Reactions of 2,4,6-trichlorophenol on model fly ash: oxidation to CO and CO_2, condensation to PCDD/F and conversion into related compounds

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Abstract

Thermal treatment of 2,4,6-trichlorophenol on a magnesium silicate-based model fly ash in the temperature range between 250°C and 400°C leads predominantly to carbon monoxide and carbon dioxide. The fraction of 2,4,6-trichlorophenol which is oxidized to CO and CO_2 increases from 3% at 250°C to 75% at 400°C. Further products are polychlorinated benzenes, dibenzo-*p*-dioxins, dibenzofurans and phenols. The homologue and isomer patterns of the chlorobenzenes suggest chlorination in the ipso-position of the trichlorophenol. The formation of PCDD from 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol on municipal solid waste incinerator fly ashes and model fly ash were compared and the reaction order calculated. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Heterogeneous reaction; 2,3,4,6-tetrachlorophenol; Fly ash; Reaction order

1. Introduction

Polychlorinated dibenzodioxins and dibenzofurans (PCDD/F) and several classes of other chlorinated aromatic compounds are formed in thermal industrial processes like municipal solid waste incineration (MSWI; Stieglitz et al., 1989a,b), metal ore sintering (Buekens et al., 1998), smelting of secondary aluminum (Lahl et al., 1995), etc. Besides carbon as a source for the generation of PCDD/F – the so-called de-novo-synthesis (Stieglitz et al., 1989a,b, 1997; Stieglitz, 1998) – chlorinated phenols (PCPh) play an important role as precursors (Dickson and Karasek, 1987; Milligan and Altwicker, 1996) or intermediates (Stieglitz et al., 1989a,b; Blaha and Hagenmaier, 1995; Hell et al., 1997) in the formation of PCDD. PCPh as well as other pre-

cursors are formed in MSWI de-novo from particulate carbon. Among the possible precursors for the formation of PCDD/F, it seems that PCPh have the highest potential to generate PCDD (Altwicker and Milligan, 1993; Addink et al., 1995; Ghorishi and Altwicker, 1996), while chlorinated biphenyls (Scholz et al., 1997) as well as biphenyl (Wilhelm et al., 1999) are the most effective precursors in the PCDF formation processes.

Similar to the oxidative degradation of particulate carbon on fly ash (Milligan and Altwicker, 1993; Stieglitz et al., 1993), phenol and monochlorophenols are mainly oxidized to CO and CO_2. Born et al. (1993) observed a steep increase in the conversion of monochlorophenols to CO and CO_2 with rising temperature, from 5% at 350°C to about 70% at 450°C. In contrast, Milligan (1994) reported no increase in the CO and CO_2 concentrations versus the de-novo baseline, when $2,3,4,6-Cl_4Ph$ was flowed over fly ash, while observing nearly complete conversion of the chlorophenol; possibly due to differences in fly ash activity and a higher degree of chlorination inhibiting the oxidation. As 2,4,

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6-Cl_3Ph can be the dominant congener among the Cl_3Ph (>90%) and among the total sum of PCPh (>40%) in the emissions of a MSWI (Aittola and Vänni, 1992; Jay and Stieglitz, 1995), we investigated the reactions of 2,4,6-Cl_3Ph on a model fly ash with emphasis on the formation of CO, CO_2, PCBz and PCDD/F. The reaction order for the condensation of 2,4,6-Cl_3Ph and 2,3,4,6-Cl_4Ph, respectively, to PCDD on different fly ashes was then calculated.

2. Material and methods

The experiments were conducted in a tubular glass reactor (1.5 cm diameter × 50 cm length) which was mounted vertically in an oven. The model fly ash (83.7% Florisil, 14.7% KCl, 1.1% $CuCl_2 \cdot 2H_2O$ and 0.5% 2,4,6-Cl_3Ph) was placed on a glass frit in the middle of the glass tube and flushed with a gas stream of 20% oxygen in helium (50 ml/min). Florisil itself is composed of 85% SiO_2 and 15% MgO. The volatile organic compounds were collected in a toluene impinger. Subsequently, the gas phase was passed through a mass spectrometer for the online measurement of CO and CO_2. Quantification was performed by means of an external standard method, using a calibration gas mixture (Messer Griesheim). The extract of the model fly ash and the solution of the toluene impinger were cleaned-up together. The PCPh, PCBz and PCDD/F were measured by HRGC/LRMS with a 30 m DB-5 column and quantified by ^{13}C internal standards.

