Gas-Phase Chemistry of Chlorinated Phenols − Formation of Dibenzofurans and Dibenzodioxins in Slow Combustion

Izabela Wiater-Protas[a][‡] **and Robert Louw***[a]

Keywords: Dioxins / Gas-phase reactions / Reaction mechanisms / Thermochemistry

The effects of the introduction of chlorine substituents onto phenol on the rates of, and products from, their slow combustion at 500–550 °C are described. Competitive experiments showed that phenol, *ortho*-chlorophenol, 2,4,6-trichlorophenol and pentachlorophenol differ little in their overall rates of conversion – mainly into CO/CO_2. Provided that an *ortho*-H moiety is available, chlorinated dibenzofurans (DFs) rather than dibenzodioxins (DDs) are formed as (cross)condensation products. Overall rates of formation, through (reversible) *ortho*-C, *ortho*-C combination of two (chloro)phenoxy radicals, are discussed on a thermokinetic basis, using new data relating to the O–H bond strengths in the target phenols. Chlorinated DDs are the predominant condensation products only when the *ortho* positions are fully chlorinated, a situation insignificant during thermal combustion of real waste. The question of mechanism is merely of scientific interest, but thermokinetic evaluation together with an experimental check on the behaviour of 'triclosan' – a model *o*-hydroxy-diphenyl ether intermediate – provides the conclusion that both radical/radical combination and radical/molecule reaction may be involved in this case, with displacement of *o*-Cl by a (chloro)phenoxy radical. As chlorinated DFs and unconverted (chloro)phenols in real incinerators are subject to further reaction – (oxy)chlorination of the DFs, and condensation of the phenols to DDs – catalysed by ashes in the pollution control devices, the mixture of polychlorinated DFs and DDs commonly found in incinerator emissions can be viewed as arising from (chloro)phenols as the only important precursors.

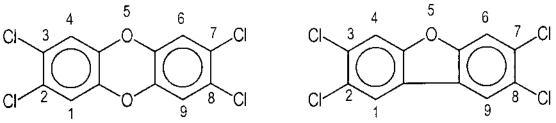
Introduction

"Of the several groups of chlorinated materials found in the environment, none has given rise to more public concern than 'dioxin' "[1] − the set of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) found in, and emitted from, a variety of processes including combustion and metallurgy.[2] Much attention has been devoted to the processes of combustion of municipal and chemical wastes. Broadly, two types of formation reactions appear to be involved:[3]

(1) at temperatures > 500 °C, over a timescale of seconds, in and directly after the primary combustor, especially from (chloro)phenol precursors. Homogeneous gas-phase (radical) reactions are important, but heterogeneous catalysis − by ashes − plays a part as well;[3,4]

(2) "de novo" formation from carbonaceous material in the ashes collected downstream in control devices (ESP, baghouse), over a timescale of hours, typically between 250−400 °C.[3,5]

The levels of the "dirty 17" congeners, with at least the 2-, 3-, 7-, and 8-positions halogenated (Figure 1) − focal in "dioxin" analysis and monitoring − at the end of stage (2) are considerably higher than those measured after stage (1).[6] This is at least in part due to catalytic conversion of certain "products of incomplete combustion" surviving from stage (1).[7,8]



2,3,7,8-TCDD **2,3,7,8-TCDF**

Figure 1. Examples of chlorinated dioxins (DDs) and dibenzofurans (DFs).

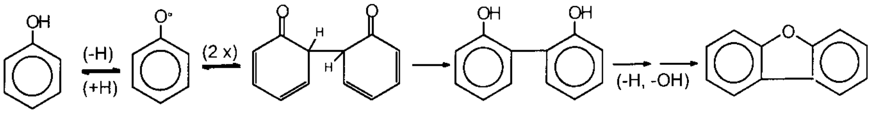
With reactive phenols apparently playing important roles throughout, a proper understanding of their rates of reaction, products, and mechanisms under well-defined and relevant conditions is of key importance. We have recently reported on the base case of the slow (partial) combustion of phenol itself. At 500−600 °C, dibenzofuran (DF) is by far the most important condensation product. The mechanism, summarised in Scheme 1, involves reversible combination of 2-phenoxy radicals, enolisation and loss of the elements of water, and the results have been quantitatively explained on the basis of thermochemical kinetics.[9]

With chlorinated phenols the same possibilities exist, provided that *ortho*-hydrogen is available. Thus, from *o*-chlorophenol, the major product is 4,6-dichlorodibenzofuran.[10] Remarkably, in the slow combustion of pentachlorophenol in a large excess of toluene − an in situ source of phenoxy radicals − the cross-condensation product is 1,2,3,4-tetrachlorodibenzofuran, with only traces of the corresponding dibenzo-*p*-dioxin.[11] The *ortho*-H present on

---

[‡] On leave (through TEMPUS grant IMG-97-Pl-2135) from Jagiellonian University, Faculty of Chemistry, Kraków, Poland

[a] Center for Chemistry and the Environment, Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
POB 9502, 2300 RA Leiden, The Netherlands
E-mail: R.Louw@chem.leidenuniv.nl



Scheme 1. Formation of dibenzofuran by dimerisation of phenoxy radicals.

one side of the radical/radical combination still allows condensation, with formation of HCl.[12] However, when *ortho*-H is totally absent, the picture changes completely: the slow combustion of, for example, 2,4,6-trichlorophenol (TCP) by itself produces tetrachlorodibenzo-*p*-dioxin (TCDD), with little if any PCDF.[12,13]

Mechanisms are still speculative. As early as 1983 Shaub and Tsang (ST) proposed a model for combustion of 2,4,6-TCP in which displacement of *ortho*-Cl in a TCP *molecule* by a trichlorophenoxy radical, reaction (a) in Scheme 2, was the key (slow) step.[14]

The resulting phenol derivative A was believed to lose the elements of HCl easily, to form a tetrachlorodioxin product. Later, slow combustion experiments by Sidhu and Dellinger (SD)[13] confirmed formation of TCDD − two isomers, due to a Smiles rearrangement (B) $\rightleftharpoons$ (B′) $\rightleftharpoons$ (B″); see Scheme 2 − but rates were much higher than those inferred from the ST model. To eliminate this discrepancy, SD chose to adjust the thermochemistry of reaction (a) (Scheme 2), by reducing the activation energy from 26 to 19.5 kcal/mol. Given the results of our study on the base case, reaction (1),[15] and of its reverse, rection (−1),[16] such a low barrier for reaction (a) seems untenable.

