

# Thermal degradation of 2-chlorophenol promoted by $\text{CuCl}_2$ or $\text{CuCl}$ : Formation and destruction of PCDD/Fs

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Accepted 26 May 2006

Available online 16 January 2007

## Abstract

The oxidative degradation of 2-chlorophenol in air (equivalence ratio  $\phi = 0.8$ ) was investigated at 350 °C by using the sealed tube technique under different conditions: in the gas phase and in the presence of copper chlorides ( $\text{CuCl}_2$  and  $\text{CuCl}$  in different proportions). Not only PCDD/Fs but carbon oxides and other organic products such as chlorophenols, chlorobenzenes, tetrachloroethylene and tetrachlorocyclopentenedione were quantified in order to evaluate the relative importance of reaction pathways. Additional experiments were performed to analyse the degradation products of octachlorodibenzodioxin and 2-monochlorodibenzodioxin. Although it was stated that chlorobenzenes could be formation precursors for PCDD/Fs, experimental data obtained in this work show that chlorobenzenes can also be degradation products of PCDD/Fs.

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**Keywords:** Sealed tubes; Chlorophenols; Dioxins; Chlorobenzenes;  $\text{CuCl}$ ;  $\text{CuCl}_2$

## 1. Introduction

Heterogeneous processes of PCDD/F formation have been extensively investigated in the last two decades. A great number of experimental conditions including different precursors, catalysts, fly ashes (model or real) or techniques have been performed. Chlorophenols have been largely used as precursors because of their high potential for PCDD/Fs formation (for comprehensive review see: Huang and Buekens, 1995; Tuppurainen et al., 1998; Stanmore, 2004). However, very few authors have been interested in the quantification of other by-products than PCDD/Fs. For example, Born et al. (1993a,b) have mentioned the formation of carbon oxides, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol, monobenzofuran, polychlorodiphenylethers, polychlorobenzenes, methylene chloride and tetrachloroethylene from the degradation of monochlorophenol on a bed of model and real fly ashes.

Chlorophenols, chlorobenzenes, tetrachloroethylene and benzoquinones were observed by Ryu and Mulholland (2002) from the ortho-chlorinated phenols degradation on copper chloride. Chlorobenzenes, chlorophenols and carbon oxides were also observed by Hell et al. (2000, 2001) from the reaction of 2,4,6-trichlorophenol on real and model fly ashes. Mixture of benzene and polychlorophenols were studied for their properties to form PCDD/Fs by Ryu and Mulholland (2005). Chlorobenzenes, chlorophenols, tetrachloroethylene and chlorinated quinones have also been observed. The role of species like chlorobenzenes in the PCDD/Fs formation is not clear as stated by Fullana et al. (2004).

In this paper we present the results obtained at 350 °C for the oxidative degradation of 2-chlorophenol (2-CP) with and without any solid matrix ( $\text{CuCl}_2$  or  $\text{CuCl}$ ). These results complete the results published elsewhere (Visez et al., 2004). To evaluate the relative importance of reaction pathways describing the processes of formation and destruction of PCDD/Fs, we have quantified as a function of residence time not only PCDD/Fs but also carbon

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oxides and organic intermediates such as chlorophenols, chlorobenzenes and other chlorinated products. Furthermore, to illustrate the potential role of chlorobenzenes as degradation products, quantitative analyses of the products from oxidative degradation of octachlorodibenzodioxin and 2-monochlorodibenzodioxin were also performed using the same experimental conditions as the ones of 2-chlorophenol.

