Formation of polychlorinated dibenzodioxins, benzenes and phenols from thermal degradation of 2-chlorophenol promoted by CuCl2

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Introduction

Numerous studies have been conducted to better understand the formation processes of PCDD/Fs from chlorophenols as precursors. These investigations have shown that other organic byproducts, potentially toxic, could also be formed with PCDD/Fs. Born et al. have studied the formation of PCDD/Fs from isomers of monochlorophenol on model and real fly ashes using a fixed bed reactor [1,2]. The reaction products observed were carbon monoxide, carbon dioxide, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol, PCDDs, monobenzofuran, polychlorodiphenylethers, polychlorobenzenes, methylene chloride and tetrachloroethylene. By investigating the PCDD/Fs formation from ortho-chlorinated phenols and copper chloride, Ryu and Mulholland have identified the following products : chlorophenols, chlorobenzenes, PCDD/Fs, tetrachloroethylene and benzoquinones [3]. Hell et al. have studied the reaction of 2,4,6-trichlorophenol on real and model fly ash using a fixed bed reactor [4,5]. They have observed that polychlorobenzenes formation was favored when time and temperature were increased.

This work is aimed at highlighting the organic compounds formed by thermal degradation of 2-chlorophenol (2CP) promoted by copper chloride using sealed tubes as closed reactors. It is clear that this experimental method is unrealistic when compared to conditions of industrial processes. However, it enables us to use residence times (from minutes to hours) long enough to get more informations on reactions pathways responsible for PCCD/Fs formation and degradation which would be difficult to obtain from experiments with much smaller residence times.

Methods and materials

All chemicals were purchased from Aldrich, except octachlorodibenzodioxin (O8CDD) and 2-chlorodibenzodioxin supplied by Interchim. Copper chloride was provided as $CuCl_2$, $2H_2O$ (99.999%). It was mechanically crushed and selected in size before use (< 100 µm). All chemicals were used without further treatment. The purities were as follows : hexachlorobenzene (99%), O8CDD (99+%), 2-chlorodibenzodioxin (99+%), tetrachoroethylene (99+%) and 2CP (99+%). The experiments were carried out using sealed tubes made of Pyrex (15 cm long, 11 mm ID). The reactants, constituted of 5 mg of hydrated copper chloride and 2 µL of 2CP, were deposited into the tube, which was then sealed under atmospheric pressure. In order to avoid any loss of 2CP by evaporation, the bottom of each tube was cooled by liquid nitrogen while sealing. The thermal treatment was performed at 350°C for a residence time ranging from 5 to 120 minutes. Preliminary work allowed us to set temperature at 350°C as a maximum for PCDD formation. After treatment, each tube was rapidly quenched at room temperature and cooled at -15°C in order to condensate the organic products formed. The products were dissolved using 2 mL of dichloromethane. The use of larger amounts of solvent has shown that only a few percents of organics were not extracted by the first operation. Identification of products was performed by means of a HP-5890 gas chromatograph equipped with a 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 µm, 50 meters length (quantification) or 30 meters length (identification). Response factors for each identified compounds were determined by injection of solutions of commercial products. The response factor determined for the 2-chlorodibenzodioxin was applied to all the chlorinated congeners of PCDD/Fs.

Results and discussion

A great variety of species were obtained from the thermal degradation of 2CP promoted by $CuCl_2$: polychlorophenols, PCDD/Fs, polychlorobenzenes, tetrachloroethylene and tetrachlorocyclopentenedione. Except tetrachlorocyclopentenedione, all these products have been mentioned by the authors previously quoted in this paper. It should be noted that the percents given in each figure are expressed in mol % (molar ratio : 100 x moles of product / initial moles of 2CP).

Decay of 2CP and formation of polychlorophenols.

Figure 1 shows the decay plot of 2CP and formation plots of the polychlorophenols as a function of residence time at 350°C. 2CP exhibited a quick decomposition under the experimental conditions. Its complete depletion was observed for residences times lower than 10 minutes. The main polychlorophenols observed were the following ones : 2,4-, 2,6- and 2,4,6- trichlorophenol. The observation of these isomers was consistent with the results of Born et al.[2].

