# **Role of Phenoxy Radicals in PCDD/F Formation**

## SUKH SIDHU, PHIL EDWARDS

Environmental Science and Engineering, 300 College Park, University of Dayton, Dayton, Ohio 45469-0132 Received 11 February 2002; accepted 6 June 2002 DOI 10.1002/kin.10083

> ABSTRACT: In this work, the role of phenoxy radicals in polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F) formation was investigated by studying the slow oxidation of 2-chlorophenol (2-CP) and 2-chloroanisole (2-CA) at a gas-phase concentration of 4 ppm ( $\sim 2.1 \times 10^4 \ \mu g/m^3$ ) over a temperature range of 400–800°C. Residence times were maintained at  $2.0 \pm 0.10$  s. PCDD/F reaction products were dibenzofuran, dibenzo-pdioxin, 4-chlorodibenzofuran, 1-chlorodibenzo-p-dioxin, 4,6-dichlorodibenzofuran, and 1,6dichlorodibenzo-p-dioxin (1,6-DCDD). Major products observed in these experiments were 2,6-dichlorophenol, 3-phenyl-2-propenal, 1-indanone, 1,3-isobenzofurandione, and 3-phenyl-2-propenoyl chloride. The 2-CP and 2-CA experiments, along with the variable concentration 2-CA experiments, showed that the concentration of radicals present in the oxidation system has a significant effect on the PCDD/F product distribution and ultimately the PCDD/PCDF ratio. Also, the observation of dichlorinated phenoxy phenol and dichlorinated dihydroxybiphenyl, the proposed intermediate species in the radical-radical mechanism, suggests that radicalradical mechanism dominates gas-phase PCDD/F formation. This information will be helpful in constructing a detailed kinetic mechanism of PCDD/F formation/destruction in combustor postcombustion zone. © 2002 Wiley Periodicals, Inc. Int J Chem Kinet 34: 531-541, 2002

### INTRODUCTION

The phenoxy radical is considered a key intermediate species in the oxidation of aromatic species that are an important fraction of automotive and aviation fuels [1–3]. The formation and destruction of phenoxy radicals are important steps that control the overall conversion of the aromatic fuel fraction into lower molecular weight aliphatic fragments. Reactions of phenoxy radicals are key reactions for the formation of many pollutants, namely soot, dioxins, and dioxin-like compounds. A phenoxy radical can thermally decompose and eliminate CO and form a cyclopentadienyl radical [4,5]. The cyclopentadienyl radical thus

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formed plays an important role in the formation of soot and polyaromatic hydrocarbons like naphthalene [6,7]. A second path for consumption of phenoxy radicals is dimerization, which leads to the formation of dibenzofurans (DF), dibenzo-p-dioxins (DD), dihydroxybiphenyls, and phenoxyphenols, with dibenzofuran being the major product under postcombustion conditions [8]. Dimerization of chlorinated phenoxy radicals can thus lead to the formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F), a class of 210 species that are known to cause adverse health effects in humans and animals [9,10]. Similarly, chlorinated cyclopentadienyl radicals formed from the decomposition of chlorinated phenoxy radicals can form polychlorinated napthalenes, which are also known to cause adverse health effects in humans and animals [11].

The structure of phenoxy radical is a hybrid of one oxygen-centered (1) and two carbon-centered (2 and 3) radicals. These resonance structures provide

 $Correspondence \ to: \ Sukh \ Sidhu; \ e-mail: \ sidhu@udri.udayton. edu.$ 

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16 kcal/mol of resonance stabilization energy to the phenoxy radical [12].



Because of this resonance stabilization energy, phenoxy radicals are usually present at higher concentrations than nonstabilized radicals like phenyl. The relative high concentration and stability enables phenoxy radicals to participate in many reactions that are key steps in pollutant formation in combustion systems [13]. Understanding these phenoxy reactions will benefit researchers who are conducting theoretical or experimental investigations of fuel ignition, soot, and pollutant formation.

