

## 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

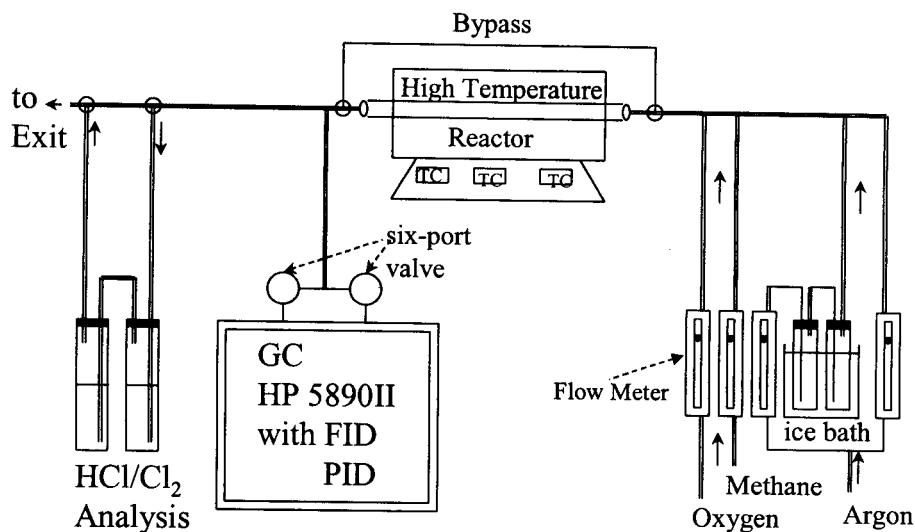
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**Figure 1.** Schematic diagram of the experimental system for  $C_2HCl_3/CH_4/O_2/Ar$ . TC denotes a thermocouple and proportional controller pair providing temperature control for the high temperature reactor.

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).