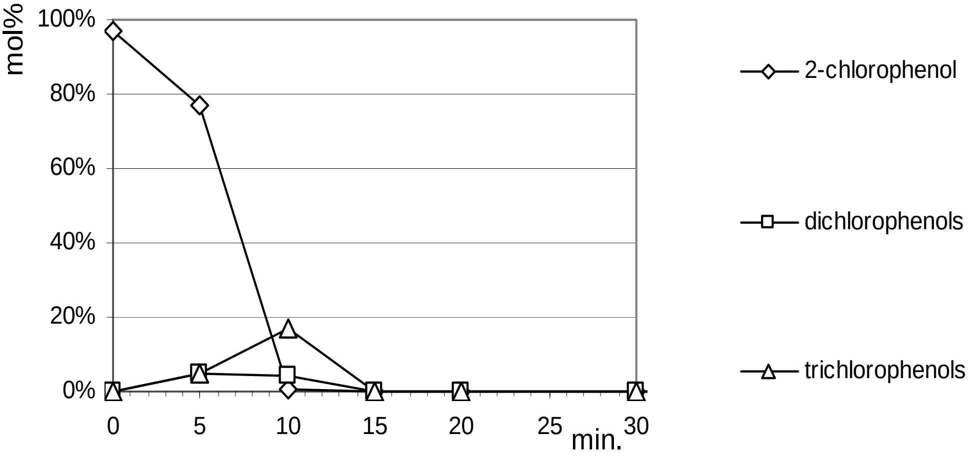
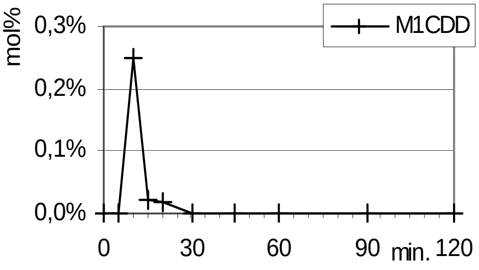


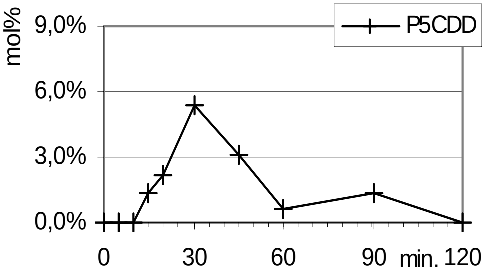
Figure 1 – Time evolution of yields of 2CP, dichlorophenols and trichlorophenols at 350°C.

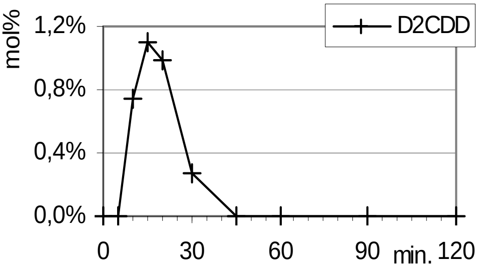
Formation of PCDDs.

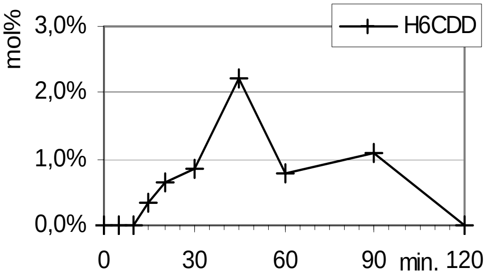
At 350°C, PCDDs were largely predominant over PCDFs. Due to their very low level of concentration, PCDFs were not quantified. This result is in agreement with the ones of Altwicker which has observed PCDF from chlorophenols only for temperatures upper than 350°C [6].

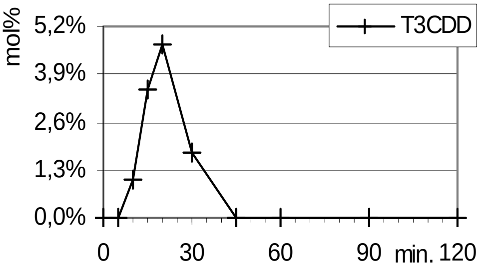
Tetra- and pentachlorinated congeners were the major PCDDs under our experimental conditions. Figure 2 shows that the lowest chlorinated congeners were formed prior to higher chlorinated ones, suggesting that lower chlorinated congeners were formed firstly and then progressively chlorinated. This result is consistant with work of Lomnicki and Dellinger about reaction of 2CP over CuO and silica surface [7]. They have suggested that dioxins formed resulted from competitive reactions of desorption and chlorination. In order to evaluate chlorination of dioxins under our experimental conditions, experiments with 2-chlorodibenzodioxin (about 1 mg) and hydrated copper chloride (5.0 mg) have been conducted at 350°C. Analysis of products resulting from thermal decomposition of 2-chlorodibenzodioxin highlighted higher chlorinated dioxins. Tetra- and pentachlorodibenzodioxins were the most abundant dioxins for a residence time of 30 min. (yield of 50 mol%). For a longer residence time of 60 min., octachlorodibenzodioxin was formed in small quantities with a yield of around 1 mol%.