It is an impossible task to study reactions of all phenoxy radicals with and without varying degrees of chlorination and other substitutions. An acceptable approach is to select a particular type of phenoxy radical based on its importance in pollutant formation and then study its reactions in detail. In this paper, we present the reactions of monochlorinated phenoxy radicals under postcombustion zone conditions. The chlorinated phenoxy radical in this study was generated from slow oxidation of 2-chlorophenol (2-CP) and 2-chloroanisole (2-CA). Both 2-CP and 2-CA were chosen as phenoxy precursors because of their presence in waste combustion effluents and also because only one of their ortho sites is chlorinated [14]. Theoretical and experimental studies of nonchlorinated phenoxy radicals have shown that phenoxy radicals exhibit a high probability for ortho-ortho C-C coupling, which then leads to the formation of DF and DD [15,16]. Since understanding the role of phenoxy radicals in the formation of chlorinated DF and DD is the main objective of this study, we wanted to study a phenoxy radical possessing one chlorinated and one nonchlorinated ortho site.

#### **EXPERIMENTAL**

All experiments were performed using a hightemperature flow reactor coupled with an in-line gas chromatograph mass spectrometer (GC–MS) system designed to simulate the reaction conditions in a combustor postflame zone. The setup is described in detail elsewhere [17]. Briefly, the reactor system consists of four integrated units: (1) A control console for precise adjustment of temperature, pressure, residence time, and the respective gas flows; (2) A thermal reactor compartment containing a high temperature Lindberg furnace housed within a gas chromatograph (HP 5890) to allow precise sample introduction into and out of the quartz reactor; (3) A gas chromatographic oven (HP 5890) containing a capillary column (J & W Scientific DB-5, 30 m, 0.25 mm ID, 0.25 µm film thickness) for separation of organic reaction products; and (4) A mass spectrometer (HP 5970B MSD) for product identification and quantification. For this study, the reactor system was fitted with a 1.0 cm ID, 27 cm<sup>3</sup> quartz gasphase reactor. The residence time distribution in the reactor simulates plug-flow behavior. Previous studies in which the reactor diameter was varied from 0.1 to 1.2 cm have shown that surface reactions of chlorinated hydrocarbons are insignificant for a reactor diameter  $\geq$ 1.0 cm [18]. Also, the high temperature region was strictly confined to the wide bore section of the reactor to prohibit end wall effects. Therefore, the system is completely homogeneous. The residence time of the reaction gas in the reactor is calculated by dividing the reactor volume by the volumetric flow rate of the reaction gas, corrected for temperature and pressure. Residence times were maintained at  $2.0 \pm 0.10$  s over a temperature range of 400-800°C. At each reaction temperature, the flow rate was adjusted to maintain the 2 s residence time. Each experiment was run for 60 min. Reactions were conducted in an atmosphere of 4% oxygen in helium.

The phenoxy precursors, namely 2-CP and 2-CA, were purchased from Aldrich Chemical and used without any further treatment. To achieve low precursor concentration and stay within detection limits, the gas-phase precursor concentration in the reaction gas was maintained at  $4 \pm 1$  ppm ( $2.1 \times 10^4 \ \mu$ g/m<sup>3</sup> at RTP). A gas-phase sample of a precursor in helium was prepared in a 0.52 l sample bulb for each run. During the runs, the sample was injected into the reactor at a constant rate by using a syringe pump (Sage Instruments Model 341A). For each run, a syringe pump flow rate setting was selected and the required concentration of precursor in the sample bulb was calculated to maintain a precursor concentration in the reaction gas of 4 ppm.

The equivalence ratios for 2-CP and 2-CA were  $6.76 \times 10^{-4}$  and  $8.26 \times 10^{-4}$ , respectively (fuel lean conditions).

The reaction products and unreacted precursor were trapped with a composite adsorptive trap consisting of 0.12 g of TENAX-TA<sup>®</sup> and 0.24 g of CARBOTRAP<sup>®</sup>. After each run, the trap was desorbed at 300°C for 20 min, and the reaction products were trapped at

30°C on a J&W Scientific DB-5 column (30 m, 0.25 mm ID, 0.25 µm film thickness). Products were analyzed using GC-MS with a temperature programming of  $30^{\circ}$ C (1 min hold) to  $300^{\circ}$ C (10 min hold) at a rate of 15°C/min. Selected ion monitoring (SIM) was used to identify and quantitate reaction products. For PCDD/F analysis, the molecular weight (M) and molecular weight +2 (M + 2) ions, along with one other prominent ion, were monitored. For other products, the molecular weight ion and two other prominent ions in the compound's spectrum were monitored. In SIM mode, we can detect up to 0.1 ng (on column) of any PCDD/F species, which means that we should observe any PCDD/F product that has a yield better than 0.00003 mol%. Quantitation was performed using external standard calibration curves for the respective product. A few minor reaction products were quantitated using standard calibration for chemically similar compounds.

