

## Dioxins and other products from the gas-phase oxidation of 2-chlorophenol over the range 450-900°C

Jean-Pierre SAWERYSYN<sup>1</sup>, Christelle BRIOIS<sup>1</sup>, Nicolas VISEZ<sup>1</sup>, Christiane BAILLET<sup>1</sup>

<sup>1</sup>Université de Lille 1 - Physicochimie des Processus de Combustion et de l'Atmosphère - UMR-CNRS 8522

### Introduction

Numerous laboratory studies have been devoted to thermal degradation processes of chlorinated aromatics because they represent the major part of toxic compounds in hazardous wastes<sup>1</sup>. Most previous studies have concentrated on the formation of seventeen toxicologically significant 2,3,7,8-substituted congeners of polychlorodibenzodioxins and polychlorodibenzofurans (PCDD/Fs, also commonly called dioxins) which have been found in both the gaseous and particle phase of effluents emitted from both industrial and distributed combustion processes. To our best knowledge, only very few authors have paid some attention on the specific analysis of low chlorinated PCDD/Fs and potential precursors of PCDD/Fs such as chlorobenzenes and chlorophenols<sup>2</sup> which may also be further sources of highly chlorinated PCDD/Fs. As key intermediates in the formation pathways of PCDD/Fs, polychlorophenols (PCP) were largely investigated but relatively few studies were devoted to the pyrolysis<sup>3,4,5</sup> or oxidation<sup>5,6,7</sup> of monochlorophenols (MCP) in the gas phase at high temperatures. In this paper, we report analytical results<sup>8</sup> on the major stable products of the high-temperature, homogeneous gas-phase oxidation of 2-chlorophenol (2-CP). The concentration profiles of 2-CP, major organic non-PCDD/F products, major PCDD/Fs and carbon oxides are determined as a function of temperature and residence time over ranges relevant to waste incinerators. Our objective is to contribute to a better understanding of the homogeneous gas-phase processes responsible for the formation / destruction of dioxins from organic precursors using a detailed chemical mechanism experimentally validated.

## Methods and Materials

### *Reagents and standards*

Synthetic air (80% N<sub>2</sub>, 20% O<sub>2</sub>) from Air Liquid had a purity of 99.999% and was exempt of CO<sub>2</sub>. 2-CP supplied by Aldrich was used without any further treatment. Its composition (mole %) was determined by Gas Chromatography / Mass Spectrometry (GC/MS) : 2-CP (99.698 %), phenol (0.141%), 2,4-dichlorophenol (0.128%), 2,6-dichlorophenol (0.021%) and 2-chlorohydroquinone (0.009%), 4-chlorophenol (0.003%).

### *Thermal degradation of 2-chlorophenol*

Thermal oxidation of 2-CP was conducted in an air environment using a flow perfectly stirred reactor (PSR). All experiments were performed at 1 atm. over the temperature range 400-900 °C and for three residence times ( 1.2 s, 2 s and 3 s). The concentration of 2-CP in synthetic air was 1000 ppmV, corresponding to an equivalence ratio of 0.03 (fuel lean conditions). The design of the set-up has been described in detail elsewhere<sup>8</sup>. Exhaust gas was withdrawn from the reactor to the analytical instruments through a stainless steel line heated at 250°C in order to assure quantitative transport of higher molecular weight products

### *Identification - HRGC/LRMS*

Identification of organic species was performed using a HP 5890 Gas Chromatograph equipped with a 5971A Mass Spectrometer (HRGC/LRMS) as a detector. Due to the large dilution of organic byproducts in air, the products were collected for identification in a cold trap at -100°C then dissolved in dichloromethane (DCM). The chromatographic conditions were as follows : column, a HP5 fused silica capillary (30 m long, 0.32 mm ID, 0.25 µm), 35°C hold for 0.1 min then ramped to 250°C at 5°C/min ; injector split mode, 1/10 ratio, 200°C ; carrier gas, helium, 1 ml/min ; detector quadrupole, 280°C, 70 eV, scan mode. Identification was achieved by comparing the experimental mass spectra to reference spectra of the data base (NBS 75 K) and, when possible, to spectra of purchased reference compounds.

