

## ABOUT HALOGENATION IN COMBUSTION REACTIONS

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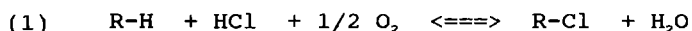
**ABSTRACT.** Organic vapors in hot air with HCl can form organic chlorine derivatives, parallel to their oxidative degradation, even without catalysis (fly-ash). Upon slow combustion with incomplete conversion, phenol - a key precursor for PCDDs - indeed gave o-/p-chlorinated phenols, together with a variety of other PICs. With HBr plus HCl, bromination of phenol is ca 10 \* faster than chlorination. These uncatalysed processes can be explained via free-radical mechanisms, with Cl<sub>2</sub> and/or HOCl as chlorine transfer agents. Bromination occurs via free Br atoms. Slow combustion of phenol plus acetone (at ca 700°C) also led to methylchloride. In real (waste) combustion, metal salts may enhance these (oxy)chlorination reactions.

## INTRODUCTION

Combustion processes are prominent sources of 'dioxins' and related PICs in the environment, and a variety of non- and less controlled combustion practices will continue to emit these pollutants. This is no longer true for advanced (domestic, and chemical) waste incinerators with up-to-date flue gas treatment, but whatever the theory, in real life even those combustors do not reach a 100% DRE of organics: The usual list of PICs, including PAHs, polychlorinated benzenes and biphenyls, and polychlorinated phenols (PCPs) still can be found at significant levels upon analysis of the effluents of combustion chambers.

Much attention has been payed to fly-ash catalysed chlorination and condensation reactions in the after-train (boiler, ESP) of incinerators, around 300°C. 'De novo' synthesis, from carbonaceous particles in the ash, and 'precursor' reactions - with PCPs as the most likely intermediates - have been advanced as pathways to the dioxins.

To date the chemistry, during combustion, of formation and survival of chlorinated PICs has been little studied. In the combustion chamber, homogeneous gas-phase (radical, radical-molecule) reactions will of course be important. But other, especially catalytic conversions - on the wall and/or by metal oxide or salt aerosols (dust) - may not be ignored. Anyway, the thermodynamics of gas-phase oxychlorination, model equation (1):



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allows very high  $[RCl]/[RH]$  equilibrium ratios, of no less than  $10^3$  -  $10^4$  at 1000K under realistic conditions. In practice, this process has to compete with oxidative degradation to  $CO_2$  and  $H_2O$ , so the question is to which extent, at partial conversion - hence under kinetic conditions - chlorination will occur.

In recent years our laboratory has already reported on fly-ash mediated (model) reactions<sup>2)</sup>, and on 'true' gas-phase processes: oxychlorination of benzene<sup>2)</sup> - a common pyrolysis product of organic matter - and slow combustion of benzene<sup>3)</sup>. Following investigations on the gas-phase thermolysis of (chloro)phenols<sup>3)</sup> - compounds commonly considered as precursors for 'dioxins' - we presently report on the gas-phase slow combustion of phenols in the presence of HCl, leading to o-/p-chlorophenol as one of the products. Results are compared with those obtained when acetone is added to the feed. The possible role of HOCl is considered. Furthermore, the effect of added HBr - with emphasis on the (mechanism of) formation of o-/p-bromophenol - is outlined.

## EXPERIMENTAL

Flow systems has been used with quartz tubular reactors at 1 bar, with dwell times of 3-17 s, at temperatures up to 700°C (Figure 1). For control runs re section I, next, there was a second inlet and transfer tube present, to allow mixing with the other gas only at the end of the reactor tube, where T is < 400°C.