## **RESULT AND DISCUSSION**

In this work, the role of phenoxy radicals in PCDD/F formation was investigated by studying the slow oxidation of 2-CP and 2-CA at a gas-phase concentration of 4 ppm ( $\sim 2.1 \times 10^4 \,\mu g/m^3$ ) over a temperature range of 400–800°C. Residence times were maintained

at  $2.0 \pm 0.10$  s. Major products observed in these experiments were 2,6-dichlorophenol (2,6-DCP), 3phenyl-2-propenal, 1-indanone, 1,3-isobenzofurandione, and 3-phenyl-2-propenoyl chloride. PCDD/F products observed were DF, DD, 4-chlorodibenzofuran (4-CDF), 1-chlorodibenzo-*p*-dioxin (1-CDD), 4,6dichlorodibenzofuran (4,6-DCDF), and 1,6-dichlorodibenzo-*p*-dioxin (1,6-DCDD).

The product profiles of non-PCDD/F products from 2-CP oxidation experiments are shown in Fig. 1. The gas-phase 2-CP is fairly stable, with slight decomposition beginning at 500°C but rapid decomposition only after 650°C. The major non-PCDD/F product is 3phenyl-2-propenal, with a mole percent yield of 0.32% at 650°C. Other products formed have mole percent yields between 0.0001 and 0.1%. Maximum yields of non-PCDD/F products occurred between 650 and 700°C. The PCDD/F product profiles from 2-CP oxidation are shown in Fig. 2. The major PCDD/F product is 1-CDD, with a maximum mole percent yield of 0.022% at 650°C. Other PCDD/F products are produced in yields of 0.0001–0.003%, with the maximum yield of PCDD/F products occurring between 600 and 650°C. All data points in these figures are an average of replicate experiments ( $\pm 10\%$ ). The observation of 1-CDD as a major PCDD/F product from 2-CP oxidation is not consistent with the results of 2-CP oxidation and pyrolysis studies conducted by the Louw, Mulholland, and



Figure 1 Thermal oxidation profiles for 2-CP and non-PCDD/F products; product yields in mole percent.  $[2-CP]_0 = 2.1 \times 10^4 \,\mu g/m^3$  (RTP),  $t_r = 2 s$  in 4% O<sub>2</sub>/He.



Figure 2 Thermal oxidation profiles for 2-CP and PCDD/F products; product yields in mole percent.  $[2-CP]_0 = 2.1 \times 10^4 \,\mu g/m^3$  (RTP),  $t_r = 2 \, s \, in \, 4\% \, O_2/He$ .

Hagenmaier groups, in which they found 4,6-DCDF to be the major PCDD/F product [19–23]. However, all the previous 2-CP studies were conducted at much higher 2-CP inlet concentrations (>1000 vs. 4 ppm) and this difference in inlet concentration could be responsible for different PCDD/F product distribution. This is discussed in detail later.

The product profiles of non-PCDD/F products for 2-chloranisole oxidation are shown in Fig. 3. The gasphase 2-CA is less stable than 2-CP, with decomposition beginning at 500°C (similar to 2-CP), but with very rapid decomposition thereafter. 2-CP is the major non-PCDD/F products observed in the 2-CA experiments. Other non-PCDD/F observed in the 2-CA experiments are similar to 2-CP experiments but with lower mole percent yields. Yields of non-PCDD/F products from 2-CA experiments range from 0.002 to 9% at 600°C. Maximum yields of non-PCDD/F products from 2-CA and 2-CP oxidation occurs around 650°C, but product formation begins at lower temperatures (500°C) for 2-CA than 2-CP. The PCDD/F product profiles from 2-CA oxidation are shown in Fig. 4. Similar PCDD/F products are observed as in the 2-CP experiments, but yields from 2-CA oxidation are lower. The major PCDD/F product from 2-CA is

4,6-dichlorodibenzofuran, with a maximum mole percent yield of 0.001% at 700°C (the major product from 2-CP was 1-CDD at 0.022% at 650°C). Other PCDD/F products are produced in yields of 0.00002–0.0005%, with the maximum yield of PCDD/F products occurring from 500–700°C. The observation of 4,6-DCDF as a major PCDD/F product from 2-CA oxidation is consistent with the results of Louw, Mulholland, and Hagenmaier [19–23].