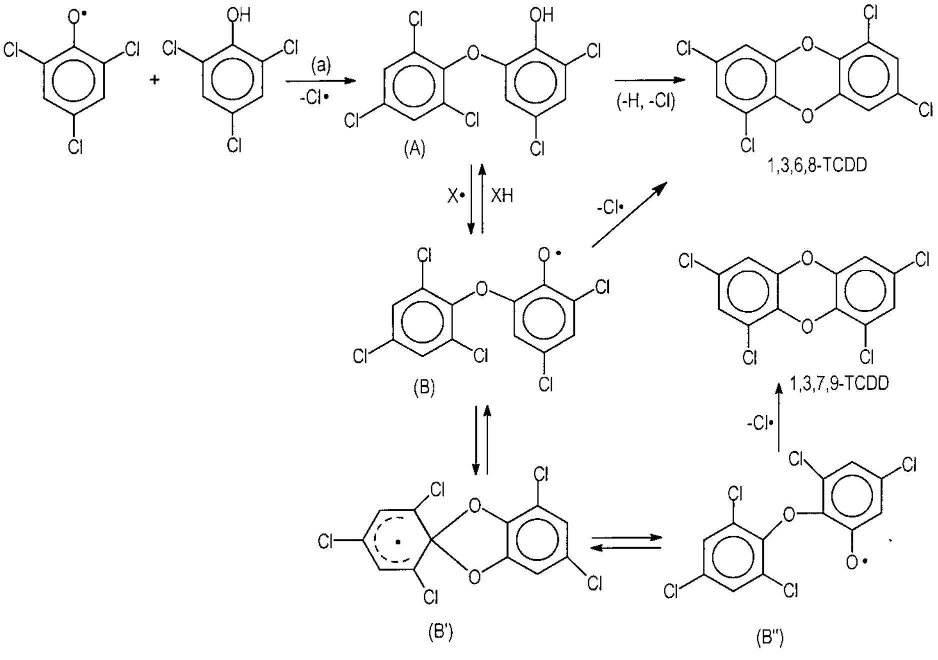
$$PhO\cdot + PhCl \rightarrow PhOPh + Cl\cdot;\ \log(k_1/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 8.7-24.5/2.3RT \quad (1)$$

On the other hand, Bozzelli et al.[17] performed calculations from which they concluded that the thermochemistry of reaction (a) differs greatly from that of reaction (1): from firmly endothermal (13−17 kcal/mol) for (1) to almost thermoneutral for (a). Such a drastic change − implying an unprecedented *change in the order of bond strengths* for Ar−Cl vs. Ar−OPh arising from introduction of chlorine substituents − is very unlikely, though. In a recent analysis, using newly obtained data on O−H bond strengths in chlorinated phenols,[18] we concluded that the endothermicity of reaction (a) should be equal to, if not somewhat larger than, that of base case (1).[19,20] If that is true, ST-type radical/molecule displacements (involving *ortho*-chlorine) should be quite slow in any case. It then remains an open question whether PCDDs − if formed in the gas phase from (poly)chlorinated phenols − arise from aryloxy/aryloxy radical condensations or not.

To help clear up this matter, we studied the following model reactions, for the reasons given:

(a) reactivity and fate of a model compound − ‘triclosan’ (T) − representative of the A-type intermediate (Scheme 2) as a possible clue to the operation of the ST mechanism;

(b) slow combustion of phenol/pentachlorophenol, for comparison with the earlier ‘toluene’ experiment;[11]



Scheme 2

(c) slow combustion of *ortho*-chlorophenol (*o*-CP) − also in competition with phenol − to determine levels and ratios of (chlorinated) DFs and DDs; and

(d) slow combustion of 2,4,6-trichlorophenol (together with phenol), to compare features with those of (b) and (c) and those in the literature.[13,14]

The aim is not only a better understanding of the rates and mechanisms in the gas-phase condensation of phenols as a function of chlorination; the product compositions may also indicate what will happen in real (waste) combustion, which should help to clarify and detail overall pathways to PCDD/Fs.

Results

(a) Triclosan

Triclosan (T) − see Figure 2 − together with phenol in benzene (molar ratio 1:5:200) was treated in an excess of synthetic air (N_2:O_2 = 80:20, O_2:phenol ≈ 135:1) at five temperatures ranging from 470−570 °C, with dwell times of ca. 42 s. Only at the lower temperatures mentioned could traces of T (< 0.2%) be found back in the condensed product mixture. On the other hand, conversions of phenol were low to modest: from at best a few percent at 470 °C to about 30% at 570 °C. As expected, DF was the major product from phenol, with selectivities up to ca. 50%; T was converted mainly into DCDD, with typical selectivities of more than 90%. Although seen as one (GC) peak, it was very probably a mixture of the 2,7- and 2,8-isomers.[21] Yet another product formed was benzobisbenzofuran (Figure 2), apparently by cross-combination of phenol and an intermediate prior to DF.[9] It amounted to ca. 1 mol % relative to DCDD.

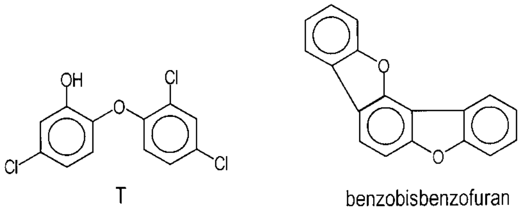


Figure 2. Structures of T (triclosan) and benzobisbenzofuran.