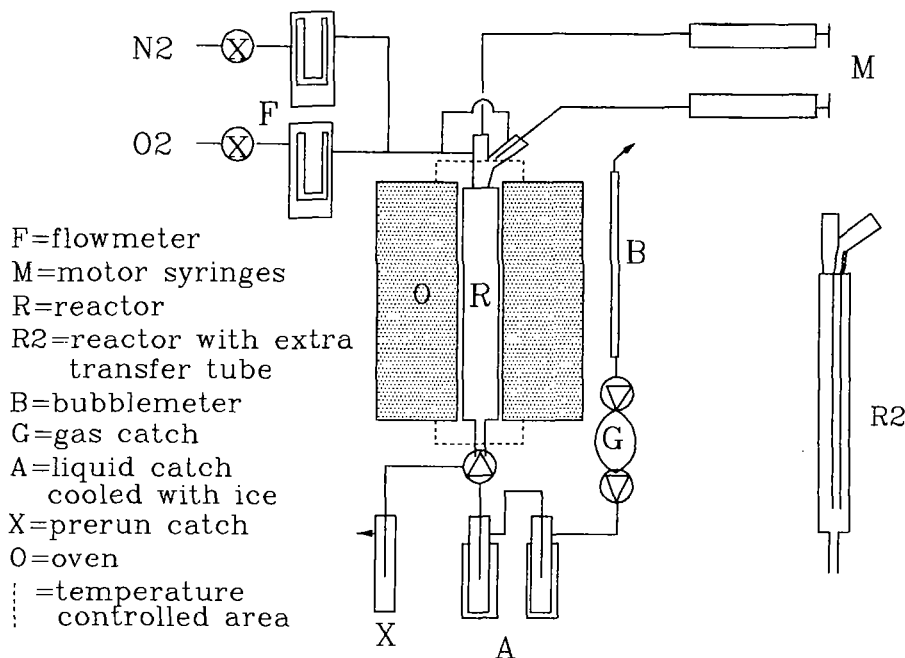


FIGURE 1

## RESULTS AND DISCUSSION

### I. Slow combustion/oxychlorination of phenol (PhOH).

With an inflow mix PhOH/HCl/H<sub>2</sub>O/O<sub>2</sub>/N<sub>2</sub>, runs were performed at 873, 903, 923 and 973K (Table 1); in run 5, a mix without HCl was fed in, whereas via the second inlet HCl was administered. To see the effect of the presence of another 'fuel', a mix involving acetone (A) was used in a second series, exps. 6-9. In run 10, A was present, but phenol was omitted.

Conversions of PhOH ranged from 33-95 % leading to a variety of 'PICs'. Most of these were Cl-free, but o-/p-chlorinated phenols were undoubtedly formed.

A full discussion of products and mechanisms is beyond the scope of this paper, but pertinent observations are:

1. The mild regime is at the threshold for combustion of CO.
2. Despite the excess O<sub>2</sub>, benzene is a fairly important product.
3. Radical-radical combinations occur: e.g. 2 PhO· → dibenzofuran (DBF), and to a lesser extent, PhO· + Me· → anisole + cresols.
4. Thermokinetic analysis shows that CO can at best only in part arise via PhO· → CO + C<sub>2</sub>H<sub>5</sub>· (with naphthalene as a product stemming from cyclopentadienyl radical). Hence, O-containing intermediate products (carbonyl derivatives, giving R(CO)·) and/or PhO-R' type compounds (to give PhO-C·(H)(R'')), then rearranging to ·OC(Ph)(H)(R''), which decomposes into ·R'' and benzaldehyde) appear to be involved.

TABLE 1 Slow combustion of Phenol (PhOH).

Exp no*)#)	1	2	3	4	5 <sup>§</sup>	6	7	8	9 <sup>§</sup>	10
T/K	873	903	923	973	903	903	903	903	903	903
PhOH conv(%)	33	41	62	95	45	57	60	66	58	-
CO (%) <sup>§</sup>	24	74	125	311	47	118	133	125	99	132 <sup>†</sup>
CO <sub>2</sub> /CO	0.15	0.14	0.11	0.15	0.50	0.14	0.15	0.16	0.4	0.06
CH <sub>4</sub> /CO	0.01	0.02	0.03	0.08	0.02	0.29	0.19	0.22	0.1	0.69
C <sub>6</sub> H <sub>6</sub> (%) <sup>§</sup>	0.06	0.29	0.90	1.3	0.40	0.66	0.79	0.72	0.71	-
m-BF (%) <sup>§</sup>	0.11	0.31	0.53	0.45	0.31	0.49	0.63	0.57	0.59	-
DBF (%) <sup>§</sup>	1.8	2.4	1.6	0.4	1.8	0.80	1.05	1.0	2.1	-
CH <sub>2</sub> Cl (mmol/h)	-	-	-	-	-	0.42	0.42	0.54	0.06	0.66
o-/p- ClPhOH (%) <sup>§</sup> *10 <sup>2</sup>	2.5	5.3	3.1	0.9	0	1.7	2.4	2.2	0	0
o/p ratio	2.6	3.5	2.8	1.9		2.8	4.3	3.6		

\* ) Intakes (mmol/h): Exps 1-5: PhOH(5.2), HCl(3.6), H<sub>2</sub>O(36), N<sub>2</sub>(282), O<sub>2</sub>(55); Exps 6-9: PhOH(4.5), HCl(3.0), Acetone(2.8), H<sub>2</sub>O(30), N<sub>2</sub>(282); O<sub>2</sub>, in exp.6(55),7(74),8(91),9(55). Exp 10: NO PhOH; Acetone(1.6), O<sub>2</sub>(74), others as before. Dwell times 11-12 s, except runs 5,9; see §, below.

§) PhOH/water mix fed in main entrance, with half of the air mix; HCl/water through extra inlet tube with other half of air; dwell time in tube ca. 2 s.