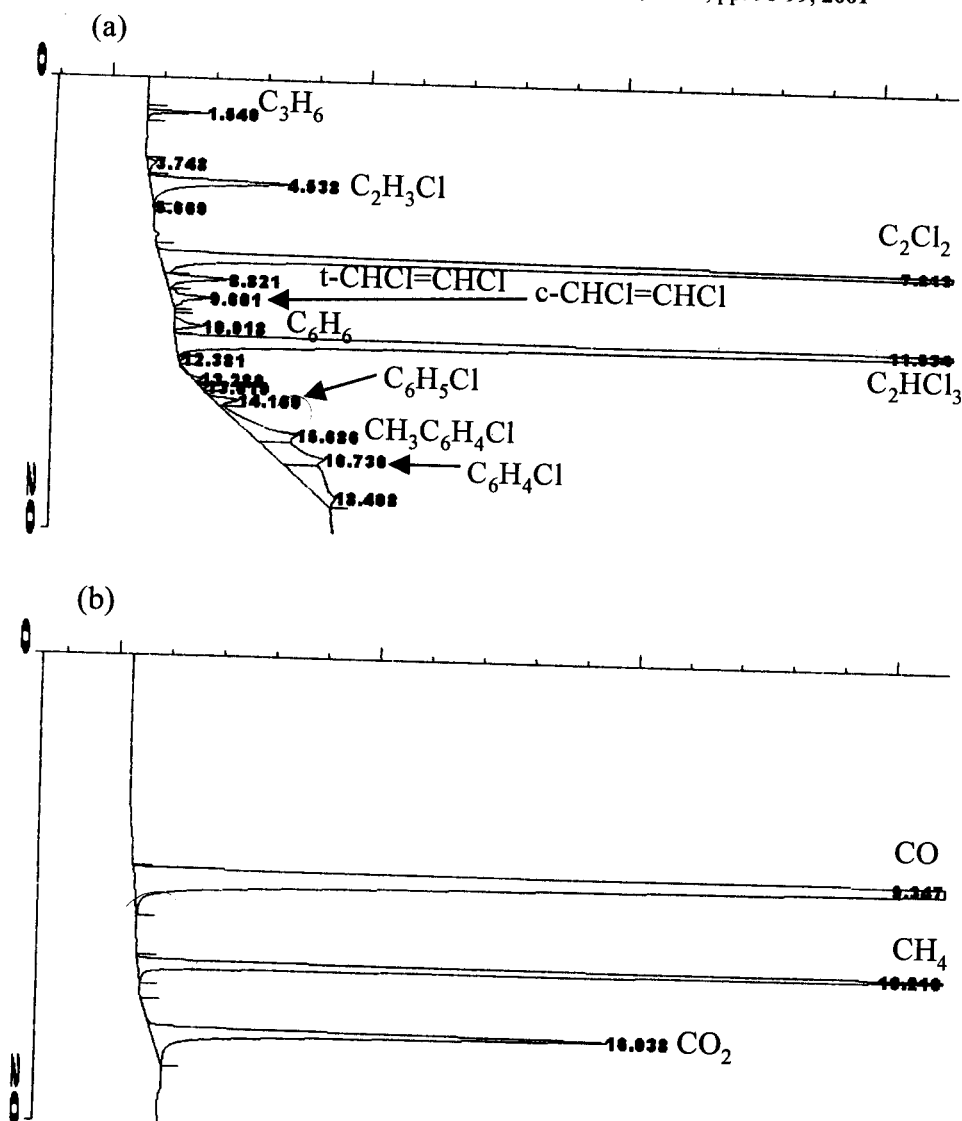
This study was performed in a tubular flow reactor of 10 mm inside diameter to examine the high temperature oxidation of  $C_2HCl_3$  with a methane argon bath. We characterize the reactant loss, intermediate and product formation as functions of time, temperature, and oxygen concentrations to describe 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<sub>2</sub>HCl<sub>3</sub>: CH<sub>4</sub>: O<sub>2</sub>=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<sub>2</sub> converter (300°C). Reaction condition: C<sub>2</sub>HCl<sub>3</sub>: CH<sub>4</sub>: O<sub>2</sub>=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<sub>2</sub> converter and then to the FID. The CO/CO<sub>2</sub> converter is a catalyzed column packed with 5% Ruthenium Alumina (Aldrich) which operated at 300 °C to convert CO and CO<sub>2</sub> to CH<sub>4</sub> by using H<sub>2</sub> as a reductant.

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

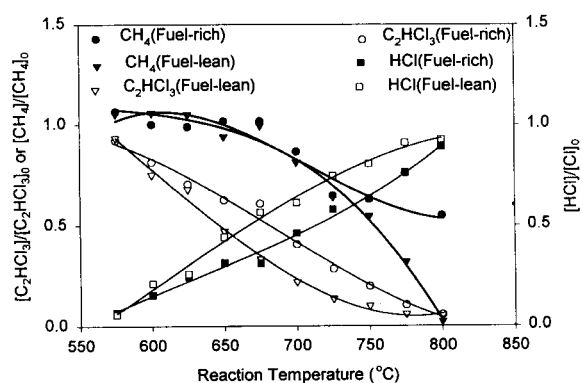
Positive identification of all reactor effluent species except CO and CO<sub>2</sub> was made by GC/MS applied to batch samples drawn from the reactor exit into previously evacuated 25ml Pyrex glass sample cylinders. A Finnigan TSQ 700 GC/MS, with a 1.0 μm, 0.32 mm × 50 m DB-1 column (J & W Scientific) 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 Cl<sub>2</sub> were performed for each run. The sample for HCl/Cl<sub>2</sub> 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 Cl<sub>2</sub> analysis, the effluent was passed through the two-stage bubbler containing the solution of 3,3-dimethylbenzidine to absorb the Cl<sub>2</sub> produced by the reaction. The concentration of Cl<sub>2</sub> was then determined by the spectrophotometric measurement of the absorbance of the resulting solution at 435 nm wavelength.