These observations confirm that T-type phenols, *o*-hydroxydiphenyl ethers bearing at least one *ortho*-Cl in the "other" ring, are unstable if formed as intermediates, and will not survive at all under conditions of (slow) combustion at temperatures >500 °C.

(b) Phenol/Pentachlorophenol

Employment of a feed mixture consisting of PCP/phenol/water in a 1:60:82 molar ratio, synthetic air (80:20 N_2/O_2, ratio O_2/phenol = 5.5), slow combustion at 550 °C and a dwell time of 77 s gave 52% conversion of PCP, whereas 49% of the phenol was consumed. The key gaseous products, CO and CO_2, amounted to 130 and 55 mol %, respectively, relative to consumed phenol, showing that slow combustion is indeed a major process. The yield of dibenzofuran DF was 5.8 mol % relative to input of phenol (which means a selectivity of 23.5% expressed in equivalents of phenol consumed). As well as DF, one other compound was produced; this turned out to be 1,2,3,4-TCDF. This cross-condensation product represented 3.1% of the converted PCP. OCDD, the product expected from reaction of two PCP moieties, amounted to only 0.37 mol % relative to 1,2,3,4-TCDF. In fact, we have used a large excess of phenol just to prevent formation of this "dirty" congener. Other PCDD/F congeners were present but at much lower concentrations. Figure 3 gives a (logarithmic!) plot. Of the TCDF group, the 1,2,3,4-isomer represented 98%; 1,2,3,4-TCDD was ≈ 100 times less abundant.

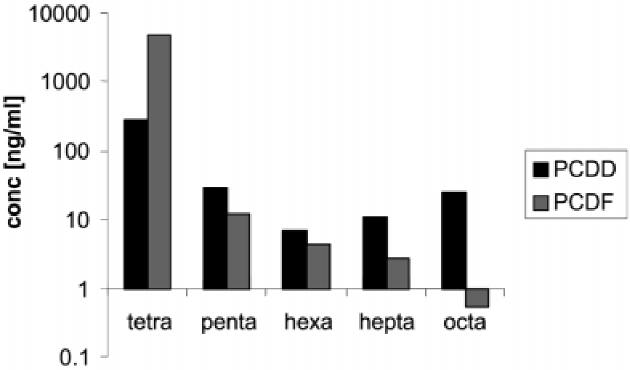


Figure 3. PCDD/Fs from slow combustion (550 °C) of pentachlorophenol and phenol (1:60).

In the small quantities (less than 1%) of higher-chlorinated congeners, formed the PCDDs are relatively more important than PCDFs. OCDF is only ca. 0.008 mol % relative to TCDF.

Several other (chlorine-free) products have been identified, with yields 1−2 orders of magnitude smaller than that of DF: isomers of benzobisbenzofuran, hydroxy derivatives of DF, xanthone and benzonaphthofuran, just as from the slow combustion of phenol alone.[9] After further concentration of the product mixture, a plethora of trace by-products including phenanthrene and other PAHs, and methyl derivatives of DF and DCDF was seen.

(c) *ortho*-Chlorophenol

To learn about the role of *ortho*-chlorine in determination of the product composition − especially the DD/DF ratio − in a relatively simple case, the slow combustion of *ortho*-monochlorophenol (*o*-CP) was studied, also in competition with phenol.

In an experiment with *o*-CP only − at 550 °C, dwell time 79 s [feed ratio: *o*-CP/water/O_2/N_2 = 1:0.4:7:35] − conversion was 39%. Next to CO and CO_2 (ratio ca. 5:2), the major condensation product was 4,6-DCDF (selectivity ≈ 2%), with smaller proportions of DD (12% relative to the DCDF) and 4-MCDF. This result can be compared with those obtained by Born,[10] who added nitromethane (ca 12% relative to the chlorophenol) in an effort to intensify radical formation. At the same temperature, with a residence time of ca. 6 s, the phenol conversion amounted to ca. 80%, the selectivity for 4,6-DCDF was ca. 2.3% and the DD:DCDF ratio was 0.21. Born also studied this reaction at lower temperatures, and noted that the latter ratio went down, to 0.06 at 500 °C, for example; this temperature effect is discussed in the final section.

Next, five competition experiments (1:1 with phenol; with 20−40 fold excesses of benzene) were performed at 500 °C with dwell times of 46 s, with quite comparable results. Typical conversions were: *o*-CP 42%, PhOH 38%, showing that *o*-CP reacts with a marginally higher rate than phenol. Now, DF (from phenol) is by far the most important condensation product, formed with a selectivity of ca. 6% based on phenol. 4-MCDF, the product expected from cross-condensation, amounted to 33 +/− 2% relative to DF. The 4,6-DCDF/DF ratio is (only) 0.025, whereas the DD/DF ratio is ≈ 0.035. Note that this DD level is now higher than that of DCDF and also some ten times larger than that obtained from experiments with phenol only;[9,18] this means that nearly all of it must have been formed from *o*-CP.

The presence of *ortho*-Cl is instrumental in forming DD, and this is underscored by results from the slow combustion of *para*-chlorophenol: here, the (chlorinated) DFs are formed without any detectable amount of DD. [In this experiment *p*-Cl-phenol was diluted with a 47 molar excess of benzene; at the temperature used (570 °C) and with a residence time of 44 s its degree of conversion was ≈ 85%]. Benzene was not completely inert under these conditions: the output of phenol was ca. 0.8% relative to the benzene input, meaning that it was 2−3 times the output of *p*-Cl-phenol. Logically, as well as 2,8-DCDF, 2-MCDF and DF were also formed, in a ratio of about 1:2:1. DD was below the detection limit.

In summary, DFs prevail, and formation of MCDF and DCDF can be explained just as DF from phenol, Scheme 1. The mode(s) of formation of DD from two *o*-CP entities are dealt with in the Discussion Section.

(d) 2,4,6-Trichlorophenol

The slow combustion of TCP was investigated under conditions similar to those mentioned in the previous sections, meaning also that conversions, though substantial, were still incomplete, allowing semiquantitative (thermo)kinetic analysis. Experiment I (Table 1) is a competition experiment with phenol, together with benzene as a diluent. When repeated three times, almost the same results were obtained. TCP turned out to be a little more reactive than phenol.

