₂H₃Cl, C₂HCl, trans-CHCl=CHCl, cis-CHCl=CHCl, COCl₂, C₂Cl₄, and C₂Cl₆ were also found in this study.

Figure 4 presents the formation profiles of C₆H₆ for the fuel-rich and fuel-lean systems as a function of temperature. The C₀ in this figure, so as in the following figures, denotes the total molar concentration of input carbons (C₂HCl₃ +

**Figure 4.** Normalized concentration (C/C_0) profiles of C₆H₆ as a function of temperature under fuel-rich ($\phi=1.25$) and fuel-lean ($\phi=0.75$) conditions.**Figure 5.** Normalized concentration (C/C_0) profiles of C₆H₅CH₃ and C₆H₅Cl as a function of temperature under fuel-rich ($\phi=1.25$) and fuel-lean ($\phi=0.75$) conditions.

CH₄). As shown in this figure, both systems formed C₆H₆ within the lower temperature range, but it decomposed faster for the fuel-lean case at temperatures higher than 650°C. These results are expected since the rate of decomposition of C₆H₆ increased with higher oxygen at higher temperatures.

Figure 5 shows distributions of C₆H₅CH₃ for both systems as a function of temperature. The profiles from both systems gave similar trends for C₆H₅CH₃ distributions. For the fuel-lean system, C₆H₅CH₃ had a lower formation tendency and decomposed faster as the temperature increased. Figure 5 also demonstrates the concentration profiles of C₆H₅Cl for the fuel-rich and fuel-lean cases as a

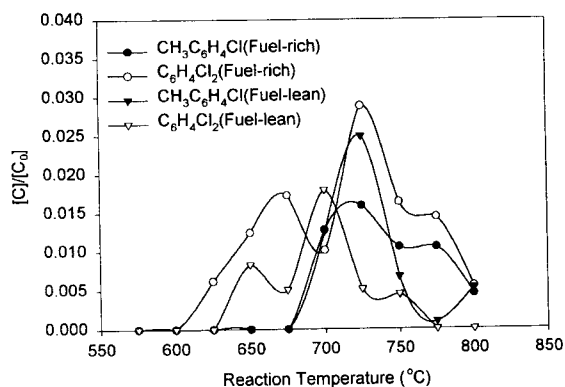


Figure 6. Normalized concentration (C/C_0) profiles of $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$ and $\text{C}_6\text{H}_4\text{Cl}_2$ as a function of temperature under fuel-rich ($\phi=1.25$) and fuel-lean ($\phi=0.75$) conditions.

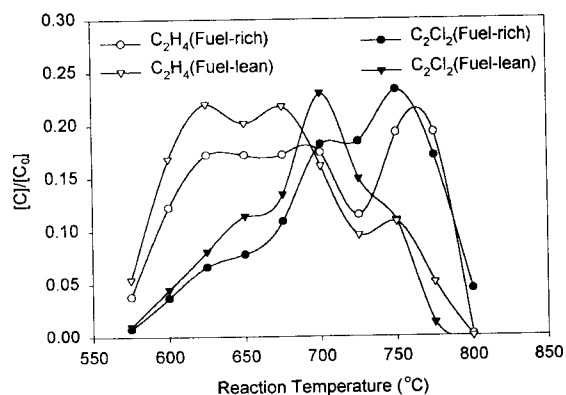


Figure 7 Normalized concentration (C/C_0) profiles of C_2H_4 and C_2Cl_2 as a function of temperature under fuel-rich ($\phi=1.25$) and fuel-lean ($\phi=0.75$) conditions.

function of temperature. There was about 25°C difference for peak formation of $\text{C}_6\text{H}_5\text{Cl}$ between the fuel-lean and fuel-rich reaction systems. It can be expected that the fuel-lean case gave faster decomposition of C_6H_6 and $\text{C}_6\text{H}_5\text{CH}_3$ as shown earlier. Both species in Figure 5 show that there were higher Cl or CH_3 radicals in fuel-rich system to attack the C_6H_6 formed.