†) Other products (in exps 1-9) include: acetylene, ethylene, naphthalene, o-/p-cresol, anisole, styrene, benzaldehyde, indene, phenanthrene, hydroxy-DBFs (3 isomers), methylene-bisphenol (3 isomers), typically at the 0.01 - 0.1 % (on PhOH) level.

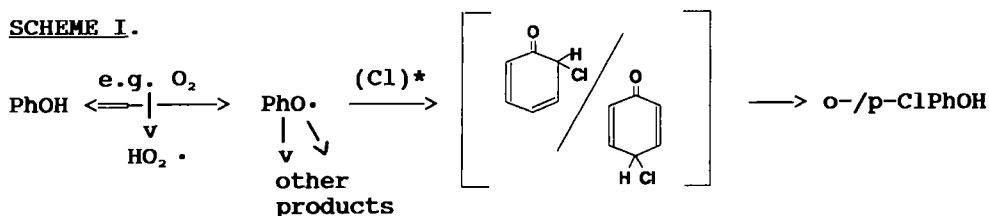
§) mol percent on PhOH in.      §) mol % on Acetone in.

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5. *o*- + *p*-ClPhOH are seen in runs 1 -4; their absence in run 5 proves that formation had occurred in the reactor, and not in the cooling section.
6. Addition of acetone (A) has little influence on the rate of reaction of PhOH, but changes the PIC composition: less DBF and ClPhOH, more methane and cresols. This is attributed to a higher concentration of methyl radicals.
7. With A, production of CH<sub>3</sub>Cl is substantial.

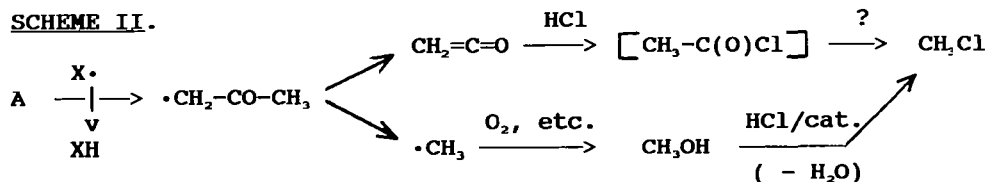
Focussing on chlorination, pathways to ClPhOH and MeCl are outlined in Schemes I and II. Although the exact nature of the chlorination agent(s) of phenol is not yet known, formation of ClPhOH can be rationalised via homolytic processes. Formation of MeCl is not so easily interpreted thusly; nonradical (ionic, surface assisted) reactions may well be involved, cf. liquid-phase nucleophilic substitution of protonated alcohols and ethers. Such types of reaction can play a more significant role if metal salts are present, as in domestic waste incineration.

## SCHEME I.



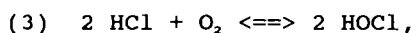
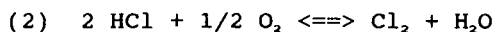
\* options: Cl·, Cl<sub>2</sub> (from 'Deacon' reaction); HOCl<sup>3)</sup>

## SCHEME II.



## II. On the role of HOCl.

In hot air, HCl may - according to thermodynamics - give several % of Cl<sub>2</sub>. Yet another possible chlorination agent is HOCl. If both agents are made rapidly enough - which is doubtful for mere gas-phase reactions<sup>4)</sup> - thermochemistry of the simple equilibria:



entails that [HOCl]  $\approx$  [Cl<sub>2</sub>] at 1000K, with HOCl becoming relatively more important at higher T, and less at lower T. The chemistry

involved in slow combustion of benzene/air/HCl - with emphasis on formation and chlorination of phenol - has been discussed<sup>2</sup>; now we report on experiments with HOCl, at 573 and 903K. To identify possible after-chlorination, excess m-cresol was placed in the liquid alkaline quench solution.

At 573K, dwell time 17 s, an intake mix HOCl/H<sub>2</sub>O/PhOH/N<sub>2</sub>/O<sub>2</sub> (mmol/h) of 0.27/67/5.0/282/74, did not result in oxidation or condensation products, but gave o-/p-chlorophenol (ratio 0.79), 12% on HOCl in. Further oxidative power due to HOCl, Cl<sub>2</sub> or whatelse was gone, and chlorinated cresol could not be detected. Presumably, much of the HOCl has given HCl, H<sub>2</sub>O and/or O<sub>2</sub>. At an oven temp. of 903K, the same feed led to some 40% conversion of PhOH and a range of (Cl free) products including dibenzofuran (DBF), benzofuran, naphthalene, indene and hydroxy-DBFs. O-/p-Cl-phenols, ratio 1.20, arose in 9% yield on HOCl. Dichlorophenols (2,4-, 2,6-) and 2,4,6-trichlorophenol were also found, their sum being about one-half of the monochlorophenols. Again the liquid catch was free of Cl-cresols. We tentatively conclude that HOCl introduced is curted up mostly to HCl, and some Cl<sub>2</sub>, the latter being able to chlorinate PhO· radicals. In the HCl/air system, Born et. al.<sup>2</sup>) observed a o-/p- ClPhOH ratio of around 3 at 900K, tending to 1.7 at 950K, when much of the (Cl)phenols will have been burnt. These higher isomer ratios point at the operation of a different chlorination agent (mechanism) with HOCl still as a candidate.

