

EFFECT OF REACTION TIME ON FORMATION OF PCB, PCDD AND PCDF IN THE SYSTEM CONTAINING EXTRACTED FLY ASH, COPPER CHLORIDE, ACTIVATED CARBON, OXYGEN AND NITROGEN ATMOSPHERE

R. Grabic, V. Pekárek¹ and J. Ullrich¹

Chemical Laboratory of the District Public Health Department, Palackého 121, 73802 Fr_{dek}-Místek, Czech Republic

¹ Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Rozvojová 135, 16502 Praha 6, Czech Republic

Introduction

In our previous work¹ we reported on the effect of oxygen and 99.999% nitrogen on formation of the title compounds. We found that these substances are formed even in the nitrogen atmosphere, which we ascribed to the oxygen present on the surface of carbon, the amount of which well corresponded to the amounts of the title compounds formed in the pure nitrogen atmosphere. The present work concerns with the question whether the mechanism of formation of PCDD/F and PCB from precursors on the carbon can be separated from novosynthetic reactions which are expected to be slower processes.

Materials and Methods

Fly ash from fabric filter of MWI CKD-Purotherm (type PL8/100) was soxhlet-extracted with toluene for 24 h, then air dried and sieved to ≤ 0.25 mm particle size. Its main chemical components were: Al 5.96, C 8.24, Ca 4.4, Fe 9.8, Mg 0.38, Si 33.96, Zn 0.2 and water 2.41, all in wt.%. Cr 0.21, Ni 0.36, Cu 0.15 and Pb 0.45, all in mg/g.

Chemicals. N₂+1% O₂ mixture, N₂ ≥ 99.999 % purity (delivered by Linde T \ddot{U} V), CuCl₂·2H₂O, (Lachema p.a. purity), activated carbon for chromatography (Merck, 35-50 mesh ASTM), toluene, hexane and nonane (all Merck SupraSolv) were used.

Experimental arrangement. The well homogenized mixture of fly ash (0.44 g), CuCl₂·2H₂O (0.0645 mmol) and carbon (1.998 mmol) was heated at 300°C (the apparatus used is described in paper 1). Prior to experiment, the system was washed with a studied gas, the temperature of 300 °C was attained by fast heating in 5 to 7 min., then the time of the reaction was recorded. After completion of the reaction, the sample was cooled in 3 to 5 min to 200 °C. The flow rate of N₂ and N₂+ 1%O₂ mixture was 10 ml/min.

Analyses. Samples of fly ash were soxhlet-extracted with toluene, after HCl-pre-treatment. The extracts were concentrated to 10 ml of hexane. 20% and 50% aliquots were analyzed. Isotope dilution method was used for PCDD/Fs and non-ortho PCBs determination. Internal standard was applied for ortho PCBs determination. GCQ^(TM) (Finnigan MAT) gas chromatograph-ion trap mass spectrometer was used with Xcalibur 1.1 software version. MS/MS detection methods were used to achieve corresponding selectivity and sensitivity. Two columns with phases of different polarity were used for chromatographic separation of PCDD/Fs congeners (DB-5ms, 60 m length x 0.25 mm ID x 0.25 μ m film; DB-17, 30 m length x 0.25 mm ID x 0.25 μ m film).

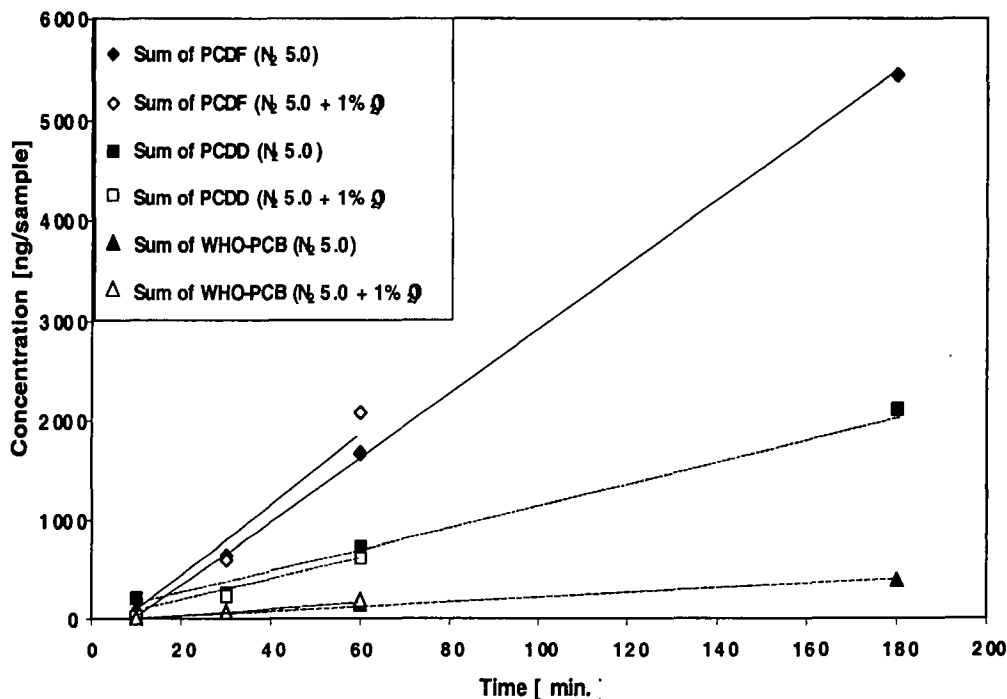
Results and Discussion

The effect of heating time on PCB, PCDD and PCDF formation in $N_2+1\% O_2$ and 99.999% N_2

Fig. 1 illustrates changes in WHO-PCB, PCDD and PCDF during 10 min to 3 h-heating .