### *Quantification - HRGC/FID*

Quantification of organics was performed on line by using a HP 6890 gas chromatograph equipped with a flame ionization detector and an automatic gas-sampling valve. A fraction of the gaseous exhaust effluents continuously flowed through a sampling loop of 0.25 cm<sup>3</sup> volume heated at 250°C. The chromatographic conditions used here were as follows: column, a HP5 fused silica capillary (50 m long, 0.32 mm ID, 1.02 µm), 95°C hold for 4 min, firstly ramped to 167°C at 6°C/min, secondly ramped to 197°C for 3 min at 30°C/min, and finally ramped to 250°C for 30 min at 8°C/min; injector, 250°C ; carrier gas, helium, 2.8

ml/min, speed gas of 39 cm/s ; flame ionization detector, 200°C. Analytical conditions were selected to separate all species with a molar mass higher than the one of benzene. Concentration of each organic product was calibrated by using a syringe pump and a vaporization chamber heated at 200°C.

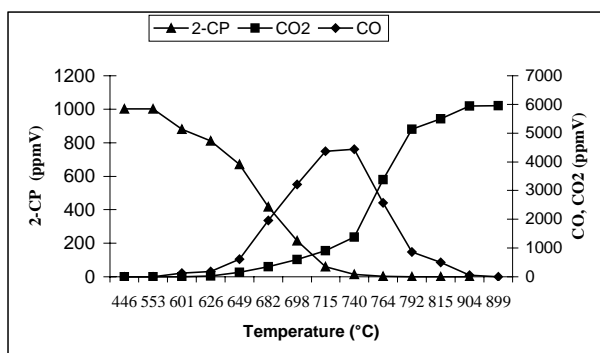
## Results and Discussion

For clarity of figures, only analytical results obtained for 2 seconds were displayed and discussed here.

### *Degradation of 2-CP and conversion to carbon oxides*

Figure 1 exhibits the concentration profiles obtained for 2-CP and carbon oxides as a function of temperature. 2-CP was fairly stable up to 500°C in the gas phase, with slight decomposition starting at 550°C. The temperatures necessary for the complete destruction of 99% and 99,99% of 2-CP were respectively 745 °C and 815°C for a residence time of 2 seconds.

**Figure1 : Concentration profiles of 2-CP, CO and CO<sub>2</sub> for 2 s over the range 440 – 900 °C**  
Gas-phase oxidation of 2-CP [2-CP]<sub>0</sub> = 1000 ppmV in air. P = 1 atm.

