PATHWAYS TO DIOXINS IN INCINERATORS. ROLE AND FATE OF (CHLORO)PHENOLS

Samuel I. Ahonkhai[a], Izabela Wiater[b] and Robert Louw*

Center for Chemistry and the Environment, Leiden Institute of Chemistry, Gorlaeus Labs, Leiden University, 2300 RA Leiden, The Netherlands.

Introduction

Despite many studies, the 'real' origin of the PCDD/Fs emitted from waste incinerators is still unknown. Some experts advocate the *'de novo'* pathway, with carbon in theflyash as the source of the dioxin skeletons[1,2]. Indeed, upon batch-wise heating of (carbon containing) ashes while stripping with air for several hours, PCDD/Fs are isolated with the right composition, but rates are very low. Other researchers hold volatile *precursors* such as (chloro)phenols - present at low levels in the exit gases of the primary combustor - responsible[1,3]. In lab studies, phenols do react rapidly and with substantial yield, to (PC)DDs, when passed over fixed beds of flyash at T> 300°C on a seconds time scale. The predominance of DDs may seem evidence against the precursor pathway. However, the use of (one single) phenol only as a 'feed' is a gross simplification; a real flue gas contains a multitude of - aromatic and nonaromatic - PICs, and also, phenol is more abundant than the (poly)chlorophenols[4]. Furthermore in heterogeneous catalysis including catalytic combustion, the behavior of components in a mix is rarely predictible from results on individual compounds[5].

In the thermal, (slow) combustion of phenols by far the most important products are the corresponding (PC)DFs; as long as ortho-H is available, little DDs arise. These noncatalyzed reactions occur via combination of two phenoxy radicals[6] rather than by displacement of (ortho) chlorine in a chlorophenol molecule by a phenoxy radical, the 'Shaub and Tsang' mechanism[7]. Even the cross-combination from the parent phenol with PCP leads to 1,2,3,4-TCDF, with negligible TCDD[8]. Such processes which do not reproduce the common PCDD/F furan:dioxin ratio from incineration may be deemed unimportant in practice again. However, the primary process can yield a collection of non-to-lower chlorinated DFs, with little DDs, next to (chloro)phenols and other types of PICs. This is exactly what has recently been found from the pilot facility in Umea[9]. The lower chlorinated DFs can be further (oxy)chlorinated on the ash, while the remaining phenols condense to esp. (PC)DDs. This *'precursor plus'* scenario can therefore satisfactorily account for key features of dioxin formation and emission without invoking 'de novo' type contributions; it also logically explains the rapid formation of substantial PCDD/F levels with the 'right' pattern in model combustions wherein carbons are not formed [10].

In this light it is important to better understand the kinetics and mechanism of the formation ofthe lower-chlorinated DFs from (chloro)phenols at elevated T (500 °C and up) in the gaseous phase.

The present contribution deals with the (quantitative) effect of (poly)chlorination on the O-H bond strength which is a pointer to the level of the phenoxy radical *vs* that of the phenol. Rates, products and mechanisms upon (cross)condensation are discussed.

---

[a] On leave from the University of Benin, Benin City, Nigeria

[b] On leave through the EU-Tempus program from Jagiellonian University, Krakow, Poland

Methods and Materials

Anisole (I), 2-Cl-anisole (II), 2,4,6-trichloroanisole (III) and pentachloroanisole (IV) were commercially available and of adequate (>99%) purity as checked by GC.

Gas-phase thermolyses were performed in a setup provided with a tubular flow reactor as described before[11]. Typical conditions: Atmospheric pressure, ~ 0.1 vol% of the anisole(s), 60-fold excess of toluene, N_2 as a makeup gas and carrier. Temperatures were between 700 – 820 K, average residence times were around 90 s, and conversions ranged from a few to over 90 %.

Organic products were collected in cold toluene (except methane) for typically 1 hour. Quantitative rate and product data were obtained after GC analysis, making use of – inert – benzonitrile as an internal standard which was added in a known amount to the feed, as wellas of coinjection standards (e.g. bromobenzene) present in the cold traps. Methane was quantified by GC analysis of 0.50 ml exit gas samples, peak surface areas being compared with those of a calibration gas.

Results and Discussion

A. *Thermolysis of (chloro)anisoles.* As an entry to the effect of (poly)chlorination on thephenolic O-H bond strength we have chosen to determine the strenghts of the corresponding O-methyl bonds by measuring the temperature dependence of the rate ofthermolysis of the anisoles I, II, III and IV. These are readily accessible compounds, easy to handle, and with bond strengths around 60 kcal/mol allowing smooth reaction under the conditions mentioned in the 'Methods' section. With reaction (1) as crucial step, reaction (2) – and (3) – preventing reversal to starting anisole, differences in Arrhenius activation parameters will show the effect ofchlorination on the O-Me bond; following Stein et al.[12], these results can be directly translated into differences in O-H bond strengths, as equilibria (5) will have $K_5 \sim 1$.