A further series of experiments was performed with model fly ash and a MSWI fly ash from the Environmental Protection Agency (termed EPA fly ash hereafter) with different 2,4,6-Cl_3Ph concentrations in the gas phase. Details of the experimental conditions and data have been published recently (Hell et al., 1998, 1999).

3. Results and discussion

3.1. Conversion of 2,4,6-trichlorophenol to other chlorinated phenols and benzenes

Thermal treatment of 2,4,6-Cl_3Ph-doped model fly ash in the temperature range between 250°C and 400°C and reaction times between 1 and 60 min leads predominantly to higher chlorinated phenols. The total conversion of 2,4,6-Cl_3Ph is >90%; <0.5% is converted into other chlorophenols (main products 2,3,4,6-Cl_4Ph and Cl_5Ph).

The yield of PCBz increases with reaction temperature and time, from 0.02% (1 μg/g at 250°C, 1 min) to 2.2% (120 μg/g at 400°C, 60 min). The 1,2,3,5-Cl_4Bz isomer is formed in the highest concentration (>50% of the total sum of PCBz and greater than 96% of the

Cl_4Bz), followed by 1,3,5-Cl_3Bz, Cl_5Bz and Cl_6Bz (Table 1). The high concentration of the Cl_4Bz and the almost exclusive formation of 1,2,3,5-Cl_4Bz isomer suggest chlorination in ipso-position: nucleophilic addition of a chlorine and elimination of the hydroxyl group.

3.2. Formation of PCDD/F

At 250°C, the PCDD concentration increases with prolonged reaction time, while at 300°C, a concentration maximum is obtained after 15 min. Even higher temperature leads to high PCDD concentrations for very short reaction times (1 min) followed by a steep decrease. This finding can be explained as follows: with increasing temperature the destruction rate grows more rapidly than the formation rate so that a concentration maximum of PCDD results at 300°C (Fig. 1). Similar results were obtained for PCDF with the difference that a concentration maximum is observed at 350°C and the concentrations are much smaller than those of PCDD. The highest conversion of 2,4,6-Cl_3Ph to PCDD/F is 1%. In a recent study, Sakurai et al. (1996) reported a yield of 1–2% of PCDD between 250°C and 300°C, while PCDF were only formed in the presence of HCl in the gas phase.

3.3. Oxidation to CO and CO_2

Despite the presence of three chlorine atoms in 2,4,6-Cl_3Ph the main reaction is the oxidative degradation. The quantity oxidized to CO and CO_2 increases from 3% at 250°C (1 min) to more than 75% at 400°C (60 min) (Table 2). No CO is formed at 250°C and 300°C (1 min). Only for reaction temperatures ≥300°C (reaction times ≥15 min) small amounts of CO could be detected. A CO_2/CO-ratio ≅ 5 is observed. This value is slightly lower than reported in the literature for monochlorophenols (CO_2/CO-ratio ≅ 6; Born et al., 1993).

In this series of experiments, a model system was doped with solid 2,4,6-Cl_3Ph, so that the data are not directly comparable with the results obtained on fly ash by Born et al. (1993) and Milligan (1994). On the Contrary to what might be expected, the high oxidation rate shows that the propensity of chlorophenols towards oxidation is not diminished by the chlorination degree. From the fact, that PCBz appear to be inert towards oxidation (their concentration increases with temperature and time), an oxygen function in the molecule seems to play a key role in the oxidation process. This suggests that the catalytically active species might interact with the adsorbed chlorophenol molecules via their oxygen function.

For two experiments, the continuously measured fractions of CO and CO_2 (volume%) in the gas phase are shown in Fig. 2, at 300°C (reaction time 1 min) and at

Table 1
Concentration of the chlorobenzenes (ng/g)

