

DIBENZOFURAN AND DIBENZODIOXIN PATTERNS FROM (CHLORO)PHENOLS IN COMBUSTION REACTIONS

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Introduction

For considerable time much attention has been given to the formation of PCDD/Fs upon incineration of esp. domestic and chemical wastes, with focus on the downstream areas (baghouse, electrostatic precipitator, in the temperature range of 300 ± 100 °C). Two distinct pathways have been advanced, viz. (I) formation via precursors, esp. chlorinated phenols, on a seconds timescale, and (II) so-called 'de novo' reaction, from carbonaceous material in the -trapped - flyash. The latter type of reaction, when studied in the laboratory over periods of hours, does yield PCDD/F congener patterns resembling those emanating from real combustors, but rates and yields are very low. So, the significance of this pathway in practice is still uncertain. Given the fact that PCDD/F patterns from incinerators vary little despite large differences in technology, feed composition, and carbon content of the ashes, it is furthermore questionable if two fundamentally different types of reaction (I), (II), can both be significant at the same time. However, type (I) model catalytic (lab) reactions lead to PCDD/F's greatly predominated by dioxins. This does not exclude the possibility that the very low concentrations of (chloro)phenols present amongst the 'PICs' of the primary combustion do react in this way, but this cannot possibly be the whole story. (Rapid) reactions of esp. phenols upstream, at higher temperatures (> 600 °C) are now getting more attention; their conversions can be thermal, of free radical nature, but heterogeneous catalysis may be important as well [1,2]. Based on the original work of Shaub and Tsang [3] - followed later on by experiments with 2,4,6-trichlorophenol [4] - this 'thermal' scenario (III) has been associated with production of dioxins, PCDDs, rather than PCDFs. Likewise, pentachlorophenol (PCP) yields OCDD, not OCDF. On the other hand, the thermal, gas-phase conversion (pyrolysis, or slow combustion) of phenol itself leads to dibenzofuran (DF), with negligible outputs of dibenzodioxin (DD) [5,6]. Remarkably, PCP upon slow combustion in excess toluene - a likely source of phenol - yielded 1,2,3,4-TCDF as the cross-condensation product, with very little, if any TCDD [7]. Regardless of mechanistic detail, condensation could involve ArO + ArO radical combination as in the case of DF from phenol [5,6,8], or might proceed via displacement of e.g. an *ortho* - Cl in a chlorinated phenol such as 2,4,6-TCP by an ArO radical [4]. We thought it worth while to study the slow combustion of (chloro)phenols in more detail, also in admixture, focusing on DD/DF outputs as a function of structure (degree of chlorination) and of conditions, with the special aim to understand mechanism(s) underlying the thermal scenario (III). When finishing our work, a paper was published also dealing with type (III) thermal conversion [9]. Some overall conclusions tally with

ours, but several key proposals are either too vague – so, not really a mechanism - or are in our view untenable.

Materials and methods

All experiments were conducted in a cylindrical, stirred-tank type reactor of 340 ml volume, placed in an electrically heated oven with temperature controlled systems. Gas flows of N₂ and O₂ (80 : 20 mol %) were regulated by needle valves and measured with capillary flowmeters. Liquid reactants were continuously introduced into the reactor by means of a calibrated motorized syringe pump via a gas-tight rubber septum and vaporized into the gas flow before entering the reactor.

Condensable products were collected in a cold trap filled with toluene with internal standard. Exit non-condensable gases were analyzed using a Packard series 428 GC-FID. Contents of a cold trap was quantified using a Hewlett Packard 5890 A GC-FID with a CP-SIL5-CB column. To identify unknown products a Hewlett Packard 5890 GC-MS was used. For more detail description of the equipment and methods see [5].

All chemicals were high grade commercial products.