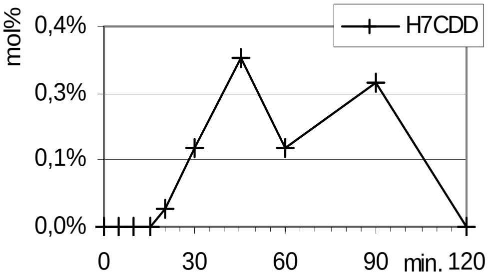












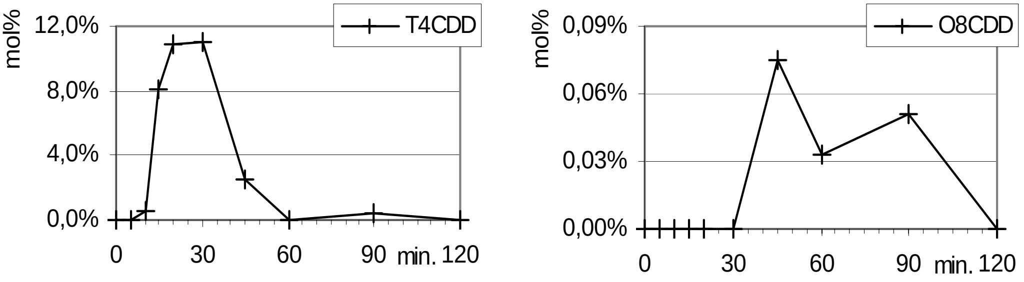


Figure 2 –Time evolution of yields of PCDDs at 350°C.

Formation of polychlorobenzenes.

Figure 3 gathers the time evolution plots of yields of polychlorobenzenes (only tri- to hexachlorinated benzenes were observed). Chlorobenzenes could be the products of chlorodehydroxylation of chlorophenols. However, hexachlorobenzene was mainly formed from 30 minutes when there were no chlorophenols left, attesting that the formation of chlorobenzenes could not only be explained by chlorodehydroxylation of chlorophenols.

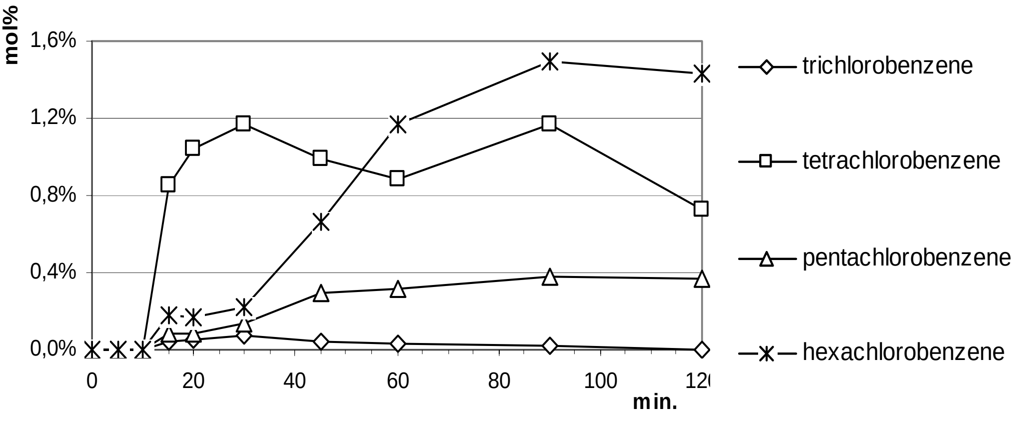


Figure 3 – Time evolution of yields of chlorobenzenes at 350°C.