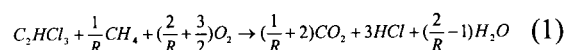
## Results and Discussion

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<sub>2</sub>HCl<sub>3</sub> and CH<sub>4</sub> 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<sub>2</sub>HCl<sub>3</sub>, CH<sub>4</sub>, O<sub>2</sub> and Ar mixture, the overall stoichiometry can be expressed as



where R is the molar ratio of C<sub>2</sub>HCl<sub>3</sub> to CH<sub>4</sub> in the mixture. The equivalence ratio,  $\phi$ , 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<sub>2</sub>HCl<sub>3</sub> and CH<sub>4</sub> together as fuel. Constant concentrations of 1% and 3% for C<sub>2</sub>HCl<sub>3</sub> and CH<sub>4</sub>, respectively, were maintained throughout the experiments. Thus, the molar ratio (R) of C<sub>2</sub>HCl<sub>3</sub> to CH<sub>4</sub> was 1/3 and the Cl/H was 0.231. O<sub>2</sub> of 5% and 10% in the influent gases were specified as fuel-rich ( $\phi=1.25$ ) and fuel-lean ( $\phi=0.75$ ), respectively.

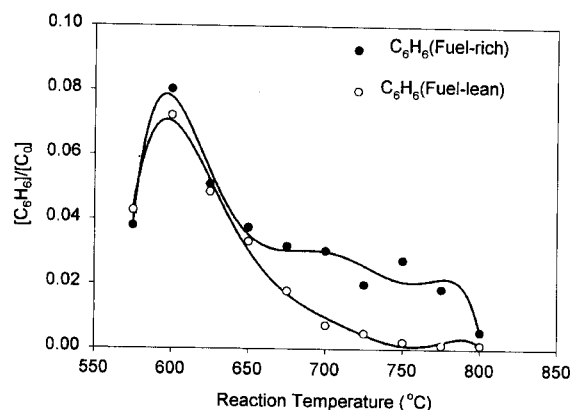
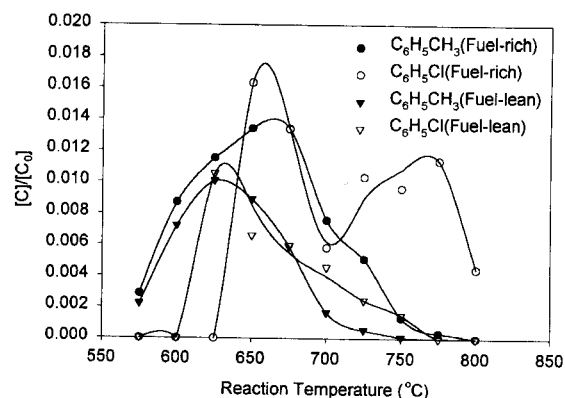
Experimental results for the decomposition of C<sub>2</sub>HCl<sub>3</sub> and CH<sub>4</sub> are shown in Figure 3, which shows normalized concentration ( $C/C_0$ ) as a function of temperature at an average residence time of 0.7 s. Since the residence times for reaction temperature above 700°C were from 0.3

**Table 1.** Reactant features.

	Mole percent				Equiv.	
	C <sub>2</sub> HCl <sub>3</sub>	CH <sub>4</sub>	O <sub>2</sub>	Ar	Ratio, $\phi$	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