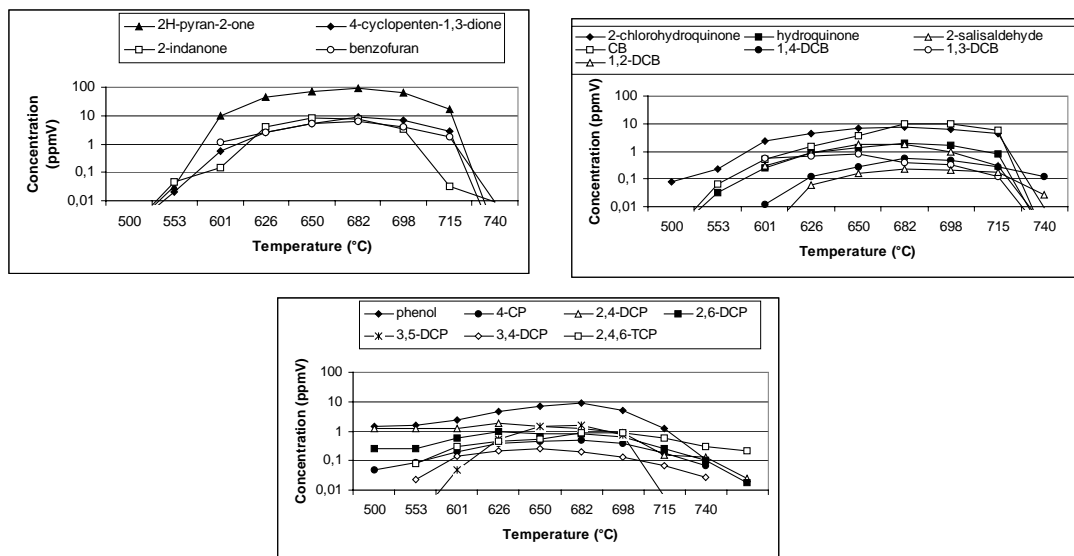


CO was the most abundant product of all intermediates. Its concentration passed through a maximum of 4400 ppmV ranged to 710-740°C. For 2 s, CO and CO<sub>2</sub> yields were around respectively 53.6% and 10 % of the feed carbon content at 700°C, and 5.3% and 91.7% at 815°C. Beyond 750°C, CO<sub>2</sub> was mainly formed by CO oxidation since all organics were nearly totally destroyed. Complete oxidation of CO to CO<sub>2</sub> occurred from 900°C, as shown by the concentration close to 6000 ppmV observed for CO<sub>2</sub>.

### *Formation of organic non-PCDD/F products*

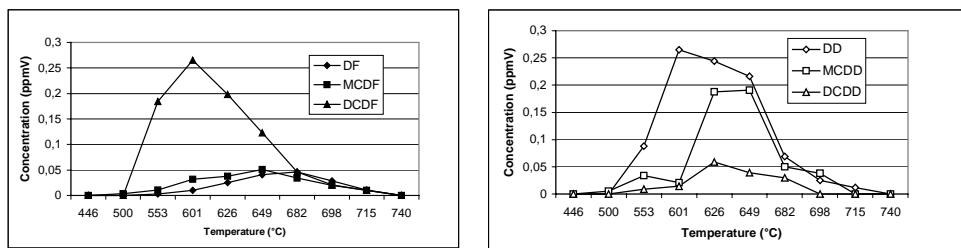
Organic non-PCDD/Fs were formed for 2 seconds over the temperature range of 550-750°C. The maximum concentration of major products occurred at about 650-700°C. As shown in figures 2, major products were ketones (2H-pyran-2-one, 4-

cyclopenten-1,3-dione and 2-indanone), aromatics compounds ( chlorobenzenes, phenol, 2-chlorohydroquinone and benzofuran). Their maximum concentration was ranged between 7 and 88 ppmV, representing 0.6 to 7.4 % of the feed carbon content. Thermal degradation of 2-CP in the gas phase led to smaller yields of hydroquinone, 2-salisaldehyde, dichlorinated benzenes (1,2-DCB, 1,3-DCB and 1,4-DCB), monochlorinated phenol (4-CP), dichlorophenols (2,4-DCP, 2,6-DCP, 3,4-DCP and 3,5-DCP) and tri-chlorinated phenol (2,4,6-TCP). A mole percent yield of about 0.15% of the initial carbon was converted to DCBs, 0.54% to other chlorinated phenols including 0.4% to DCPs. It is well known that these intermediates (chlorinated benzenes and phenols) can also contribute to the formation of PCDD/Fs. It should be noted that phenol, 2-chlorohydroquinone, 2,4-DCP and 2,6-DCP were initially present in the commercial 2-CP as impurities and that all these species were also produced by the oxidation of 2-CP from 550°C for 2 seconds.



**Figure 2 : Concentration profiles of non-PCDD/F products over the range 500 – 750 °C for 2 seconds. Gas-phase oxidation of 2-CP  $[2\text{-CP}]_0 = 1000 \text{ ppmV}$  in air.  $P = 1 \text{ atm}$ .**