DF was found at an expected level, with DCDF and DCDD (in a ratio of ≈ 1:5) as the cross-condensation products, although at lower levels. TCDD, the product expected from TCP alone,[13,14] was even less abundant, barely detectable by our standard GC analysis.

If benzene was left out and water used instead − experiment (II) (Table 1)− the (relative) reactivity of the two phenols did not change. The output of DF was also comparable: in (I) the 0.026 mmol/h represent 15% of the converted phenol, while the 0.11 mmol/h from (II) amounts to ca. 17.5%. There is a considerable change, however, in the composition of the cross-combination product: the DCDF:DCDD ratio is now about 10:1, up by a factor of 50 from the 1:5 of exp. I. A plausible explanation is given in the Discussion Section.

In exp. III, no phenol was used, acetone serving as a carrier and "co-fuel" for TCP. The only detectable condensation products were TCDD (two isomers in near-equal abundance, beyond doubt the 1,3,6,8- and 1,3,7,9-isomers, compare Scheme 2) and TCDF (one-third of the amount of TCDD, isomer composition as yet unknown) − a result not unlike that observed by Sidhu et al.[23] in the combustion of 2,4,6-TCP with added hexane.

Discussion

(i). First we shall analyse the observations with *o-chlorophenol*; beginning with the formation of chlorinated DFs.

Table 1. Slow combustion of 2,4,6-trichlorophenol

No.		I	II	III
T (°C)		500	550	550
res time (s)		45	45	79
INPUT[a] [b]	PhOH	0.780 [44%]	2.49 [51%]	−
	2,4,6-TCP	0.253 [54%]	0.308 [62%]	4.61 [40%]
	Other	21.0 (benzene)	1.19 (water)	3.94 (acetone)
OUTPUT[a] [c][d]	DF	0.026 (≡1)	0.111 (≡1)	−
	DCDD	(0.0144)	(0.00045)	nd
	DCDF	(0.0029)	(0.0045)	(≈0.075)
	TCDD	(≈0.0008)	(≈0.0008)	0.008(≡1)
	TCDF	nd	nd	(0.375)
	$CO + CO_2$ (CO/CO_2)	≈1.0 (≈1:1)	≈4 (≈1:1)	≈12 (≈3:1)

[a] in mmol/h, carrier N_2/O_2 (4:1), total for I and II ≈430 mmol/h and for III ≈260 mmol/h [b] between brackets[]: percentage converted [c] between brackets(): relative amounts [d] nd- below detection limit

Although the molar ratio in the competition experiments of *o*-CP with phenol was close to one, the levels of the condensation products DF, MCDF and DCDF decreased quite markedly from 1 to 0.35 to 0.025, respectively. If it is assumed that the corresponding phenoxy radicals are present in (pseudo)equilibrium with the phenols,[9] the recently obtained data on O−H bond strengths[19,20] imply a larger (e.g., sixfold) ratio of [ClPhO·]/[PhO·] compared with that of the parent phenols.[24] In the model Equations (2) − (4), the ratio of the overall rate constants, then, is $k_2{:}k_3{:}k_4 \approx 1{:}0.06{:}0.0007$.

$$2\,\mathrm{PhO}\cdot \rightarrow\rightarrow \mathrm{DF}\ (\text{cf. Scheme 1}) \tag{2}$$

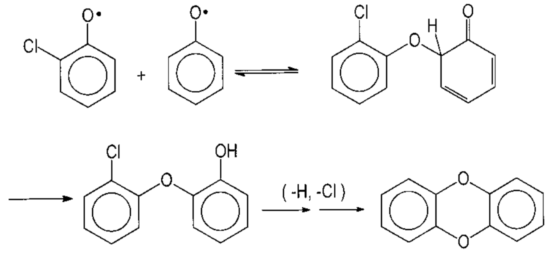
$$\mathrm{PhO}\cdot + o\text{-}\mathrm{ClPhO}\cdot \rightarrow\rightarrow \mathrm{MCDF} \tag{3}$$

$$2\,o\text{-}\mathrm{ClPhO}\cdot \rightarrow\rightarrow \mathrm{DCDF} \tag{4}$$

Accepting $k_2 = 3 \times 10^8$,[15] k_3 is $\approx 10^7$ and $k_4 \approx 10^5$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$.

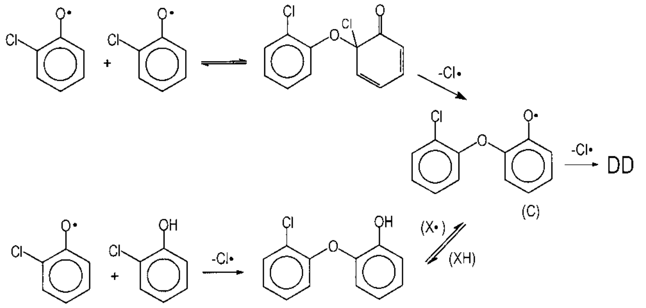
The reason(s) for this downward trend could be a decreasing *o*-C, *o*-C bond strength[25] and/or a decreasing efficiency for further reaction (enolisation, for example) in the (reversibly formed) dimers, due to the introduction of one or two *ortho*-chlorine atoms. The statistical factor [of four, comparing reaction (4) with reaction 2] offers only a partial explanation. Anyway, with the above set of data and assumptions, it is possible to model (equilibrium) concentrations for both PhO· and *o*-ClPhO· :[26] for the specific example, with (average) concentrations of the two phenols of ca. 1×10^{-5} M, [PhO·] is ca. 4×10^{-9} M, while that of *o*-ClPhO· is 6 times larger, implying a ratio of [*o*-ClPhO·]/[*o*-ClPhOH] $\approx 2 \times 10^{-3}$.