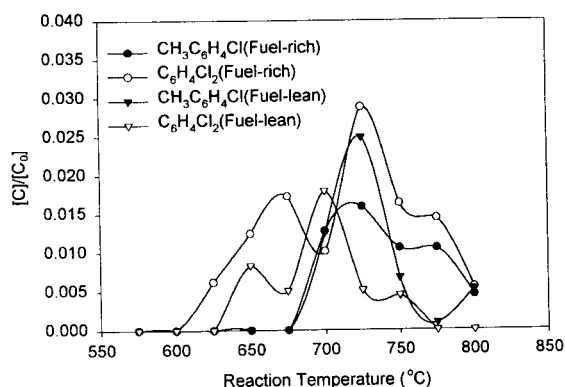
to 1.0 s, 0.7 s was chosen for comparison in this study. C<sub>2</sub>HCl<sub>3</sub> concentration consistently decreased with increasing temperature in both reaction environments. CH<sub>4</sub> concentration stayed in peak levels for the low-medium temperature range for both reaction systems, and then decreased with increasing temperature as those in fuel-lean system gave faster decay as expected. Major products for both reaction systems included C<sub>2</sub>Cl<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CO, CO<sub>2</sub> and HCl. Figure 3 also presents the formation profiles of HCl for the fuel-rich and fuel-lean systems. C<sub>l0</sub> denotes the total molar concentration of Cl from the inlet. HCl concentrations increased for both systems since the chlorinated reactant-- C<sub>2</sub>HCl<sub>3</sub>-- decomposed with increasing temperature and showed slower formation in fuel-rich cases since C<sub>2</sub>HCl<sub>3</sub> had a slower decay. Aromatic compounds, including benzene (C<sub>6</sub>H<sub>6</sub>), toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), chlorobenzene (C<sub>6</sub>H<sub>5</sub>Cl), chlorotoluene (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Cl, isomers included) and dichlorobenzene (C<sub>6</sub>H<sub>5</sub>Cl<sub>2</sub>, isomers included) were detected. In addition to the aromatic products, trace intermediates including C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>4</sub>, CH<sub>3</sub>Cl, C<sub>2</sub>H<sub>3</sub>Cl, C<sub>2</sub>HCl, trans-CHCl=CHCl, cis-CHCl=CHCl, COCl<sub>2</sub>, C<sub>2</sub>Cl<sub>4</sub>, and C<sub>2</sub>Cl<sub>6</sub> were also found in this study.

Figure 4 presents the formation profiles of C<sub>6</sub>H<sub>6</sub> for the fuel-rich and fuel-lean systems as a function of temperature. The C<sub>0</sub> in this figure, so as in the following figures, denotes the total molar concentration of input carbons (C<sub>2</sub>HCl<sub>3</sub> +

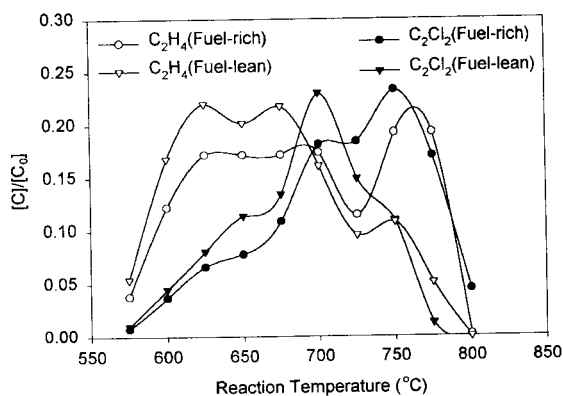
**Figure 4.** Normalized concentration ( $C/C_0$ ) profiles of C<sub>6</sub>H<sub>6</sub> as a function of temperature under fuel-rich ( $\phi=1.25$ ) and fuel-lean ( $\phi=0.75$ ) conditions.**Figure 5.** Normalized concentration ( $C/C_0$ ) profiles of C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>Cl as a function of temperature under fuel-rich ( $\phi=1.25$ ) and fuel-lean ( $\phi=0.75$ ) conditions.

CH<sub>4</sub>). As shown in this figure, both systems formed C<sub>6</sub>H<sub>6</sub> 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 C<sub>6</sub>H<sub>6</sub> increased with higher oxygen at higher temperatures.

Figure 5 shows distributions of C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> for both systems as a function of temperature. The profiles from both systems gave similar trends for C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> distributions. For the fuel-lean system, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> had a lower formation tendency and decomposed faster as the temperature increased. Figure 5 also demonstrates the concentration profiles of C<sub>6</sub>H<sub>5</sub>Cl for the fuel-rich and fuel-lean cases as a