Qualitative experiments were achieved to investigate the degradation pathways of dioxins. Thermal degradation of O8CDD (≈ 0.5 mg) in presence of copper chloride (5.0 mg) at 350°C for 30 min. produced large amounts of C_2Cl_4. Tetrachlorocyclopentenedione and hexachlorobenzene were also formed. Trichlorobenzene, pentachlorobenzene and tetrachlorocarbon were only observed in low concentrations. All of these compounds were not experimentally obtained when O8CDD was thermally treated without copper chloride. It is clear that polychlorobenzenes were thermal degradation products of dioxins. However they could be also formed directly and/or via condensations reactions of C_2Cl_4.

Formation of C_2Cl_4 and CCl_4.

Tetrachloroethylene and tetrachlorocarbon were identified by mass spectrometry but only semi-quantification of tetrachloroethylene has been performed due to its very high volatility.

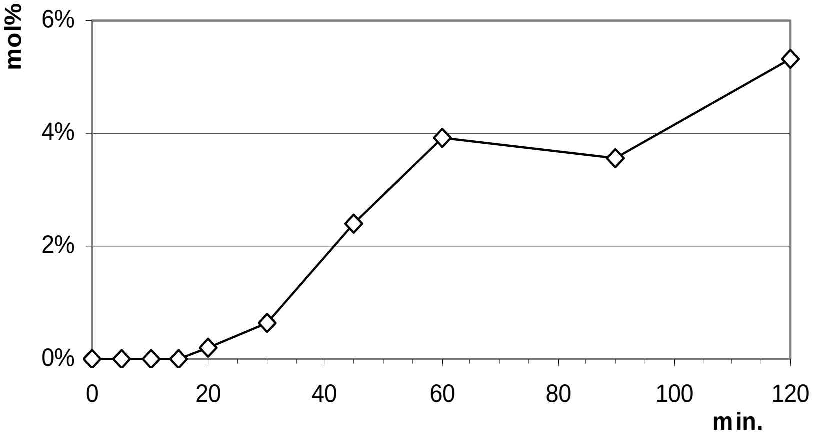


Figure 4 – Time evolution of yield of tetrachloroethylene at 350°C.

Tetrachloroethylene and tetrachlorocarbon have been observed simultaneously to chlorobenzenes during thermal degradation of O8CDD. Taylor and Dellinger have reported possible formation of hexachlorobenzene from C_2Cl_2 in the presence of $CuCl_2$ over the range 150-350°C [8]. In order to clarify possible reactions pathways between chlorobenzenes and C_2Cl_4, additionnal sealed tubes experiments were performed using about 1.3 mg of hexachlorobenzene and 5.0 mg of hydrated copper chloride and about 1.6 mg of C_2Cl_4 and 5.0 mg of hydrated copper chloride. At 350°C for a residence time of 30 minutes, there was no evidence of reactions pathways between hexachlorobenzene and C_2Cl_4. Only hexachloroethane was formed in small quantities (estimated to less than 0.5 mol%) by chlorination of tetrachloroethylene.

Organic carbon and chlorine balances.

Figure 5 shows the organic carbon and chlorine balances at 350°C as a function of residence time.

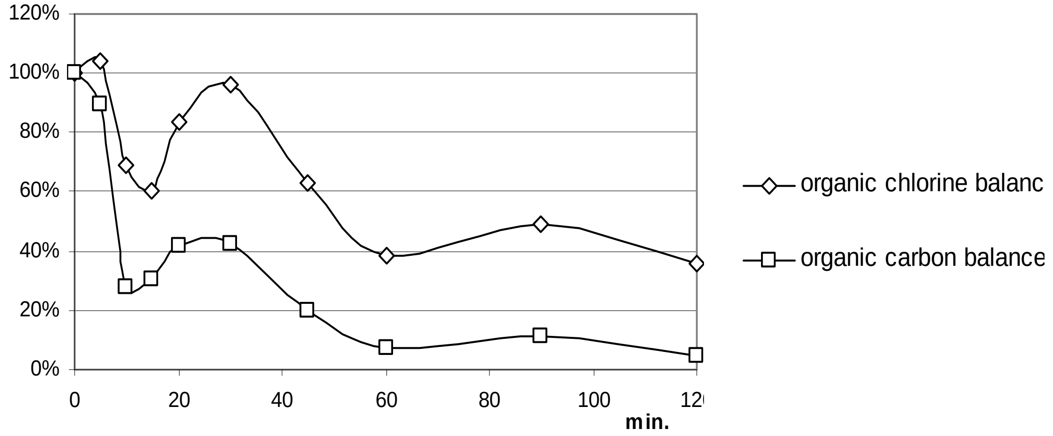


Figure 5 – Organic carbon and chlorine balances as a function of residence time at 350°C.