The formation of di- and trichlorophenol is explained as a consecutive reaction of (keto)monochlorophenols (see Scheme I) which can undergo H-abstraction to ClPhO· and then chlorination.

### III. Bromination due to HBr.

Domestic waste also contains bromine, typically around 1 % on Cl. This is known to lead to e.g. Br containing PCDD/Fs with a relatively large Br content. We have conducted slow combustion experiments at ca 973K, exemplified by that with an intake mix (mmol/h) of HBr/HCl/H<sub>2</sub>O/PhOH/N<sub>2</sub>/O<sub>2</sub> of 0.3/3.3/37/5.2/210/52, dwell time 3-4 s. Some 80% of PhOH is now converted. Many 'PICs' are seen, including CO (35 mol% on PhOH), benzene (2.5%), and again the halogen-free compounds DBF, benzofuran, naphthalene, all at the 0.1 - 1% level; benzaldehyde - at the 0.01% level only, but significant as a possible precursor of benzene. O-/p-chlorophenol (ratio 3.0), was found in 0.05 % on PhOH in, o-/p-BrPhOH (ratio 1.9) emerging in equimolar amounts. Bromination, therefore was ten times more efficient than chlorination, given the HBr/HCl intake ratio of 0.1. Checks with cresol in the alkaline quench did not reveal any halogenated cresols, proving that halogenation had taken place in the reactor.

Variation of the HBr input led to the plot seen in Figure 2. The output of BrPhOH nicely parallels [HBr]; interestingly, more HBr also leads to some increase in chlorophenol.

Thermokinetic analysis supports our view that Br· is the brominating agent of phenoxy; both species equilibrate via:

- (4)  $\text{PhO} \cdot + \text{HBr} \rightleftharpoons \text{PhOH} + \text{Br} \cdot$ , followed by:  
 (5)  $\text{Br} \cdot + \text{PhO} \cdot \rightleftharpoons \text{keto-o-/p-bromophenol}$ .

'Enolisation' of keto-halophenols (symmetry-rule forbidden as a unimolecular step) is relatively slow.

Relation HBr Intake and Br/Cl-phenols in outflow

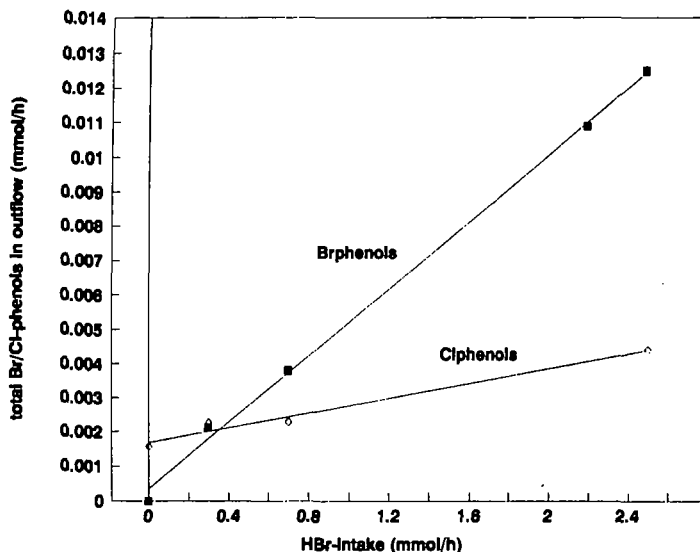


FIGURE 2

## CONCLUDING REMARKS

Obviously 700°C is an inadequate temperature for reaching a level of >99.9.. % DRE, but the conditions used in our investigation mimic inlets or outlets of, and 'pockets' in, combustors. Without the 'help' of catalysts, chlorination does occur, but not to a large extent. Experiments involving real municipal solid waste<sup>4</sup> show that - without flyash - reactor walls develop catalytic properties, enhancing formation of Cl<sub>2</sub> from HCl - and chlorination. Under poor combustion practices, organochlorine compounds already present in the feed may to some extent survive, but under regular circumstances nonchlorinated and chlorinated PICs will be newly formed. Phenols are peculiar in the sense that - via electrophilic and via free radical reaction - **polychlorinated** phenols can arise, which may condense to PCDD/Fs in boiler or ESP sections of (domestic waste) combustion facilities.

## REFERENCES

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