Whereas formation of the (chlorinated) DFs can be fully explained by aryloxy/aryloxy radical condensation (reactions 2−4), the pathway(s) to DD require special consideration. With *o*-CP only, the DD output was about an order of magnitude smaller than that of DCDF. From the competition runs with phenol, relatively more DD was obtained, which can be explained as follows (Scheme 3).



Scheme 3. Formation of dibenzo-*p*-dioxin by condensation of chlorophenoxy and phenoxy radicals.

For DD to arise from *o*-Cl-phenol *only*, pathways involving H-abstraction or transfer (enolisation) must be absent. Below, a quantitative analysis is made of two alternatives: radical/radical combination with loss of a chlorine atom, and radical/molecule reaction with net displacement of a chlorine atom (cf. the original proposal by Shaub and Tsang[14]) (reactions 5 and 6; Scheme 4).



Scheme 4. Formation of dibenzo-*p*-dioxin from *o*-chlorophenol.

$$2\,o\text{-}\mathrm{ClPhO}\cdot \rightarrow \mathrm{Cl}\cdot + o\text{-}\mathrm{ClPhO\text{-}PhO}\cdot\ (\mathrm{C})\ (\rightarrow \mathrm{DD} + \mathrm{Cl}\cdot) \tag{5}$$

$$o\text{-}\mathrm{ClPhO}\cdot + o\text{-}\mathrm{ClPhOH} \rightarrow \mathrm{Cl}\cdot + o\text{-}\mathrm{ClPhO\text{-}PhOH},\ \text{etc.} \tag{6}$$

Scheme 4 also shows that the key intermediate radical (C) can in principle be formed by either route: radical/radical (5) or radical/molecule (6), if interconversion (equilibration) between the intermediate *o*-(*o*-chlorophenoxy)phenol and its radical (C) is assumed. The step from (C) to DD is firmly endothermic; by analogy with base case (1) by ca. 17 kcal/mol, meaning that this reaction is not very fast. This leaves some room for bimolecular reaction, especially with (chloro)phenoxy radical, to produce trinuclear species of the benzobisbenzofuran type.[9,16]

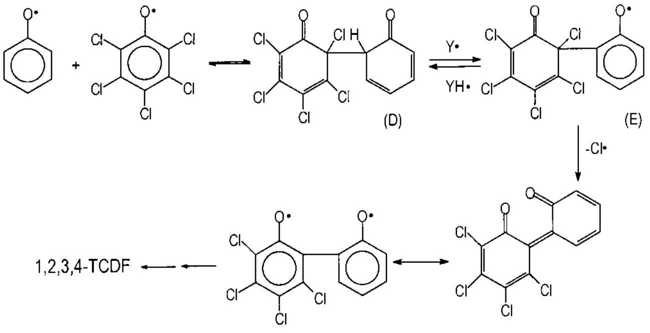
Applying the best available thermochemistry,[27] the reaction (5) to give Cl· and C is ca. 20 kcal/mol endothermic. To cover the experimental rate of formation of DD from *o*-CP (ca. 10^{-11} $\mathrm{M}\,\mathrm{s}^{-1}$)[28] would require $k_5 \approx 2 \times 10^4\ \mathrm{M}^{-1}\mathrm{s}^{-1}$, feasible with $E_5 = 20$ kcal/mol, $\log A_5 / \mathrm{M}^{-1}\mathrm{s}^{-1} = 10.0$.

For alternative (6), the concentrations of ClPhOH and ClPhO·, together with the rate parameters measured for the reaction (1) base case ($\log A/\mathrm{M}^{-1}\mathrm{s}^{-1} = 8.7$, $E = 24.5$ kcal/mol), *also* result in a modelled rate of ca. 10^{-11} $\mathrm{M}\ \mathrm{s}^{-1}$ [28] at the given temperature of 773 K. On this basis no final conclusions can be drawn − or in other words, both mechanisms may be followed under the given slow combustion conditions . Note that reactions (5) and (6) both have substantial (well over 20 kcal/mol) activation barriers to displacement of the chlorine atom. In this context, it is of interest that Born noted an increasing [DD]/[DCDF] output ratio with increasing temperature,[10] which corresponds to a temperature coefficient of ca. 30 kcal/mol. In all likelihood, the [ArO·]/[ArOH] pseudo-equilibrium ratio should rise with temperature, which would then disfavour reaction (6) in comparison with reaction (5). Furthermore, one factor in play may be that condensations involving *o*-H to DFs (hence, with enolisation possible) may proceed with much smaller activation barriers than those associated with removal of Cl.

(ii). At this point it is appropriate briefly to comment on the results with *triclosan* (Results, section a). This model compound easily reacts to give the corresponding dibenzodioxin with loss of the elements of HCl, which proves that this part of Shaub and Tsang's assumptions was correct. The oxy radical derived from T – expected to be in pseudo-equilibrium with T itself – will react in the same way as (C) (Scheme 4) and as (B)/(B′)/(B″), Scheme 2.

(iii). The results with *phenol + PCP* show that cross combination even of a fully chlorinated phenol entity with a partner containing *ortho*-hydrogen moieties results in a (PC)DF rather than a DD product. Its formation can be qualitatively understood both in terms of condensation of PhO· with the radical of PCP (hereafter denoted PCPO·) and by reaction of PhO· with PCP itself.[12]

The PhOH/PCP ratio was ≈ 60; results relating to anisole thermolysis[20] suggest a 3.9 kcal/mol difference in O–H bond strength, implying a tenfold preference for PCPO· over PhO·. If it is accepted that TCDF is formed by cross-combination of the two radicals (reaction 7; Scheme 5), the product ratio DF/TCDF of 170, together with the calculated radical concentrations, then implies $k_7 = 0.035 \times k_2$ or $\approx 10^{7.0}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.[29]



Scheme 5. Condensation of phenoxy and pentachlorophenoxy radicals.