This difference in product distribution between 2-CA and 2-CP experiments can be attributed to weaker O-CH<sub>3</sub> bond strength of 2-CA (~64 kcal/mol) compared to O-H bond strength in 2-CP (~88.7 kcal/mol) [24,25]. Because of this weaker O-CH<sub>3</sub> bond strength, 2-CA generates phenoxy radicals and methyl radicals at lower temperatures than from 2-CP. In 2-CP oxidation experiments, the destruction of 2-CP occurred initially via thermal decomposition,

$$C_6H_5OH \longleftrightarrow C_6H_5O \cdot + H_5$$

but the recombination rate of phenoxy radical and H is very high  $(2.5 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$  and this is the reason that rapid destruction of 2-CP is observed only at higher temperatures (>650°C) [26]. On the other hand,



Figure 3 Thermal oxidation profiles for 2-CA and non-PCDD/F products; product yields in mole percent.  $[2-CA]_0 = 2.1 \times 10^4 \,\mu g/m^3$  (RTP),  $t_r = 2 \, s \text{ in } 4\% \, O_2/He$ .



Figure 4 Thermal oxidation profiles for 2-CA and PCDD/F products; product yields in mole percent.  $[2-CP]_0 = 2.1 \times 10^4 \,\mu g/m^3$  (RTP),  $t_r = 2 \, s \, in \, 4\% \, O_2/He$ .

the 2-CA thermal decomposition profile shows a rapid decomposition of 2-CA because the initial decomposition products of 2-CA, phenoxy and methyl radical recombine but mostly form cresol and not anisole. This is why product formation from 2-CA occurs over a broader temperature range than from 2-CP. The methyl radicals formed from the initial dissociation of 2-CA create a radical pool that is not present in chlorophenol, in which many reactions take place such as

$$CH_{3} \cdot + O_{2} \longleftrightarrow CH_{2}O + OH \cdot;$$
  

$$CH_{3} \cdot + O_{2} \longleftrightarrow CH_{3}O \cdot + O \cdot$$
  

$$O \cdot + CH_{3} \cdot \longleftrightarrow CH_{2}O + H \cdot;$$
  

$$CH_{3}O \cdot + M \longleftrightarrow CH_{2}O + H \cdot + M, \text{ etc.}$$

H radical thus formed can also combine with phenoxy radical to form 2-CP, which is the major product observed in 2-CA experiments. A weaker initial dissociation bond combined with a lack of recombination to form parent compounds and reactive methyl radicals create a very reactive system, in which it is more difficult to form large molecular growth molecules such as PCDD/F. This can be clearly observed in Fig. 5, which compares product yields (mole percent yields based on precursor input) from 2-CP and 2-CA oxidation at 600°C. From Fig. 5 it can also be observed that dioxin formation is reduced more than furan formation such that the major PCDD/F product from 2-CA is 4,6-DCDF, where it was 1-CDD in the 2-CP experiments, and the furans in general become dominant PCDD/F products in 2-CA oxidation.

PCDD/F products observed in both 2-CP and 2-CA experiments are probably formed via radicalmolecule or radical-radical reactions between the 2-chlorophenoxy radicals and the 2-CP/2-CA molecules. Thermochemical and kinetic analysis has previously concluded that the molecule-molecule reaction is infeasible in 2-CP/2-CA oxidation under the reaction conditions of this study [27]. In the radical-molecule reaction (see Fig. 6), the initial step is the displacement of the molecule's chlorine by the phenoxy radical. The resulting compound can then either abstract HCl to directly form DD or can lose a hydrogen atom by OH. abstraction to form a phenoxy ether intermediate (11 in Fig. 6). The intermediate then undergoes Smiles rearrangement to form either DD through intraring elimination of the second chlorine atom or 1-CDD through intraring elimination of the hydrogen atom. Smiles rearrangement is a well-documented occurrence in these types of reactions [8,21-23,28]. Alternatively, in dibenzofuran formation the initial step is instead the displacement of OH· by the phenoxy radical. The resulting



Figure 5 Yield comparison for 2-CP and 2-CA.  $T = 600^{\circ}$ C, [2-CP, 2-CA]<sub>0</sub> 2.1 × 10<sup>4</sup> µg/m<sup>3</sup>,  $t_r = 2 \text{ s in } 4\% \text{ O}_2/\text{He}$ .



