Formation of PCDFs during Chlorination and Oxidation of Chlorobenzene in Chlorine/Oxygen mixtures around 340 °C

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Abstract

Homogeneous gas-phase chlorination of chlorobenzene (CB) in the presence of oxygen at 330-350°C gives substantial amounts of PCDFs, up to 6% on the major product, the dichlorobenzenes.
Chlorine atoms abstract H from chlorobenzene, the resulting chlorophenyl radicals reacting rapidly with Cl_2, or with O_2. The latter reaction leads to chlorophenoxyl radicals. Part of these appear to be further chlorinated before condensation to mainly D_2CDF, T_3CDF and T_4CDF takes place. This chemistry is compared to that of other thermal processes leading to PCDD/PCDF.

Introduction

Formation of PCDD and PCDF in combustion processes of chlorine containing organic materials has been frequently studied. It has been recognized that fly ash, acting as a heterogeneous catalyst, plays a crucial role in the formation of PCDDs and PCDFs in the afterburning zone of municipal waste incinerators[1,2,3]. Precursors for PCDDs/PCDFs are aromatic structures like toluene[3] or phenol[4]. In the absence of heterogeneous catalysis, and without HCl/Cl_2, slow combustion of benzene at ca 600°C gives partial conversion, fair yields of phenol, and ca 1% of dibenzofuran (DF) on phenol[5]. When HCl is present, 2- and 4-chlorophenol are also formed (ca 1% on phenol); MCDF is not detectable by regular GC and therefore negligible compared with DF. Hence, under these conditions, (oxy)-chlorination is minimal and polychlorinated products are essentially absent[6].
Slow combustion of chlorobenzene at ca 500°C gives phenol, the three chlorophenols, DF, the four isomers of MCDF and ten DCDFs, but DD/MCDDs were not observed (less than 0.1% on DF)[7]. Starting with a mixture of phenol and the chlorophenols, the same products were formed; with yields of DF/MCDF/DCDF above 5%, DD+MCDD could be observed at a level of 0.4% on the DFs. Interestingly, carefully controlled slow combustion of phenol at T< 600°C can yield DF with a selectivity of 70%[8].

FORM

The present paper deals with results we have obtained thus far when using reactant gases, very rich in chlorine; departing from regular chlorination, oxygen has been admitted. Chlorobenzene was chosen as the model substrate; it allows observation of regioselectivity (e.g. isomer distribution of the dichlorobenzenes) and it was expected not to give rise to large proportions of highly toxic PCDDs/PCDFs. Another purpose of this study was to determine the rate constant for reaction (2) [9] (see scheme).

Regular gas-phase chlorination is known to proceed smoothly above 300°C[10] ; oxygen should be able (step 2) to compete with chlorine (1) for $ClC_6H_4\cdot$ radicals, a third -minor- reaction being arylation of chlorobenzene (3).

Scheme Elementary steps in gas-phase oxychlorination of chlorobenzene.
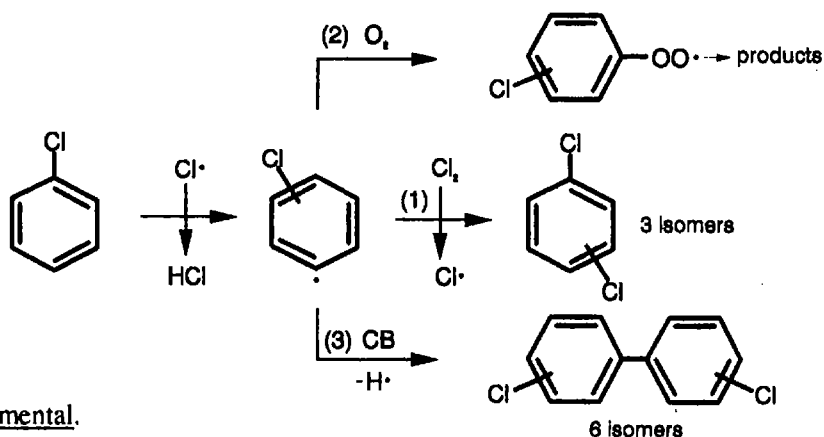
Experimental.

A conventional flow system (atmospheric pressure) with a pyrex tubular flow reactor (590 ml) was used. Experimental details are described elsewhere [9]. Effluents were quenched in a cold trap (0°C) containing carbontetrachloride and aqueous NaOH to quench chlorine ($2OH^-$ + Cl_2 --> Cl^- + ClO^- + H_2O). After workup residual chlorine and HCl were determined by iodometric and potentiometric titration respectively. Organic products were identified using GC-(FID or MSD). Quantification was carried out by means of GC-FID comparing product peak areas to the peak area of an internal standard present in the CCl_4/NaOH trap.

Results and Discussion.

Example a, without oxygen (see Table), tallies with earlier results[10]; the three dichloroben-zenes (DCBs) and the six isomers of $ClC_6H_4C_6H_4Cl$ (DDPs) have been formed with the expected rate and ratios. Admitting oxygen (exp. b) lowers the rate of chlorination as noticed before[10], leaves the DDP/DCB ratio unchanged, **and leads to PCDFs.** With more oxygen (exp. c) less DCB is formed, but the PCDF/DCB ratio is doubled.

Increasing the temperature to 350°C, as in exp. d, not only gave rise to an increased rate of chlorination, but PCDF formation has also become more important (exp e).