## 2. Experimental

Experiments were performed using the sealed tube technique. This technique was chosen because it was well suited to a wide range of residence times (from minutes to hours). Although long reaction times were unrealistic for industrial processes, those conditions were also really of a great interest to compare potential abilities of different species for PCDD/Fs formation, chlorination and/or degradation. The experiments were carried out by using sealed tubes made of Pyrex (15 cm long, 11 mm ID). 2-CP and copper chloride were separately deposited in the bottom of the tubes. For each experiment, 1.6  $\mu\text{l}$  of liquid 2-CP (i.e., 16 mmol of 2CP per tube) were introduced in a Pyrex capillary. Sealing of the tubes under atmospheric pressure was achieved with great care. In order to preserve the initial composition of the reactants deposited in the bottom, this part of the tube was frozen at the liquid nitrogen temperature while the sealing was done below 5 cm of the opening of the tube. All experiments involving 2-chlorophenol were conducted with an air/2-chlorophenol equivalence ratio of around 0.8. It should be noted that the sets of experiments presented here (compared to Visez et al., 2004) were obtained with a better control of temperature conditions during and after the thermal treatment which have allowed reaction rates occurring much faster and has made possible thermal treatment with residence times lower than 5 min. Otherwise, the 2-chlorophenol/air equivalence ratio was now estimated to be around 0.8 due to a better measurement of initial amounts of 2-chlorophenol used in each tube. The thermal treatment was performed at 350 °C for a residence time ranging from 1 to 120 min. After treatment, each tube was quenched at room temperature and cooled down to -15 °C in order to condense the organic products on the inner wall of the tube. The tube was then opened and organic products were collected by washing the inner surface of each tube with 2 ml of methylene chloride. PCDD/Fs and other organic compounds were analysed without further purification or treatment. Their identification was performed by means of a HP-5890 gas chromatograph equipped with a low resolution mass selective detector 5971-A. They were quantified using a HP-6890 equipped with an ionisation flame detector. HP-5 capillary columns were used for separation: ID 0.32 mm, film thickness 1.05  $\mu\text{m}$ , 50 m length (for quantification) or 30 m length (for identification). Carbon oxides were analysed by means of an IRTF spectrometer

(Thermo Nicolet Avatar 360). Calibration curves for the quantification of different compounds were determined by injection of solutions of commercial products. Regarding PCDDs quantification was determined for one specific isomer and then applied to all the isomers with the same number of chlorine atoms.

Four sets of experiments have been done at 350 °C as a function of residence time. For simplicity, they are named: sets “2CP”, “CuCl<sub>2</sub>”, “CuCl” and “(CuCl) × 2”, respectively. Sets “2CP” correspond to the oxidative degradation of 2-CP in air in the gas phase without any solid promoter. They were performed as ‘blank’ experiments to highlight the effects of heterogeneous processes in presence of copper chlorides. Experiments entitled “CuCl<sub>2</sub>” were all carried out under the same conditions as the ones used for the sets “2CP” but in the presence of 30 mmol of CuCl<sub>2</sub>, 2H<sub>2</sub>O. In “CuCl” experiments, CuCl has replaced CuCl<sub>2</sub> as a promoter using a nearly identical molar quantity (29 mmol). Water (1 mg) was added to keep the same humidity level. For sets “(CuCl) × 2”, the quantity of CuCl was nearly multiplied by a factor of 2 (59 mmol of CuCl).

## 3. Results

It should be noted that the yields of analysed species were expressed in molar percentage (i.e., 100 × moles of product/initial moles of 2-CP). In the contrast of most studies conducted in this field, our approach was to have a look over the global reactivity of investigated systems in order to better check the quality of our analyses and to evaluate the relative importance of different reaction pathways observed under operating conditions.

The species observed from the thermal degradation of 2-CP in the gas phase at 350 °C (set “2CP”) were as follows: CO, CO<sub>2</sub>, non-chlorinated, mono- and di-chlorodibenzofuran, non-chlorinated and monochlorinated dibenzodioxin and chlorophenoxyphenol. Identification of these species was consistent with the work of Sawerysyn et al. (2004) and Briois et al. (2006) devoted to the gas phase degradation of 2-CP.

The presence of copper chloride modified the number and the variety of organic products. Using CuCl<sub>2</sub> and CuCl as promoters, the following species were identified: 2,4- and 2,6-dichlorophenol and 2,4,6-trichlorophenol, PCDDs (with 1–8 atoms of chlorine), chlorobenzenes (with 3–6 atoms of chlorine), CCl<sub>4</sub>, C<sub>2</sub>Cl<sub>4</sub>, C<sub>2</sub>Cl<sub>6</sub> and tetrachlorocyclopentenedione (C<sub>5</sub>Cl<sub>4</sub>O<sub>2</sub>). The extents of the oxidative degradation of 2-CP and the ones of the chlorination of products were much more important than previously. Furthermore, PCDDs were predominantly observed under these conditions. With CuCl<sub>2</sub> and CuCl (both sets), the main final products were CO<sub>2</sub> and CO. For long residence times, carbon oxides completed the carbon balance to around 100%. The ratio between CO<sub>2</sub> and CO was raising as a function of residence time. At 120 min., this ratio was greater with CuCl<sub>2</sub> ( $\approx$ 8) than with CuCl ( $\approx$ 5) suggesting that CuCl<sub>2</sub> was a better oxidative agent than CuCl.

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