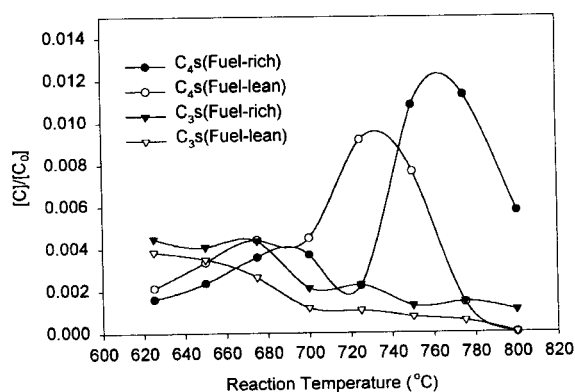
**Figure 6.** Normalized concentration ( $C/C_0$ ) profiles of  $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$  and  $\text{C}_6\text{H}_4\text{Cl}_2$  as a function of temperature under fuel-rich ( $\phi=1.25$ ) and fuel-lean ( $\phi=0.75$ ) conditions.



**Figure 7** Normalized concentration ( $C/C_0$ ) profiles of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{Cl}_2$  as a function of temperature under fuel-rich ( $\phi=1.25$ ) and fuel-lean ( $\phi=0.75$ ) conditions.

function of temperature. There was about  $25^\circ\text{C}$  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  $\text{C}_6\text{H}_6$  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  $\text{CH}_3$  radicals in fuel-rich system to attack the  $\text{C}_6\text{H}_6$  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  $\text{CH}_3$  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  $\text{C}_3\text{s}$  ( $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_4$ ) and  $\text{C}_4\text{s}$  ( $\text{C}_4\text{H}_6$  and  $\text{C}_4\text{H}_4$ ) 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.

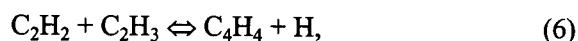
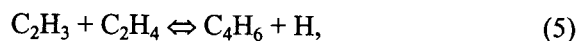
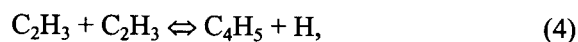
It should be helpful to present the profiles for other products,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{Cl}_2$ ,  $\text{C}_3\text{H}_6$  and  $\text{C}_4$  compounds, in order to analyze the formation pathways of aromatic compounds. Figure 7 presents the formation profiles of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{Cl}_2$  for both the fuel-rich and fuel-lean systems in the studied temperature range. For the fuel-lean system, as expected,  $\text{C}_2\text{H}_4$  had a higher formation tendency and gave a faster decay. Figure 7 also shows a  $\text{C}_2\text{H}_4$  formation-decomposition tug for both reaction systems since temperature was higher than  $675^\circ\text{C}$ . The concentration of  $\text{C}_2\text{H}_4$  for both systems first decreased as the temperature got higher than  $675^\circ\text{C}$ , then increased as the temperature reached  $725^\circ\text{C}$ , and then decreased again as the temperature increased. This was due to the decomposition of the aromatic compounds at temperatures higher than  $650^\circ\text{C}$ , as discussed earlier, and to the

recombination of  $\text{CH}_3$  radicals, which are well recognized to be responsible for  $\text{C}_2\text{H}_4$  formation at higher temperatures. Figure 7 also shows  $\text{C}_2\text{Cl}_2$  profiles for the fuel-rich and fuel-lean cases. These two systems show similar profiles; however, the fuel-lean case had a lower peak temperature for the formation of  $\text{C}_2\text{Cl}_2$  and then decomposed faster than the fuel-rich one. These profiles also show that  $\text{C}_2\text{Cl}_2$  was mainly formed from the decomposition of  $\text{C}_2\text{HCl}_3$  and that there were insignificant amounts of highly chlorinated aromatics formed in the course of the decomposition.