$$\mathrm{PhO\cdot} + \mathrm{C_6Cl_5O\cdot}\ (\mathrm{PCPO\cdot}) \rightarrow (-\mathrm{Cl,H,O}) \rightarrow \text{1,2,3,4-TCDF} \qquad (7)$$

$$\mathrm{PhO\cdot} + \mathrm{C_6Cl_5OH}\ (\mathrm{PCP}) \rightarrow (-\mathrm{Cl,\ HOH}) \rightarrow \text{1,2,3,4-TCDF} \qquad (8)$$

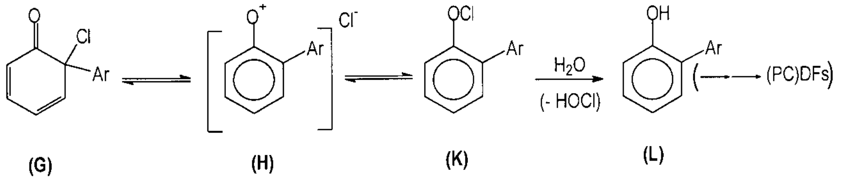
If, on the other hand, reaction (8) is viewed as responsible, the respective concentrations together with proper rate parameters – $\log A_8/\mathrm{M}^{-1}\mathrm{s}^{-1} = 9$, $E_8 = 28$ kcal/mol[30] – imply a rate more than two orders of magnitude below that observed. If the endothermicity of the displacement of *o*-Cl in PCP by PhO· (≈ 22 kcal/mol [30]) is respected, reaction (8) appears to be slow compared with reaction (7).

Once intermediate (E) (Scheme 5) has been formed – again by tautomerisation and/or ArOH/ArO· equilibration – it can rapidly lose the chlorine atom, which in fact is in the β-position to the free-radical centre, part of the phenoxy radical system.

(iv). From the *phenol/2,4,6-TCP/water* experiment II (Table 1) the most prominent product is DCDF; this is analogous to the result obtained with phenol/PCP, and the formation of DCDF (by cross-combination of PhO· and the radical from 2,4,6-TCP, hereafter denoted TCPO·) can be explained in the same way as that of TCDF in Scheme 5. It is therefore most probably the 2,4-isomer. The second product, DCDD, can also be explained by cross-condensation, in full analogy with the formation of DD from PhO· and *o*-ClPhO· (Scheme 3), which should yield the 1,3-isomer. Calculation of rates of formation and average radical concentrations, as performed in these earlier cases, produces overall rate constants for the two processes of ≈ 10^6 and ≈ $10^5\ \mathrm{M}^{-1}\mathrm{s}^{-1}$, respectively – in fair agreement with the values derived for k_7 and k_5. Whereas the outputs of DF – and the values calculated for [PhO·] to match this (close to 10^{-8} M) – for experiments I and II are quite comparable, the DCDD:DCDF ratio is altered from ≈ 10 (exp II) to 0.2 (in exp. I). This phenomenon does not appear to stand alone; Sidhu et al. found TCDD with much less, if any, TCDF in the slow combustion of 2,4,6-TCP alone. Combustion of TCP together with excess hexane, in the temperature region of ca. 600–700 °C, resulted in the formation of comparable amounts of TCDF and TCDD.[13,23] An important difference was the presence of water (produced from the combusted hexane), which seems to promote formation of the DFs.

Our experiment III, on TCP with added acetone, produced TCDF and TCDD (each as two isomers) in a ratio of ca. 1:3, which tallies well with Sidhu and Dellinger's results.[23]

A tentative interpretation would be the existence of an additional (nonradical) process operating on some intermediate to produce 'extra' (PC)DF. A common structural entity in the pertinent primary *o*-C, *o*-C radical combination products [see dimer (D), Scheme 5, for example] is that of (G), see Scheme 6. Here, Cl has a special position in the sense that a formal $-\mathrm{O}^+$ structure (H) would arise upon heterolysis – with a restored aromatic sextet. This would therefore be much more favourable than in the nonaromatic cases of α-chloro-carbonyl compounds subject to solvolysis (hydrolysis), as discussed in (for example) Lowry and Richardson's book.[31] Scheme 6 shows an interpretation for reaction with water. The overall process from (K) to (L) is mildly endothermic, but this can be overcome at the temperatures used.



Scheme 6. Non-radical reaction to give DFs.

Whatever the merits of this proposal, given the nature of chlorine compound (G) it is hard to believe that it would be inert in the environment of a real postcombustion zone of a waste incinerator, with reactive polar surfaces and a lot of steam.

Conclusions

(1) The SD conclusion,[13] that the actual rate of formation of DCDD from 2,4,6-TCP is much higher than that to be expected from a 'ST' radical/molecule reaction − which prompted them to adjust the thermochemistry and kinetic parameters − suggests in itself that a reaction faster than 'ST' had taken place, obviously with the radical/radical pathway as the most likely candidate.

(2) Whereas our present analyses − for condensation to DDs, requiring loss of two chlorines − under the conditions used do not imply any clear preference of radical/radical condensation over radical/molecule pathways, it should be kept in mind that this is a dilemma concerning model systems only; in real-world thermal combustion, DD/DF formation − if occurring through phenol precursors − will nearly always involve at least one species with a hydrogen in an *ortho*-position. Then, as our analysis shows, radical/radical pathways (with enolisation, etc. facilitated by water and polar surfaces) appear to be efficient enough to make ST-like reactions insignificant.

(3) (Chlorinated) DFs are by far the most prominent products from these condensations − rather than (chlorinated) dioxins, as commonly believed after ST's paper. As we have pointed out earlier, (chloro)phenols surviving primary combustion in an incinerator and the region immediate thereafter, will react quite rapidly, catalysed by ashes, in the ESP and baghouse to give PCDDs rather than DFs. Together, these processes may well explain the overall incinerator PCDD/F pattern with fairly constant DF:DD ratios (>1); whether the rather typical congener distribution can also be covered by reactions of phenols only needs to be verified by further, relevant, model experiments.