The fastest concentration increase is observed for PCDF, the slower for PCDD, while the concentration of nonortho- and monoortho-PCBs increases most slowly. Essentially identical amounts of these compounds formed in both atmospheres confirm the assumption that the presence of oxygen in 10^{-4} - 10^{-6} percent range suffices for PCDF and PCDD formation. Remarkable PCDF concentration difference between 1% O_2 and 99.999 % N_2 found in our previous experiments² can be thus ascribed to the markedly smaller amounts of chlorine present now in the studied system as a precursor of novosynthetic reactions, as we have not used here KCl as reaction system component. Another reason to be considered seriously is the fact that in previous experiments $N_2+1\%O_2$ was moistened with water.

Fig. 1. Time dependence of PCDD, PCDF and WHO-PCB formation at 300°C



Effect of reaction time on isomer distribution

PCDF: For 5 min-reaction time, HxCDF(28%) and PeCDF(25%) prevail in congener profiles, while after 3 h-reaction prevailing isomers are HpCDF (29%) and HxCDF (28%). At the same time the isomeric pattern changes only little.

PCDD: The congener profile after 5 min shows PeCDD (33%) and TCDD (31%) as prevailing components ; after 3 h-reaction the predominant isomers are in particular OCDD (42%), HpCDD and HxCDD (both ca. 21%), while TCDD decreased to 3 per cent. The isomeric pattern undergoes significant changes in dependence on reaction time.

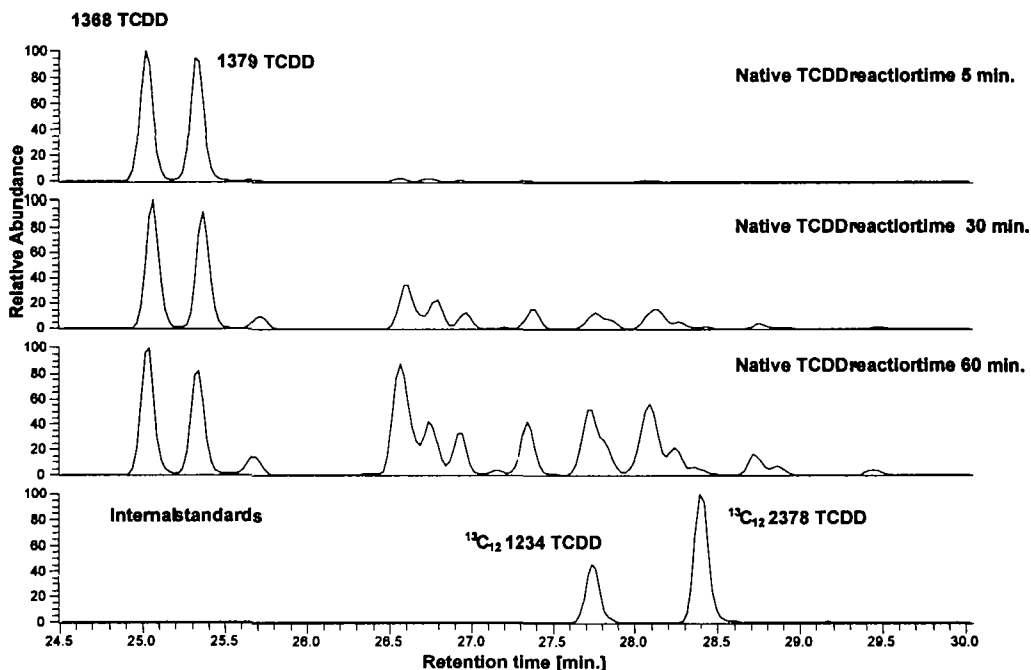
WHO-PCB: The isomeric pattern for both short and long-time thermal treatment is characterized by the greatest amounts of the most toxic PCB 126 (19.4-24.6%) and is shifting slightly with time toward the higher chlorinated isomers.

Mechanism of formation of isomers in dependence on time, represented by TCDD as an example

Fig. 2 shows the chromatograms of TCDD for 5, 30 and 60 min-reaction times.

The Figure documents that at the shortest reaction time, 1368 and 1379 TCDD are formed practically as sole reaction products. These isomers are present in considerable amounts also in all long-time experiments, but their relative proportion decreases with time. Other TCDD isomers are produced only after longer reaction times, the most toxic 2378 TCDD being detected in the greater amounts only after 1 h-reaction. We believe that the time-separated formation of both compounds might result from different mechanisms of their formation. It is worth mentioning that both isomers are formed practically selectively at the very moment at which the reaction temperature attains the temperature of their possible formation. In our opinion these compounds arise from precursors residing on the carbon of fly ash and on activated carbon. It is well known that polymeric disordered structure of carbon contains, according to Huang et al³, many organic precursors from which dioxin isomers can be first formed. The general process of carbon aromatization and novosynthetic reactions leading to dioxin formation are, therefore, much more time demanding, as indicated by the example just discussed. Analogous results were also obtained for other dioxin isomers, PCDF and PCB.

Fig. 2. Chromatograms of TCDD for different reaction times



FORMATION AND SOURCES - POSTERS

Acknowledgement

The authors acknowledge the support of the Grant Agency of the Czech Academy of Sciences No. A4072901/1999.

References

1. Pekárek V., Grabic R., Marklund S., Pun_ochá_ M. and Ullrich J. (1999) Effect of oxygen on formation of PCB and PCDD/F on extracted fly ash in the presence of carbon and cupric salt, Chemosphere, Special Issue Dioxin 1999, in print.
2. Grabic R., Marklund S., Pekárek V., Pun_ochá_ M. and Ullrich J. (1999) Organohalogen Compd. 41, 251-254.
3. Huang H., Biesemans M., Schoonenboom M. (1999) Organohalogen Compd. 41, 105-109.