Organic chlorine balance was slighty higher than 100% for a residence time of 5 and 30 minutes indicating that chlorine from copper chloride was transfered from inorganic to organic matter. The deficit in organic carbon balance at 10 minutes was likely due to compounds which could not be extracted by dichloromethane. It is assumed that these species were strongly bounded to copper. In this way, Lomnicki and Dellinger have proposed reaction pathway for PCDD from 2CP which was including a carbon-centered phenoxyl radical adsorbed on copper and PCDD adsorbed on copper [7]. One or both of this adsorbed species could explain this lack in organic carbon balance.

Degradation of 2CP without copper chloride.

For comparison, thermal degradation of 2CP without copper choride has been also studied at 350°C under the same experimental conditions. As expected, 2CP was much less decomposed . Less than 50% of initial amount was only destroyed for a residence time of 2 hours while only 10 minutes were enough to completely destroyed 2-CP in the presence of $CuCl_2$. Dibenzofurans were formed predominantly (yield of 1.5 mol%), only non chlorinated to dichlorinated congeners were formed. Dibenzodioxins and monochlorodibenzodioxins were formed with a total yield of 1.0 mol%. Trace amounts of chlorophenoxyphenol have been identified (yield of 0.1 mol%). There was no evidence of the formation of polychlorophenols, polychlorobenzenes or tetrachloroethylene. The maximum yield for the sum of PCDDs when $CuCl_2$ was present is close to 20 mol% (fig. 6).

As $CuCl_2$ could be decomposed into CuCl at 350°C, further work will be focused on detailed role played by $CuCl_2$ and CuCl.

Conclusion and perspectives

Conluding remarks can be illustrated by figure 6. This figure shows time evolution of yields measured for the sum of chlorophenols, PCDDs and chlorobenzenes at 350°C in the presence of copper chloride.

The following reaction pathway could be proposed : first of all, 2-chlorophenol is chlorinated into polychlorophenols which form PCDDs via condensation reactions. Intermediates are probably strongly bounded to copper chloride. PCDDs are then chlorinated. As residence time increases, PCDDs are destroyed to form chlorobenzenes, tetrachloropentenedione, tetrachloroethylene and undoubtedly CO and CO_2. Some chlorobenzenes, formed for earlier reaction time, could proceed from chlorodehydroxylation of polychlorophenols. Additionnal experiments are actually performed with another promoters of reaction, such as CuCl, $FeCl_2$ and $FeCl_3$. We also planned to get more informations about species bounded to copper chloride by using infrared and Raman spectroscopy.

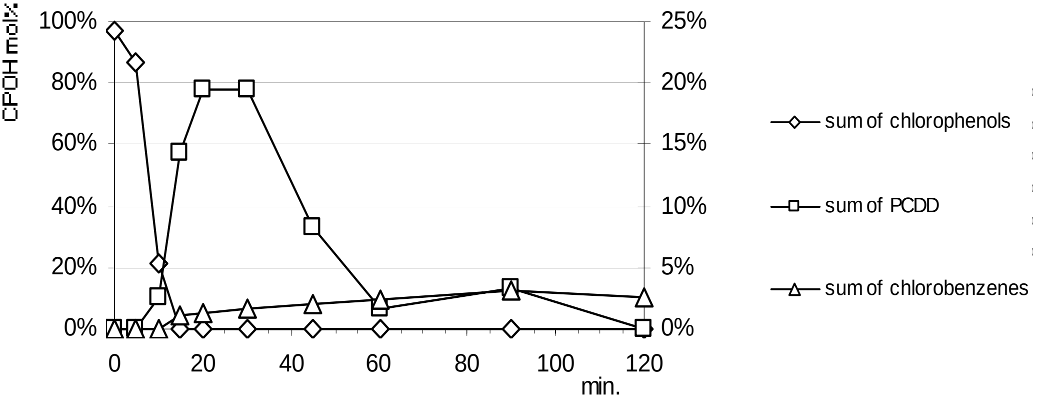


Figure 6 – Time evolution of yields of chlorophenols, PCDDs and chlorobenzenes at 350°C.

Acknowledgments

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