(4) A final point to comment on is as follows. Phenol, TCP and PCP differ very little in their (overall) rates of (slow) combustion to give − ultimately − CO and CO_2, materially by far the most important product channel. The proportions of the corresponding ArO· radicals will, however, increase in that order, due to the decreasing O−H bond strengths. Without going into mechanistic details here, ArO· radicals are the intermediates likely to undergo oxidative breakdown. In this case, the rates for the initial step(s) − whether unimolecular or by bimolecular reaction − e.g., with O_2 − will decrease with increasing degree of chlorination, consonant with general principles (and other observations) relating to oxidisability.

Experimental Section

General: All experiments were conducted in a cylindrical quartz, stirred-tank type flow reactor of 340 mL volume, placed vertically in an electrically heated oven. For details on the set-up and procedures, see refs.[10,15]

Each experiment, after conditioning for at least 20 min, was carried out for 1 hour (occasionally 2 h) and was repeated at least twice. Details on inflows, and residence times, are given in the respective Results sections. − Condensable products, collected in a cold trap containing toluene with an internal standard (bromobenzene), were quantified with a Hewlett Packard 5890A gas chromatograph with FID using a CP-SIL5-CB column (50 m × 0.32 mm ID) operated by HP Chem Stations. Portions (2 μL) of liquid samples were injected by a Hewlett Packard 6890 Series auto sampler. Absolute concentrations were deduced from the peak areas, after calibration by injection of standard mixtures of known composition. − A Hewlett Packard 5890 GC-MS was used to identify unknown products. − Non-condensable exit gases were analysed using a Packard series 428 GC equipped with FID detector, Carboplot 007 column and a methaniser, calibrated by independent injections of a standard gas mixture.

Chemicals: Tank N_2 (99.99%) and O_2 (99.99%) were supplied by Hoekloos in standard cylinders. Phenol (Merck, pro analysis), benzene (Merck, pro spectroscopy quality, distilled), toluene (J. T. Baker, >99.5%), *o*-chlorophenol, 2,4,6-trichlorophenol and pentachlorophenol (Aldrich) were checked for adequate purity (>99%) by GC and were used as such. Triclosan was kindly provided by the Colgate Company. Reference compounds (bromobenzene, dibenzofuran, dibenzo-*p*-dioxin) were all high-grade commercial products.

Acknowledgments

The authors are indebted to Dr. Kees Olie, University of Amsterdam, for the detailed congener-specific PCDD/F analysis of the phenol/PCP reaction product, and to Mariusz K. Cieplik for helpful discussions. I. W-P. would like to thank the Tempus Foundation (grant IMG-97-Pl-2135) and the Polish State Committee of Scientific Research (KBN grant no. 3T09A 093 18) for financial support. Part of this research was performed under the aegis of 'MINIDIP', EU Project no. ENV4-CT97−0587.

---

[1] N. Winterton, *Green Chemistry* **2000**, 173−225.
[2] H. Fiedler, *Organohalogen Compounds* **1999**, *41*, 473−476.
[3] R. Addink, K. Olie, *Environ. Sci. Technol.* **1995**, *29*, 1425−1435.
[4] J. Kanters, R. Louw, *Chemosphere* **1996**, *32*, 89−97.
[5] M. S. Milligan, E. Altwicker, *Environ. Sci. Technol.* **1993**, *27*, 1595−1601
[6] E. Benfenati, G. Mariani, R. Faneli, S. Zuccotti, *Chemosphere* **1991**, *22*, 1045−1052.
[7] J. G. P. Born, P. Mulder, R. Louw, *Environ. Sci. Technol.* **1993**, *27*, 1849−1863.
[8] E. Wikstrom, S. Marklund, *Environ. Sci. Technol.* **2000**, *34*, 604−609.
[9] I. Wiater, J. G. P. Born, R. Louw, *Eur. J. Org. Chem.* **2000**, 921−928.
[10] J. G. P. Born, *PhD Thesis* **1992**, Leiden University (in English).
[11] J. Kanters, R. Louw, *Chemosphere* **1996**, *33*, 1889−1896.
[12] I. Wiater, R. Louw, *Organohalogen Compounds* **1999**, *41*, 77−82.
[13] S. S Sidhu, L. Maqsud, B. Dellinger, G. Mascolo, *Comb. and Flame* **1995**, *100*, 11−20.
[14] W. M. Shaub, W. Tsang, *Environ. Sci. Technol.* **1983**, *17*, 721−730.
[15] H. H. Grotheer, R. Louw, *Combust. Sci. And Tech.* **1998**, *134*, 45−63.

[16] I. Wiater, R. Louw, *Eur. J. Org. Chem.* **1999**, 261−265.

[17] J. W. Bozzeli, Y. G. Wu, E. R. Ritter, *Chemosphere* **1991**, *23*, 1221- 1232.

[18] R. Louw, I. Wiater, *The 6th International Congress on Toxic Combustion By-products*, University of Karlsruhe, June 27−30, **1999**, 187−188.

[19] S. I. Ahonkhai, I. Wiater, R. Louw, *Organohalogen Compounds* **2000**, *46*, 74−77.

[20] R. Louw, S. I. Ahonkhai, *Chemosphere* **2001**, in press.

[21] While 2,8-DCDD would be the product from straightforward displacement of Cl by the intermediate aryloxy radical of T, the 2,7-isomer should be present in about the same abundance, through a Smiles rearrangement analogous to that included in Scheme 2. The two isomers are known to coincide upon GC analysis even on the best suited columns (see ref.[22]) an observation also made in other (qualified) dioxin analysis labs.

[22] R. Bacher, M. Swerev, K. Ballschmiter, *Environ. Sci. Technol.* **1992**, *26*, 1649−1655.

[23] S. Sidhu, B. Dellinger, *Organohalogen Compounds* **1997**, *31*, 469−474.

[24] The Arrhenius parameters for thermolysis of anisole: PhO−Me → PhO· + ·Me are:[19,20] $\log A$ /s^{-1} = 15, E = 62.5 kcal/mol, those for the methyl ether of *o*-CP being 14.6 and 59.1. This implies a relative rate at 773 K of 4; this factor may also be used to express the equilibrium proportions of the respective aryloxy radicals. When only the 3.4 kcal/mol energy difference is taken into account, the factor becomes 10. In the analysis an intermediate value of 6 was adopted.