Results and Discussion

First, we focus on the ‘base case’ - DF formation from phenol, via phenoxy radicals. Knowing that oxidative conversion of phenol in the liquid phase at $T < 200$ °C leads to all five possible *o*-, *p*-C combination products [10], it has to be understood why upon slow combustion at $T > 500$ °C DF is produced as about the only condensation product. Upon radical-induced gas-phase reaction between 300 - 550 °C, products other than DF - e.g. 2-hydroxy-diphenylether and 2,2'-dihydroxybiphenyl - are indeed obtained at the lower T end, but the picture rapidly shifts to DF at higher T. Based on insights into rates and mechanisms of tautomerization of intermediate PhO/PhO combination products, and using best available thermochemical data - entailing for example a difference in enthalpy of formation of phenol and its ‘*ortho*-keto’ tautomer of ca 15 kcal/mol [5] - this behaviour, as we will show, can be satisfactorily rationalized.

Introducing chlorine in phenol does not perceptibly change this picture (formation of essentially only DF's from *m*- or *p*-chlorophenols). Even if *ortho* positions are in part substituted by chlorine, DF's predominate greatly. So, the slow combustion of *o*-monochlorophenol gives the ‘expected’ DCDFs with much less (Cl-free) DD.

We confirm the observation of Sidhu et al. [4] that the slow combustion of 2,4,6-TCP leads to 1,3,6,8- and 1,3,7,9- TCDD, not to TCDF. Typical conditions: T between 500 and 650 °C, dwell times around 90 s, ArOH ca 1.7 mol% in (synthetic) air. When 2,4,6-TCP was reacted together with an equimolar amount of acetone, some TCDF was also seen, next to TCDD. We then turned to the reaction of phenol/TCP (ca 3:1). In addition to DF (from PhO + PhO) DCDD and DCDF as crossed products were obtained. Upon slow combustion of the two phenols diluted with benzene (which, on its own, gave a little phenol and traces of DF), DCDD outweighed DCDF (ratio ca 5:1). However, when the two phenols were fed in diluted with water, DCDF became more important than DCDD.

The slow combustion of PhOH/PCP (ca 60:1) diluted with water (58 mol%), at 550 °C (both phenols converted for about 50%) gave DF (5 % on the PhOH input) and 1,2,3,4-TCDF (1.7% on PCP in). Next to these results by our own GC analysis, a detailed PCDD/F MS-analysis on the tetra-to-octa congeners revealed also some TCDD (4% on TCDF) and smaller proportions

of higher chlorinated PCDD/Fs, see Figure 1. The congener distribution within discrete isomers reveals predominance of 1,2,3,4- chlorinated derivatives, but other isomers are also present, as we will show. Whereas Cl₅ -Cl₈ derivatives clearly stem from PCP, some (hydro)dechlorination is evident. Possible mechanism(s) for this will be presented. Our rationale for the formation of 1,2,3,4-TCDF is shown in Figure 2; the remarkable selectivity to this single DF congener can, will, be explained based on a thermochemical kinetic analysis of the discrete steps involved, and of *a priori* logical alternatives.

We wish to point out that results based on (model) experiments with phenols fully chlorinated at *ortho* positions - giving PCDD only - are not representative for real combustion processes. The organic structures in the waste will lead to aromatics, hence phenolics, to begin with benzene and phenol. (Poly)chlorinated phenols - whether already present in the feed or made 'under way', by catalyzed (oxy)chlorination - have a much better chance to undergo cross-coupling, leading to DFs rather than DDs. Water vapour appears to increase the DF/DD ratio. In this 'thermal' (partly catalyzed) scenario, generation of Cl₁ - Cl₃ DFs (with little DDs) is even more likely than that of the (toxic) Cl₄ -Cl₈ family. However, these 'pre'(toxic) furans/dioxins could be subject to further chlorination in the APC devices, while any remaining (chloro)phenols yield PCDDs concomitantly. We have conclusively demonstrated that upon feeding a mix of phenol vapour and chlorobenzene in excess air to a fixed bed of (real) MSW flyash at T between 300 and 500 °C, the former reacted to completion at 350 °C while the latter was still at its onset at 500 °C [11]. So, simple, volatile aromatics without a means for effective chemisorption - benzene, lower chlorinated benzenes - do not act as precursors in the rapid, flyash-mediated PCDD/F formation. Depending on conditions, esp. the catalytic activity of the ash and the carbon content/type, 'de novo' formation of PCDD/Fs may contribute to some extent in real combustors. If so, we wish to point out also that the mechanisms, pathways, leading from macromolecular, polyaromatic carbon to PCDD/F (scenario II) may altogether not differ very much from those of the 'precursor' scenario (I). Published results obtained with mixtures of regular and isotopically labeled carbons tally with formation of (partially chlorinated) biphenyls and/or DFs first, which then can undergo further oxidation and (oxy)chlorination, whereas DDs, at least in part, are formed via mononuclear species, especially phenols.