Figure 6 shows the formations of $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$ for the fuel-rich and fuel-lean cases as a function of temperature. The profiles show similar trends for both cases, but it shows a higher formation of $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$ for the fuel-lean system. It was caused by, with reference to Figure 5, the decomposition of $\text{C}_6\text{H}_5\text{Cl}$ (which may be attacked by CH_3 radicals to form $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$) or the decomposition of $\text{C}_6\text{H}_5\text{CH}_3$ (which may be

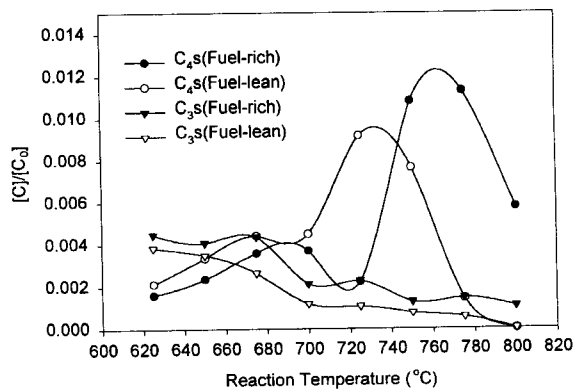
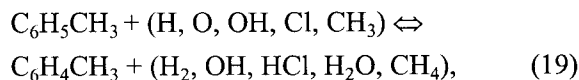
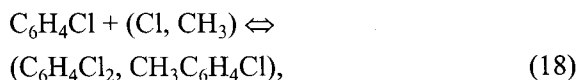
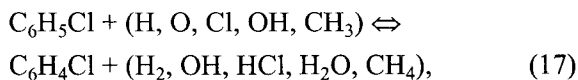


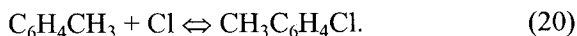
Figure 8 Normalized concentration (C/C_0) profiles of C_3s (C_3H_6 and C_3H_4) and C_4s (C_4H_8 , C_4H_6 and C_4H_4) as a function of temperature under fuel-rich ($\phi=1.25$) and fuel-lean ($\phi=0.75$) conditions.

attacked by Cl radicals to form $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$, which were faster in the fuel-lean system. Figure 6 also compares the formation of $\text{C}_6\text{H}_4\text{Cl}_2$ for both reaction systems. Both systems gave similar trends for $\text{C}_6\text{H}_4\text{Cl}_2$, but the fuel-lean system shows a lower formation and requires lower temperatures for its decomposition. This result shows it has a lower chance for highly chlorinated aromatics formation.

It should be helpful to present the profiles for other products, C_2H_4 , C_2Cl_2 , C_3H_6 and C_4 compounds, in order to analyze the formation pathways of aromatic compounds. Figure 7 presents the formation profiles of C_2H_4 and C_2Cl_2 for both the fuel-rich and fuel-lean systems in the studied temperature range. For the fuel-lean system, as expected, C_2H_4 had a higher formation tendency and gave a faster decay. Figure 7 also shows a C_2H_4 formation-decomposition tug for both reaction systems since temperature was higher than 675°C . The concentration of C_2H_4 for both systems first decreased as the temperature got higher than 675°C , then increased as the temperature reached 725°C , and then decreased again as the temperature increased. This was due to the decomposition of the aromatic compounds at temperatures higher than 650°C , as discussed earlier, and to the



and



There are other possible pathways for the formation of these aromatics from some other cyclic species (Mitchell *et al.*, 1995; Xieqi *et al.*, 1993). However, these pathways were not present in this study since these species were not observed in our experiment.

Conclusions

The oxidation of C_2HCl_3 with CH_4 in an Ar bath gas was carried out at 1 atmosphere total pressure in a 10 mm ID tubular flow reactor under fuel-rich ($\phi=1.25$) and fuel-lean ($\phi=0.75$) conditions. The high temperature tubular flow reactor was operated isothermally and isobarically in the range 575 – 850 °C, with the average gas residence times in the range of 0.3 to 1.5 seconds.

The major products for both reaction systems include C_2Cl_2 , C_2H_4 , CO, CO_2 and HCl. Aromatic compounds, including C_6H_6 , $C_6H_5CH_3$, C_6H_5Cl , $CH_3C_6H_4Cl$ and $C_6H_5Cl_2$ were detected. Experimental data also show that in the higher oxygen environment, major products, such as C_2Cl_2 , CO, CO_2 and HCl, were detected in the lower reaction temperatures. Final products

such as CO_2 and HCl were found for reactions at temperatures greater than 750°C.

The formation pathway for aromatic species were believed to be due to the subsequent additions of C_2 to C_4 species, followed by the cyclization and dehydrogenation of the adducts. The chemically activated adducts involving C_3 species have also been considered.

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