Figure 6 Radical-molecule pathway to PCDD/F formation from oxidation of 2-CP.

compound can then either abstract HCl to directly form 4-CDF or lose hydrogen with the help of OH· to form a phenyl ether intermediate (12 in Fig. 6). The intermediate then undergoes Smiles rearrangement to form either DF through intraring elimination of the second chlorine atom or 4-CDF through intraring elimination of hydrogen. However, the PCDD/F product distribution obtained from radical-molecule mechanism is not consistent with the results of this study, as it gives DD and 4-CDF as main PCDD/F products, whereas the experimental results show 1-CDD and 4,6-DCDF as main PCDD/F products. Another problem with the radicalmolecule mechanism is that it requires chlorine and hydroxyl displacement as first steps, and these steps are not energetically favored under the conditions of the present study [8].

Exclusion of the radical-molecule mechanism leaves us with a radical-radical mechanism to explain PCDD/F formation in the present study. Phenoxy or chlorophenoxy radicals exist as oxygen-centered radicals ("eno" form) or as carbon-centered radicals ("keto" form). Theoretical and experimental studies have shown that keto form is the more stable form of the phenoxy radical [29,30]. In the radical-radical reaction to PCDD, keto and eno react to form an ether adduct, which is then followed by hydrogen tautomerism. The resulting compound, dichlorophenoxyphenol (*13*)

in Fig. 7), can then either abstract HCl to directly form 1-CDD or lose a hydrogen atom by OH· abstraction to form a chlorophenyl-chlorophenoxy ether intermediate. This intermediate then undergoes Smiles rearrangement to form either 1-CDD through intraring elimination of the second chlorine atom or form a DCDD (1,6- or 1,9-) through intraring elimination of hydrogen. The rotation of the five-membered Smiles rearrangement ring at the apex results in two possible DCDD isomers. However, we observed only one DCDD isomer (1,6-DCDD); this perhaps could be attributed to higher stability of 1,6-DCDD than 1,9-DCDD [31]. The intermediate I3 (2,6'-dichloro-2phenoxyphenol; listed as 2,6'-DC2PP in Fig. 2) has been consistently observed in the 2-CP experiments but not in 2-CA experiments. 2,6'-DC2PP was identified based on a good match of product spectrum with NIST mass spectral library. This identification was later verified and quantified using a synthesized standard.

In the radical–radical reaction to PCDF (see Fig. 8), chlorophenoxy radicals in the keto form combine at the ortho-carbon site to form dichlorinated biphenoxy intermediate (with two ketone groups). This intermediate then undergoes hydrogen tautomerism to form dichloro-2,2'-dihydroxybiphenyl. Dichloro-2,2'-dihydroxybiphenyl can lose a hydrogen atom via



Figure 7 Radical-radical pathway to PCDD formation from oxidation of 2-CP.

abstraction and then eliminate a hydroxyl radical to form 4,6-dichlorodibenzofuran or eliminate water directly to form 4,6-dichlorodibenzofuran. Similarly, a chlorophenoxy radical can react with a nonchlorinated phenoxy radical to form 4-CDF, and two nonchlorinated phenoxy radicals can form DF. Dichloro-2,2'dihydroxybiphenyl was observed in both the 2-CP and 2-CA experiments with yields very close to detection limit (0.00003 mol%). We were able to identify dichloro-2,2'-dihydroxybiphenyl but were not able to quantify it within our acceptable experimental scatter limits ( $\pm 10\%$ ). This is the reason that dichloro-2,2'-dihydroxybiphenyl is not shown in Figs. 2 and 4. From the earlier discussion, it is evident that the radical-radical mechanism is consistent with the observed intermediates and PCDD/F product distribution. Radical-radical PCDD/F formation mechanism can also explain why 1-CDD was the major PCDD/F product in our 2-CP experiments, whereas 4,6-DCDF was the major product in the 2-CA experiments and 2-CP oxidation studies conducted by Louw, Mulholland, and Hagenmaier groups [19–23]. As shown in Fig. 7, dioxin formation occurs via combination of eno and keto forms of phenoxy radicals and thus relies upon the eno-keto radical equilibrium. As the radical pool increases because of large initial concentrations of phenoxy precursor (33 and 684 ppm 2-CP experiments)