(1) $ArO\text{-}CH_3$ →(slow)→ $ArO\bullet + \bullet CH_3$

Ar = phenyl (I), o-Cl-phenyl (II), 2,4,6-trichlorophenyl (III), pentachlorophenyl (IV).

(2) $\bullet CH_3 + PhCH_3 \rightarrow CH_4 + PhCH_2\bullet$

(3) $ArO\bullet + PhCH_3 \rightarrow ArOH + PhCH_2\bullet$

(4) $2\ PhCH_2\bullet \rightarrow$ bibenzyl

(5) $ArOMe + Ar'OH \leftrightarrow ArOH + Ar'OMe$

Results on a selected number of individual runs with I, II or III, each at conversions in the range of 40-90% have shown that material balances were satisfactory. Also, few other products, if any, were seen. A large number of individual runs, as well as pair-wise competitions (I+II, II+III) led to rate data and first-order rate constants (Figure 1). The Arrhenius parameters are given in Table 1. Clearly, ortho-Cl lowers the O-Me – hence, also the O-H bond strength in the phenol derivative, a result tallying well with earlier VLPP work[12]. With both ortho-positions chlorinated and a third chlorine at para (as in III), bonds are further weakened. Accepting a BDE(O-H) in the parent phenol of 87 kcal/mol[13], that in 2,4,6-trichlorophenol becomes ~82 kcal/mol. With results on IV not yet available one may *speculate* that owing to the two additional Cl substituents its O-H bond is below 82. It is useful to point out that in a series of *mono*substituted phenols (in solution),

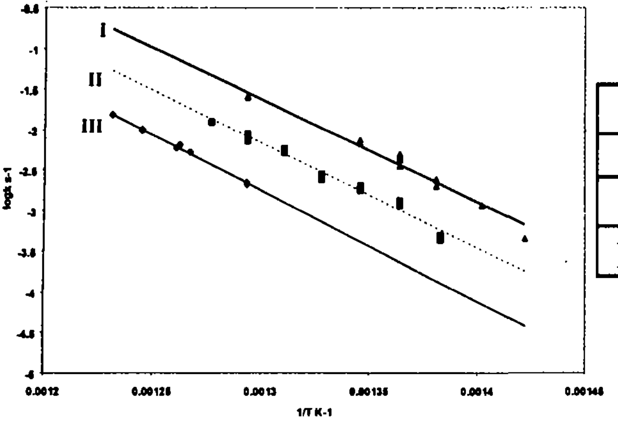


Figure 1. Arrhenius plots for Anisole (I), 2-Cl-Anisole (II) and 2,4,6-Trichloroanisole (III)

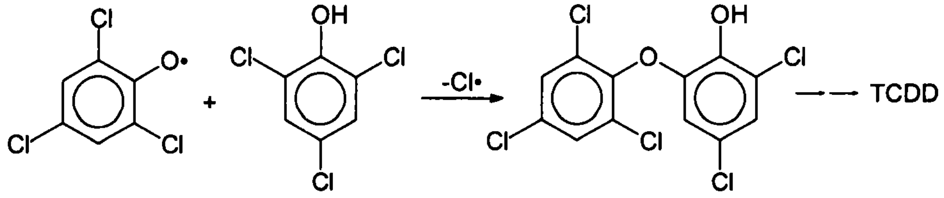
	Log A/s^{-1}	E_a(kcal/mol)	k_{rel}@500°C
I	15.0	62.5	(1)
II	14.6	59.1	4
III	14.8	57.7	12.5

Table 1. Arrhenius parameters

electron-attracting groups *increase* the O-H bond strength, while 'donors' lead to lower BDE(O-H) values. Data obey a Hammett $\rho\sigma^+$ correlation, including $\sigma_o^+ = 0.66\ \sigma_p^{+}$ [14,15]. If that systematics would hold also for (poly)chlorination, the O-H bond in 2,4,6-trichlorophenol is then 'calculated' to be 2 kcal/mol - and that in pentachlorophenol no less than 7 kcal/mol -*stronger* than O-H in phenol. One may conclude that additivity of substituent effects does not hold for these polychlorinated analogues, and that trustful data have to be obtained by experiment.

