

## GAS-PHASE PATHWAYS TO 'DIOXINS' FROM HALOGENATED PHENOLS.

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### Abstract.

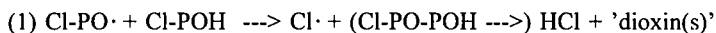
The key step (1) of the 'Shaub and Tsang' mechanism for gas-phase formation of dioxins from chlorinated phenols has been substantiated by measurements on the analogous reaction of phenoxy with chlorobenzene (2). Such phenoxy radical + (chloro)phenol/arene reactions are indeed slow and insignificant in real combustions, but a more efficient pathway exists in combination of two (chloro)phenoxy radicals (3). Products therefrom may be precursors for the family of toxic PCDD/Fs formed in the cooling zone of incinerators. Results on bromobenzene (4) and on the reverse reactions of (3) and (4), diphenylether with Cl or Br, substantiate rates and mechanisms involved.

### 1. Introduction

Combustion of Cl containing matter is afflicted with the emission of 'dioxins'. An important part of the chemistry of PCDD/F formation in incinerators involves catalyzed conversions in the post-combustion

train, air pollution control devices, but the formation and survival of 'pre-dioxins', esp. (chloro)phenols, and generation of (chlorinated) dibenzodioxins and dibenzofurans is no doubt inherent in the combustion itself.

In 1983 Shaub and Tsang<sup>1)</sup> have addressed the question of the mechanism of gas-phase formation of dioxins from chlorophenol, and came up with the displacement of an (ortho) chlorine in a (poly) chlorinated phenol **molecule (Cl-POH)** by a (chloro)phenoxy **radical (Cl-PO·)** as the only important pathway and consequently as the key step (reaction 1).



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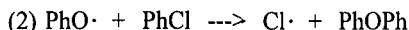
The activation barrier for displacement of Cl was modelled at 26 kcal/mol and the overall conclusion was that dioxin formation via this mechanism was insignificant in real incinerators.

Recently, Dellinger et. al.<sup>[2]</sup> have experimentally found rates for gas-phase formation of 'dioxins' from 2,4,6-trichlorophenol to be much larger than compatible with the S&T mechanism. They adjusted S&T's model activation energy  $E_1$  down to 19.5 kcal. Other pathways to dioxins were not considered.

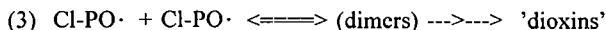
In the analogous case of tribromophenol, rates were about 500 times faster (around 600 °C), and the modelled activation energy for Br displacement came out as 8.8 kcal/mol<sup>2</sup>.

## 2. Results and Discussion

In order to obtain a better insight in this matter, we have investigated the slow combustion of phenol [PhOH] together with chlorobenzene [PhCl], i.e. we used PhCl as a model substitute for chlorophenol (reaction 2). The advantage is that the specific product is diphenylether, PhOPh.



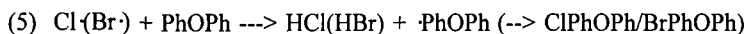
Using a quartz backmix-flow reactor at atmospheric pressure, we measured PhOPh for 728<T<984 K relative to dibenzofuran (DF), known to arise from PhOH via condensation of 2 PhO· radicals<sup>3</sup>. Rate and product data will be presented and discussed, showing that PhOPh is indeed formed but it is very minor to DF. The activation energy for reaction (2) was found to be 24.5 kcal/mol, so S&T's thermokinetic model is underscored, as is their conclusion that the 'phenoxy + phenol' reaction pathway (1) is unimportant. By analogy with ref. 3 we conclude that the self-reaction of chlorinated phenoxy radicals (reactn 3) is the preferred pathway for gas-phase dioxin formation - not only in model reactors like Dellinger's and ours but also in real incinerators.



This conclusion is further based on an assessment of the ratio of concentrations of Cl-PO· and Cl-POH under relevant conditions.

For comparison, reactions involving bromobenzene(s), with (4) as an example, are also investigated; preliminary results show that displacement of Br is only little faster than that of Cl. This has important consequences for the activation energies associated with Cl, and Br, displacement by phenoxy radicals.

To understand and quantify reaction pathways and energy profiles better, a study of the **reverse** of reactions (3) and (4) is appropriate. In those cases, splitting of the ether via ipso-addition of Cl· or Br· could compete with the - endothermic - **abstraction** of (o-,m-, or p-) hydrogen (reaction 5), *key step in the gas-phase chlorination or bromination of benzene derivatives*<sup>4,5</sup>.



It has been reported that chlorination of PhOPh does give ClPhOPh, and no mention was made of formation of PhCl<sup>5)</sup>. Chlorobenzene may have been a minor side product, and we plan to reinvestigate that. Anyway, the energy diagram shown next substantiates that the barrier for reaction (3) must be (at least) some 24 kcal/mol. Results on the gas-phase reaction of PhOPh with **bromine** show that H-abstraction (5), hence bromination, is also the major reaction, which on a per-site basis is about twice as fast as splitting (reaction - 4). Combined data on the forward and reverse reactions here indicate an activation barrier for (4) close to that for (3), despite the ca. 15 kcal/mol difference between the C-Cl and C-Br bond strengths.

In conclusion, the S&T pathway to 'dioxins' is indeed insignificant, but there is a better, faster entry via combination of two (chlorinated) phenoxy radicals. This has also been the case in Dellinger's experiments. Depending on Cl(Br) substitution, both DDs and DFs can arise with *k* values above 10<sup>8</sup> M<sup>-1</sup>.s<sup>-1</sup>. These PCDD/Fs will be lower halogenated, and be outside the category of toxic, 2,-3,-7,-8,- congeners. Next to chlorophenols, these 'pre-dioxins' may act as precursors for the usually measured 'dirty' PCDD/F family, formed in the fly-ash mediated reactions in the cooling zone<sup>6)</sup>.

### 3. References

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