4,6-DCDF

**Figure 8** Radical–radical pathway to PCDF formation from oxidation of 2-CP.

or because of weak initial dissociation bond of phenoxy precursor (2-CA), the reactions of phenoxy radical with other nonphenoxy radicals also increases. This depletes the total phenoxy radical concentration and further lowers the chances of phenoxy-phenoxy radical recombination to form PCDD/Fs. The concentration of the eno form of the phenoxy radical decreases more than that of the keto form, as keto is the more stable form of the phenoxy radical [29,30]. Since furan formation involves only the more stable keto form of the radical, the decrease in furan yields is less than the observed decrease in dioxins. This higher decrease in dioxin yields when compared to furan yields is clearly shown Fig. 5, which compares product yields from 2-CP and 2-CA experiments at 600°C. This is consistent with results from our previous study in which oxidation of 2,4,6-trichlorophenol (2,4,6-TCP) with and without hexane was investigated. The introduction of the extra radicals produced from the decomposition of hexane caused a decrease in the yields of PCDD products, while PCDF yields did not show the same effect, and were even observed to increase [32].

To further test our hypothesis that radical concentration can impact the PCDD/PCDF ratio and to better understand the role of radical concentration on PCDD/F formation, experiments were conducted for 2-CP oxidation at a temperature of 600°C and variable inlet 2-CP precursor concentrations of 4, 33, and 684 ppm  $(2.1 \times 10^4, 1.73 \times 10^5, \text{ and } 3.57 \times 10^6 \text{ ng/m}^3 \text{ at RTP}).$ As postulated, similar reaction products were observed at all three concentrations, but the yield distribution of PCDD/F products did change. The dominant PCDD/F product in the 4 ppm 2-CP oxidation experiments was found to be 1-CDD, while the dominant PCDD/F product in the 33 and 684 ppm experiments was found to be 4,6-DCDF. This reaffirms the previous conclusion that when the concentration is increased, the increased number of radicals available hinders the formation of PCDD more than the formation of PCDF, which is not dependent on chemistry involving the less stable eno form of phenoxy radicals. However, the reduction of dioxin products with an increase in 2-CP concentration is much less noticeable than when a new species such as hexane or anisole is introduced. PCDD/F product distributions for 4, 33, and 684 ppm experiments are shown in Fig. 9. Figure 9 also shows that no 1,6-DCDD was observed in 33 ppm experiments. Mechanistically it is not possible for 1,6-DCDD to not form in 33 ppm 2-CP experiments. The most plausible explanation is that 1,6-DCDD was formed, but was just below the detection limit.

The 2-CP and 2-CA experiments, along with the variable concentration 2-CA experiments, showed that the concentration of radicals present in the oxidation system has a significant effect on the PCDD/F product distribution and ultimately the PCDD/PCDF ratio. Also, the observation of dichlorinated phenoxy phenol and dichlorinated dihydroxybiphenyl, the proposed intermediate species in the radical-radical mechanism, suggests that radical-radical mechanism dominates gas-phase PCDD/F formation in the combustor postcombustion zone. The only scenario in which radical-molecule PCDD/F formation mechanism might be dominant would be the combustion of phenol whose ortho and para sites are chlorinated (e.g., 2,4,6-trichlorophenol or pentachlorophenol) such that the radical-radical combination at ortho sites would require chlorine tautomerism, a step that is thermodynamically not feasible under the postcombustion zone conditions. However, in most practical combustion situations, other hydrocarbon species will be present along with 2,4,6-trichlorophenol or pentachlorophenol and the chlorine at the ortho or para sites of these phenols could be easily displaced, opening reaction routes for radical-radical mechanism. Thermochemical and kinetic modeling of this data and data from other



Figure 9 Yield comparison for PCDD/F products at various initial 2-CP concentrations.  $T = 600^{\circ}$ C,  $t_r = 2 \text{ s in } 4\% \text{ O}_2/\text{He}$ .

chlorophenol studies would be useful in clarifying aspects of the various pathways to PCDD/F formation from precursors.

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