### Formation of PCDD/F products



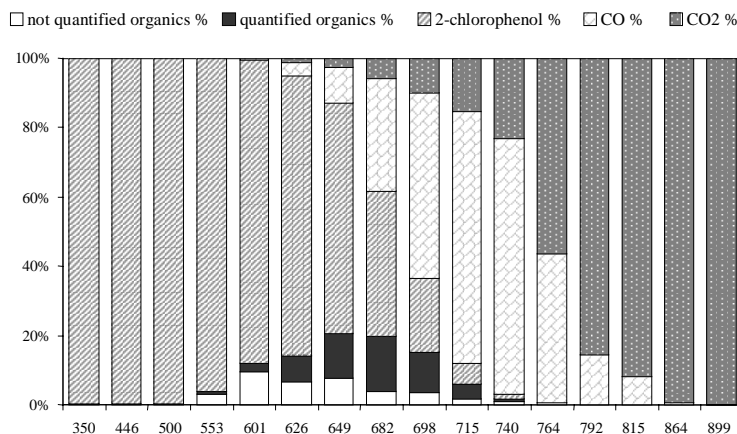
**Figure 3 : Concentration profiles of PCDD/F products over the range 500 – 750 °C for 2 seconds. Gas-phase oxidation of 2-CP [2-CP]<sub>0</sub> = 1000 ppmV in air. P = 1 atm.**

As shown in Fig.3, only low chlorinated or non chlorinated furans/dioxins were produced from the gas-phase 2-CP oxidation for a residence time of 2 s. These products were observed over the temperature range 500-750°C. Under our experimental conditions, the most abundant PCDD/F product was one dichlorodibenzofuran (DCDF) i.e 2,8-DCDF<sup>8</sup> or 4,6-DCDF as suggested in previous works<sup>3,4,5</sup>. Its maximum concentration occurred around 600°C and corresponded to a mole percent yield of 0.050%. Other furans (monochlorodibenzofuran, MCDF, and dibenzofuran, DF) were also obtained at lower concentration. Their maximum concentration were observed at higher temperatures than the one of DCDF, suggesting a possible dechlorination of DCDF. DF can also be formed from phenol which was a relatively abundant intermediate. As mentioned by numerous authors<sup>2</sup>, the *ortho* position of chlorine atom in 2-CP favors the formation of dioxins. Dibenzodioxin (DD) was the major dioxin under operating conditions. Like DCDF, its maximum concentration corresponding to a mole percent yield of 0.051% was observed around 600°C. Mono- and dichlorodibenzodioxin (MCDD and DCDD) were also formed with a lower yield ( 0.04 % and 0.01 % respectively, at 650°C). Similar PCDD/F products were previously observed from pyrolysis<sup>3,4,5</sup> or oxidation<sup>5,6,7</sup> of 2-CP in the gas phase over the same temperature range but in different distributions, depending on experimental conditions. Presence of oxygen, 2-CP concentration and temperature seem to be important factors determining the relative abundance of PCDD/F products observed.

#### Carbon balances

Carbon balances were defined by the total carbon content in analysed species with respect to the feed carbon introduced within 2-CP. As the initial concentration of 2-CP used in this study was 1000 ppmV, the total carbon content was 6000 ppmV.

Carbon balances showed a slight deficit of about 3 to 11% over the temperature 550-700°C (fig.4) because only organic species with at least six carbons were quantified here. As expected, the best results of carbon balances were obtained at temperatures below 450°C and above 780°C, respectively when 2-CP was not yet consumed and when no organic species was present in the effluent gases. The most abundant intermediate was CO with a yield of 80% at around 750°C.



**Figure 4 : Carbone balances as a function of temperature for a residence time of 2 seconds. Gas-phase oxidation of 2-CP [ $2\text{-CP}]_0 = 1000 \text{ ppmV}$  in air.  $P = 1 \text{ atm}$ .**

### Conclusion

In this work, the gas-phase oxidation of 2-CP in air was studied over the temperature range of 450-900°C using a flow PSR for a residence time of 2 seconds. Degradation of 2-CP and conversion to carbon oxides, organic non-PCDD/F products and PCDD/F products were investigated as a function of temperature. All these analytical results provide a very useful data set for the validation of a chemical detailed mechanism proposed to understand the formation/destruction processes of PCDD/F products from precursors in the gas phase. Such a detailed model is underway in our laboratory.

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