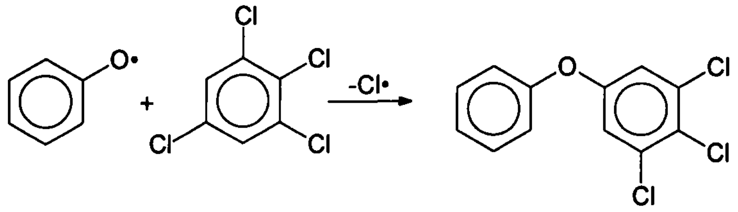
B. *Consequences for – thermal, precursor - dioxin formation.* Taking 2,4,6-trichlorophenol as a key example, what do the aforementioned results mean for the understanding of the gas-phase, thermal condensation to dioxins? Since Shaub and Tsang's 1983 paper[7], focus has been on displacement of an (ortho) chlorine in the chlorinated phenol by an aryloxy radical (eqn 6). Later on, we have shown that in the base case (6a) the activation barrier is no less than 24 kcal/mol[11], which for a major part is due to the overall endothermicity of ~ 17 kcal/mol, as the C-Cl bond in chlorobenzene (94 kcal/mol) is replaced by the Ph-O bond in diphenylether, of (only) 77 kcal/mol.

(6)



(6a) PhO• + PhCl → PhOPh + Cl•

(6b)



Whereas condensation of two (chloro)phenoxy radicals is a rather easy process, with rate constants of over 10^8 M^{-1} s^{-1}, [11] radical/molecule reactions as in (6) are likely to be (much) slower than radical/radical pathways, especially if one takes into account that in a hot oxygen-containing, dilute environment the [ArOH]/[ArO•] ratio will not be very large. To compensate for a 24 kcal/mol barrier at say 800 °C, that ratio must be at least 10^5. It is only if the activation barrier of e.g. displacement (6) is very much lower than that of the simple case (6a), will a radical/molecule pathway become competitive.

That view was advanced by Bozzelli et al. some time ago[16] ; calculations led him to conclude that - in the case of example (6b) the overall process was even 2 kcal/mol *exo*thermal, with a concomitantly low overall barrier.

To alter the respective C-Cl and C-OPh BDE's that drastically by introducing 3 more chlorines in the aromatic ring, so as to even *invert* the order, is to our knowledge unprecedented and therefore untenable. The large database on well-defined BDE's for many R-Cl and R-OR' derivatives shows that for example R-Cl and R-OMe are nearly equally strong, with – of course - some fluctuation with R, within +/- 3 kcal/mol. Given the resonance stabilization in phenoxy of ~16 kcal/mol, the heat of reaction of (6a) is explained. The Ar-Cl and Ar-OPh bonds in reactions (6) - and also (6b) - will *both* be lowered by possibly several kcal/mol, due to the substituents in the molecule, to leave the heats of reaction very comparable to that of (6a). Furthermore, the 3 chlorines in the aryloxy radical lower its bond strength: to H, methyl, and thence also to the aryl moiety in the ether product to increase even the endothermicity of reaction (6) by 2-3 kcal/mol, compared with base case (6a). In conclusion, the radical/molecule reaction (6) will not be faster than the model example (6a), leaving radical/radical pathways as the most likely route here as well.

Apparently, calculations of thermochemical properties on a much more advanced level are required to adequately (re)produce data on structures as discussed above, which are so relevant for the elucidation of the mechanism of dioxin formation in incinerators.

The behavior and fate of (chlorinated) phenols, at levels in a PIC-environment common for real incinerators, and representative for conditions in APC devices should also be much better known; studies in this direction are now under way as well.

References

1. Addink R. and Olie K. (1995) Environ. Sci. Technol. 29, 1425
2. Stieglitz L., Zwick G., Beck J., Roth W. and Vogg H. (1989) Chemosphere 18, 1219
3. Born J.G.P., Louw R. and Mulder P. (1989) Chemosphere 18, 401
4. Jay K. and Stieglitz L. (1995) Chemosphere 30, 1249
5. Van den Brink, R.W., Louw R. and Mulder P. (2000) Appl. Catal. B 25, 229
6. Wiater I., Born J.G.P. and Louw R. (2000) Eur. J. Org. Chem., 921
7. Shaub W.M. and Tsang W. (1983) Environ. Sci. Technol. 17, 721
8. Kanters M.J. and Louw R. (1996) Chemosphere 33, 1889
9. Wikstrom E. and Marklund S. (2000) Environ. Sci. Technol. 34, 604
10. Ghorishi S.B. and Altwicker E.R. (1995) Environ. Sci. Technol. 29, 1156
11. Grotheer H.H. and Louw R. (1996) Twenty-Sixth Symp. (Int.) on Combustion, 2405
12. Suryan M.M., Kafafi S.A. and Stein S.E. (1989) J. Am. Chem. Soc. 111, 4594
13. Arends I.W.C.E., Louw R. and Mulder P. (1993) J.Phys.Chem. 97, 7914
14. Jonsson M., Lind J.,Eriksen T.E and Merenyi G. (1993) J.Chem.Soc. Perkin Trans.II, 1567;
15. Laarhoven, L.J.J. (1997), Ph.D. thesis Leiden University.
16. Bozzelli J.W., Wu Y-P.G. and Ritter E.R. (1991) Chemosphere 23, 1221