When 1 mol% of dibromobenzene is added to the feed, the rate of chlorination is

increased further, the PCDF formation again becoming relatively more important

A search for PCDDs, by GC-SIM-MS, in the product of exp. d led to values, if any, well below 1% on PCDF. Hence, the very high preponderance of DF is quite general for homogeneous oxidative conversions of benzene derivatives. A graphic representation of the production of DDPs and PCDFs is given in the figure.

In the practice of combustion, e.g. of municipal solid waste, emissions involve rather comparable levels of PCDD and PCDF. Whatever the exact nature of their precursors, it is generally accepted that fly-ash mediated reactions play a dominant role[11]. In those cases homogeneous gas-phase chemistry - with phenols as key intermediates[7] - merely serves as a source of the requisite products of incomplete combustion. That formation of PCDD/F 'in the oven' is relatively unimportant is mainly due to the low chlorine contents of the feed. Our data on the chlorobenzene/chlorine/air system show that this picture becomes different when more chlorine is present. Obviously it is not advisable to run this type of thermal oxychlorination with di- or higher-chlorinated benzenes. Also, oxychlorination of benzene derivatives with air/HCl and a (Deacon-type) catalyst forming Cl_2 in situ can be expected to give levels of PCDD/F, spectacular to those involved in monitoring regular combustion, or environmental samples.

Product compositions tally with the mechanism shown in the Scheme.

Chlorine atoms are the sole H abstractors, and in a sense mimic OH· in normal autoxidation/combustion. Details on the thermochemical kinetics will be published elsewhere[9]. The $ClC_6H_4OO·$ radicals will largely decompose into $ClC_6H_4O·$ and $O(^3P)$, the latter reacting with chlorobenzene to give phenol and the three chlorophenols[12]. To some extent, the chlorophenoxyl radicals appear to react with Cl_2, a relatively slow step due to its endothermal character. The resonance stabilized, relatively unreactive mono- and dichlorophenoxyls mainly undergo reversible coupling. The ortho-C/ortho-C coupled dimers are capable of conversion to stable, analyzable products, viz. the observed PCDFs. The net loss of water takes place with an overall effective rate constant of ca 10^8 $M^{-1}s^{-1}$ [6].

References

1 Goldfarb, Th.D. Evidence for postfurnace formation of PCDDs and PCDFs -- Implications for control. Chemosphere, 18 (1989), 1051-1055.

2 Stieglitz, L. and H. Vogg. On formation conditions of PCDD/PCDF in fly ash from municipal waste incinerators. Chemosphere, 16 (1989), 1917-1922.

3 De Leer, E.W.B., R.J. Lexmond and M.A. de Zeeuw. "De novo"-synthesis of chlorinated biphenyls , dibenzofurans and dibenzo-p-dioxins in the fly ash catalyzed reaction of toluene with hydrochloric acid. Chemosphere, 19 (1989), 1141-1152.

4 Born, J.G.P., R. Louw and P. Mulder. Formation of dibenzodioxins and chlorobenzenes in fly ash catalyzed reactions of monochlorophenols. Chemosphere, 19, (1989), 1629-1633.

5 Born, J.G.P., Thesis, Leiden University, The Netherlands, 1992.

6 Born, J.G.P., H.W.A. van der Wart, P. Mulder and R. Louw. Gas phase oxychlorination of benzene. Recl. Trav. Chim. Pays Bas, 112 (1993), 262-270.

7 Born, J.G.P., R. Louw and P. Mulder. Formation of dibenzodioxins and dibenzo-

FORM

furans in homogenous gas-phase reactions of phenols. Chemosphere, <u>19</u> (1989), 401-406.

8 Mulder, P. and J. Joosting Bunk. Unpublished observations from this laboratory.

9 Sommeling, P.M., P. Mulder, R. Louw, D.V. Avila, J. Lusztyk, K.U. Ingold. Rate of reaction of phenyl radicals with oxygen in solution and in the gas phase J. Phys. Chem., submitted

10 Dorrepaal, W. and R. Louw. The mechanism of the vapor phase chlorination of benzene derivatives. Int. J. Chem. Kinet., <u>10</u> (1978), 249-275.

11 Born, J.G.P., P. Mulder and R. Louw. Fly ash mediated reactions of phenol and monochlorophenols: oxychlorination , deep oxidation and condensation. Environ. Sci. Technol., in press

12 Sol, V.M., M.A. van Drunen, R. Louw and P. Mulder. Gas phase oxygenation of benzene derivatives at ca 300 K with O(^{3}P) atoms produced by microwave discharge of N_2O. Part 1. Rates and mechanism of phenol formation . J. Chem. Soc., Perkin Trans. 2 (1990), 937-942.

Table. Gas phase Chlorination and Oxydation of Chlorobenzene[1]

exp	T (°C)	intake (mmol/h)			DCB yield on CB (%)	DDP	PCDF % on DCB	ratio PCDF $D_2/T_3/T_4$
		N_2	Cl_2	O_2				
(a)	330	246	10.1	–	5.1	1.4	–	–
(b)	330	245	10.1	4.8	1.6	1.6	0.34	68/25/7
(c)	330	227	10.4	20.7	0.37	1.4	0.68	66/31/3
(d)	350	231	11.4	20.9	1.4	1.2	1.8	58/39/3
(e)[2]	350	233	10.6	20.9	2.7	2.7	4.9	58/37/5

notes
1 intake chlorobenzene : 29.8 mmol/h; dwell time : 140-150s
2 in exp (e) 1 mol % of $C_6H_4Br_2$ was added to the feed

Figure

Formation of PCDF and dichlorobiphenyls (DDP)

■ % DDP on DCB ⬚ % PCDF on DCB