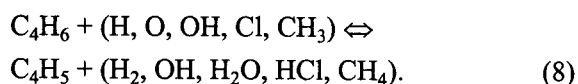
Figure 8 shows the formation of  $\text{C}_3$  ( $\text{C}_3\text{s}$ ) and  $\text{C}_4$  compounds ( $\text{C}_4\text{s}$ ) for both reaction systems as a function of temperature. We have to note that the  $\text{C}_3$  compounds include  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_4$  and that  $\text{C}_4$  compounds include  $\text{C}_4\text{H}_8$ ,  $\text{C}_4\text{H}_6$ , and  $\text{C}_4\text{H}_4$  species. These profiles all show that in the higher oxygen environment,  $\text{C}_3$  and  $\text{C}_4$  compounds decomposed faster, as expected. The profiles of  $\text{C}_4\text{s}$  also show more significant peak levels than those of  $\text{C}_3\text{s}$ . The fact that the profiles of  $\text{C}_4\text{s}$  rise again was due to the fact that  $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$  and  $\text{C}_6\text{H}_4\text{Cl}_2$  started to decompose earlier at temperature higher than  $700^\circ\text{C}$ . The formation of these higher molecular weight intermediates is typical in fuel-rich hydrocarbon and chlorinated hydrocarbons systems (Qun and Senkan (1990, 1994)).

The formation pathways for aromatic species were believed to be due to the subsequent additions of  $\text{C}_2$  to  $\text{C}_4$  species, followed by the cyclization and dehydrogenation of the adducts (Weissman and Benson (1984); Frenklach et al. (1984); Benson (1992)). The chemically activated adducts involving  $\text{C}_3$  species also has been suggested (Westmoreland et al. (1989); Miller and Melius (1992)). The formation pathways responsible for the aromatic species discussed above are as follows. The higher molecular weight intermediates,  $\text{C}_4\text{s}$ , for example, can be

formed via

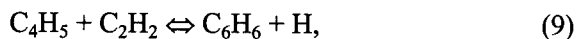


and



$\text{C}_2\text{H}_2$  can be formed via the decomposition of  $\text{C}_2\text{H}_4$ .

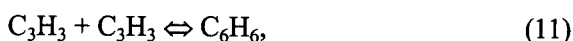
The possible pathways for  $\text{C}_6\text{H}_6$  formation, as suggest by Westmoreland et al. (1989), would be



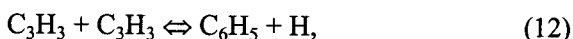
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or as proposed by Miller and Melius (1992),

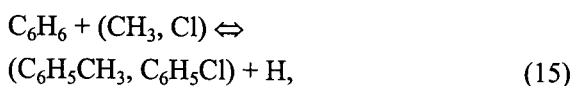
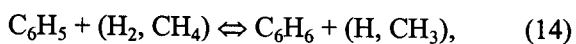
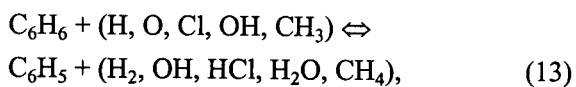


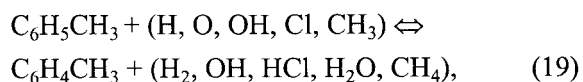
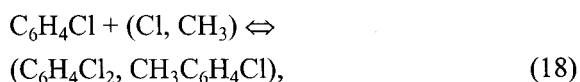
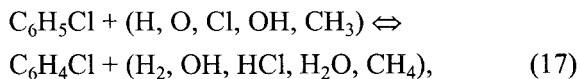
and



where  $\text{C}_3\text{H}_3$  can be formed from the dissociation of  $\text{C}_3\text{H}_4$ .

Other related pathways for these aromatics include,





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  $\text{C}_2\text{HCl}_3$  with  $\text{CH}_4$  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  $\text{C}_2\text{Cl}_2$ ,  $\text{C}_2\text{H}_4$ , CO,  $\text{CO}_2$  and HCl. Aromatic compounds, including  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_5\text{CH}_3$ ,  $\text{C}_6\text{H}_5\text{Cl}$ ,  $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$  and  $\text{C}_6\text{H}_5\text{Cl}_2$  were detected. Experimental data also show that in the higher oxygen environment, major products, such as  $\text{C}_2\text{Cl}_2$ , CO,  $\text{CO}_2$  and HCl, were detected in the lower reaction temperatures. Final products

such as  $\text{CO}_2$  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  $\text{C}_2$  to  $\text{C}_4$  species, followed by the cyclization and dehydrogenation of the adducts. The chemically activated adducts involving  $\text{C}_3$  species have also been considered.

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