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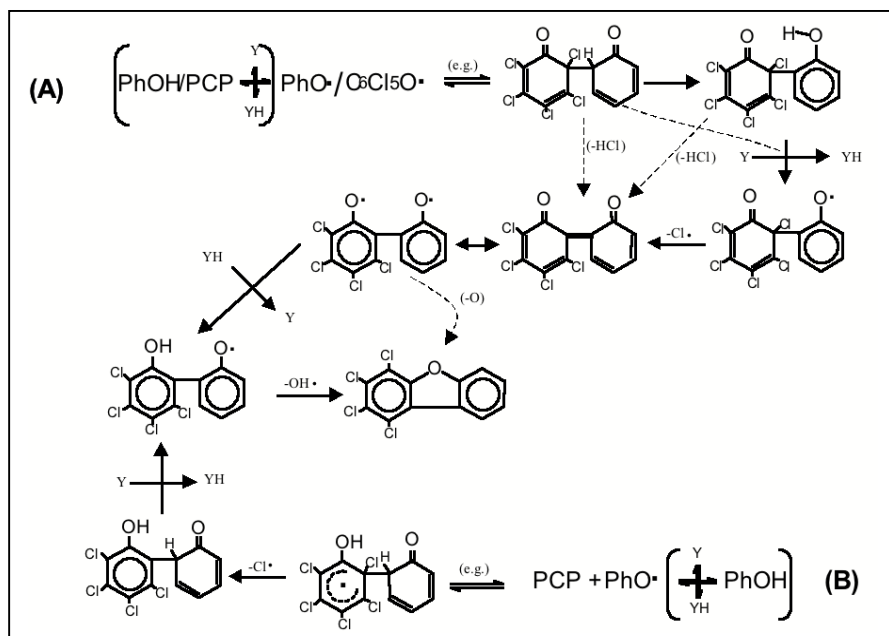
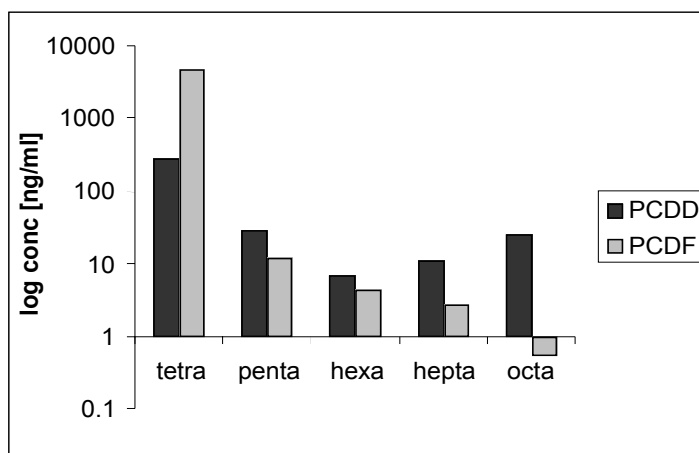
Figure 1. PCDD/Fs distribution pattern for the slow combustion of PhOH/PCP (*Note the LOG scale*)

Figure 2. Formation of 1,2,3,4-TCDF from phenol and PCP

(A) via radical cross combination

(B) via radical/molecule Cl-displacement

Y = e.g. ArO·, HO₂·, O·, ·OH,



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