[25] The dimer, reversibly formed by bonding between the H-bearing *ortho*-sites of 2-chlorophenoxy radicals and an intermediate in the formation of DCDF (reaction 4), is likely to have a C−C bond considerably weaker than the 37 kcal/mol of the Cl-free analogue[9] (Scheme 1, eqn 2). If the heat of enolisation is not measurably affected by the Cl substituent, its C−C bond will be about 2 × 3.4 = 6.8 kcal/mol less, or ca. 31 kcal/mol. This would lower the equilibrium concentration and hence the apparent rate constant k_4 relative to k_2 by a factor of about 100.

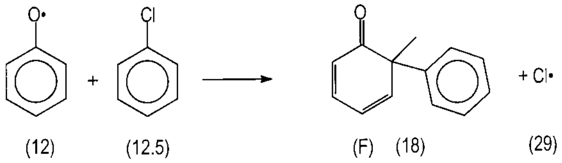
[26] The inflows mentioned imply a mixing ratio (mol fraction) of the two phenols of 1.0×10^{-3} (equal to $\approx 1.6 \times 10^{-5}$ M at 773 K). With partial conversion the average concentrations are $\approx 1.2 \times 10^{-5}$ M. The output of DF (formed in 46 s) is 1.6×10^{-5} mol fraction or 2.5×10^{-7} M, implying a rate $R_2 \approx 5.4 \times 10^{-9}$ M·s^{-1}. With $k_2 = 3 \times 10^8$ M^{-1}s^{-1}, [PhO·] $\approx 4.2 \times 10^{-9}$ M; accepting the factor 6,[24] [*o*-ClPhO·] = 2.5×10^{-8} M, and [*o*-ClPhO·]/[*o*-CP] = 2×10^{-3}.

[27] The standard heat of 17 kcal/mol for reaction (1) should remain essentially the same for the overall process: PhO· + *o*-ClPhO· → *o*-PhO-PhO· (P) + Cl·, due to (near) cancelling of the effect brought about by introduction of an *o*-O· moiety into chlorobenzene and diphenyl ether, respectively. In the target process of reaction (5), the chlorine of *o*-ClPhO· is replaced by an *o*-ClPhO group rather than by PhO; the *o*-C−O bond in Q should be weaker by about the same amount as O−H is weakened in *o*-CP compared with phenol. This, then, would increase the endothermicity of reaction (5) from 17 to ca. 20 kcal/mol.

[28] With rate $R_4 \approx 0.025$, $R_2 \approx 1.3 \times 10^{-10}$ M·s^{-1}, composed of $k_4 = 0.0007\ k_2$ (= 2.0×10^5 M^{-1} s^{-1}) and [*o*-ClPhO·] = 2.5×10^{-8} M, see ref. [26]. If it is assumed that (DD) formed from *o*-CP is due only to reaction (5), $k_5 \approx 0.1$, $k_4 \approx 2 \times 10^4$ M^{-1}s^{-1}. At 773 K, the pair, E_5 = 20 kcal/mol, $\log A_5$/M^{-1}s^{-1} = 10 (or: 24, 11.0) would match that rate constant. Should, however, (DD) be formed by reaction (6), the corresponding rate may be estimated by using the given values for [*o*-CP] and [*o*-ClPhO·] together with the parameters for reaction (1) as a substitute for those of reaction (6), giving $\log k_6 = 1.8$ at 773 K and $R_6 = 10^{-10.7}$ M·s^{-1}.

[29] The in- and outflow data imply (average) concentrations: [PhOH] = $10^{-3.4}$ M, [PCP] = $10^{-5.2}$ M (molar ratio ≈ 60), and from DF formed (rate $10^{-6.4}$ M·s^{-1})), [PhO·] = $10^{-7.4}$ M. Hence, [PhO·]/[PhOH] = 1.0×10^{-4}. With a 3.9 kcal/mol weaker O−H bond in PCP − resulting in a factor 10 difference in equilibrium ratio at 823 K − [PCPO·]/[PCP] = 10^{-3}, and [PhO·]/[PCPO·] ≈ 60:10 = 6. With a product ratio DF/TCDF = 170, k_7/k_2 = 6/170 = 0.035, so $k_7 \approx 1.0 \times 10^7$ M^{-1}s^{-1}. Note that the C−C bond in (D) (Scheme 5) is expected to be ca. 4 kcal/mol weaker than that in the Cl-free dimer I (Scheme 1, reaction 2), which disfavours its equilibrium concentration − and hence k_7 vs. k_2 − by a factor of 10. This covers an important part of the difference between these overall rate constants.

[30] To assess the endothermicity of the first step of reaction (8) it is appropriate to consider the analogous Cl-free example: $\Delta_f H°_{298}$(F) = + 18 kcal/mol is derived from that of ketophenol (− 8 kcal/mol, see ref.[9] by using the increment for propane → 2-phenylpropane (cumene) of + 26 kcal/mol. Then, formation of F from PhO· and chlorobenzene: PhO· + PhCl → F + Cl·



is at least 22 kcal/mol endothermic, the balance of 47 and 24.5 kcal/mol. For the analogous step in reaction (8), a comparable value will hold. If one accepts 'ST-like'[15] Arrhenius parameters, $\log A$/M^{-1}s^{-1} = 9, E = 28 kcal/mol (accounting for an intrinsic activation energy of 6 kcal/mol), for the key step of reaction (8), $\log k$ = 1.5 (823 K). With the values for [PCP] and [PhO·] − see ref.[29]− the computed value for R_8 is $\approx 10^{-11}$ M. s^{-1}, more than 2 orders of magnitude lower than the observed value for TCDF formation, $10^{-8.6}$ M. s^{-1} (compare note 29: $10^{-6.4}$/170).

[31] T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, chapter 4, 3rd Edition, Harper & Row, Publishers, New York, **1987**, 390−391.

Received February 13, 2001
[O01069]