Temperature	250°C				300°C				350°C				400°C			
Time (min)	1	15	30	60	1	15	30	60	1	15	30	60	1	15	30	60
1,3-Cl$_2$Bz	0	0	0	0	0	0	160	180	110	240	240	350	380	720	1190	800
1,4-Cl$_2$Bz	0	0	0	0	250	340	14	100	10	40	60	80	160	380	430	410
1,2-Cl$_2$Bz	0	0	0	0	0	0	50	210	90	200	200	340	730	1770	2490	1490
Cl$_2$Bz	0	0	0	0	250	340	224	490	210	480	500	770	1270	2870	4110	2700
1,3,5-Cl$_3$Bz	260	290	760	950	710	2950	3260	5690	4310	7890	9470	8120	6550	11530	12120	16000
1,2,4-Cl$_3$Bz	40	40	0	50	90	120	150	290	190	760	940	870	1050	2110	2030	2080
1,2,3-Cl$_3$Bz	0	0	0	170	0	280	870	550	490	1290	1250	2570	1910	4260	8100	4500
Cl$_3$Bz	300	330	760	1170	800	3350	4280	6530	4990	9940	11660	11560	9510	17900	22250	22580
1,2,3,5-Cl$_4$Bz	610	1490	3090	3910	2860	10120	16770	25510	9450	15560	20820	31040	43970	55060	51180	61100
1,2,4,5-Cl$_4$Bz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1,2,3,4-Cl$_4$Bz	0	0	0	60	0	140	460	380	190	400	490	1230	1040	1720	2360	2500
Cl$_4$Bz	610	1490	3090	3970	2860	10260	17230	25890	9640	15960	21310	32270	45010	56780	53540	63600
Cl$_5$Bz	0	60	130	240	110	1480	3680	5580	2030	4360	5400	9230	13700	16080	15150	19310
Cl$_6$Bz	0	40	120	210	100	990	3290	3810	1930	3690	4970	10750	9850	17400	8120	14090
PCBz	910	1920	4100	5590	4120	16420	28704	42300	18800	34430	43840	64580	79340	111030	103170	122280

350°C (reaction time 30 min), respectively. For a heating time of only 1 min (Fig. 2(a)), CO_2-evolution is detected over 25 min. Measurement was stopped only after the baseline value was reached. It is interesting to note that for reaction temperatures $\geq 300°C$ (time ≥ 15 min), the online CO_2 concentration profile shows two maximums (Fig. 2b). The main maximum results from oxidation of 2,4,6-Cl$_3$Ph. The second maximum was observed for experiments in which the PCDD concentration already decreases after short reaction times (300°C, time ≥ 15 min and 350–400°C). Thus, the second rise of the CO_2 concentration might be related to the oxidation of the products of the 2,4,6-Cl$_3$Ph, e.g., PCDD/F or oligomerization and polymerization products.

3.4. Conversion of chlorophenols to PCDD on model fly ash and MSWI fly ashes

The rates of formation of PCDD/F from precursors as well as from carbon are crucial to understand the concentration levels of PCDD/F in the effluents of MSWI. In earlier studies, the reactivities of several chlorophenols to PCDD/F over a single fly ash were compared at one temperature (300°C) (Altwicker and Milligan, 1993; Milligan and Altwicker, 1996). From that investigation it was concluded that 2,3,4,6-Cl$_4$Ph is 7–8 times more reactive than 2,4,6-Cl$_3$Ph. In subsequent studies, fly ash dilution of 1:10 (with inert glass beads) was required to approach differential reactor conditions (i.e., $[Cl_xPh]_{(in)} \cong [Cl_xPh]_{(out)}$) which would facilitate kinetic analysis of the results. The EPA fly ash used in this study appears to be much more reactive (a better catalyst) than the model fly ash. Even with a 10-fold dilution of the fly ash with inert glass beads differential reactor conditions could not be obtained for 2,4,6-Cl$_3$Ph on EPA fly ash as well as on model fly ash; most of the 2,4,6-Cl$_3$Ph were converted. Unfortunately, the fly ash (Ontario fly ash) used in the original study (Milligan and Altwicker, 1996) with 2,3,4,6-Cl$_4$Ph is no longer available. The PCDD formation rate (Table 3) from 2,4,6-Cl$_3$Ph on EPA fly ash (Hell et al., 1998) is similar to that from 2,3,4,6-Cl$_4$Ph in the original study (Milligan and Altwicker, 1996) and approximately three times higher than on model fly ash (Table 3). The results suggest that the nature of the fly ash may be crucial in controlling the absolute and relative reactivities of chlorophenols to form PCDD/F. Nevertheless, the results can be used to derive the reaction order for the formation of PCDD from 2,4,6-Cl$_3$Ph on EPA and model fly ash and from 2,3,4,6-Cl$_4$Ph on Ontario fly ash. The PCDD concentrations formed on the model fly ash and two MSWI fly ashes (10-fold diluted with inert glass beads) as a function of gaseous chlorophenols in the inflow are summarized in Table 3.
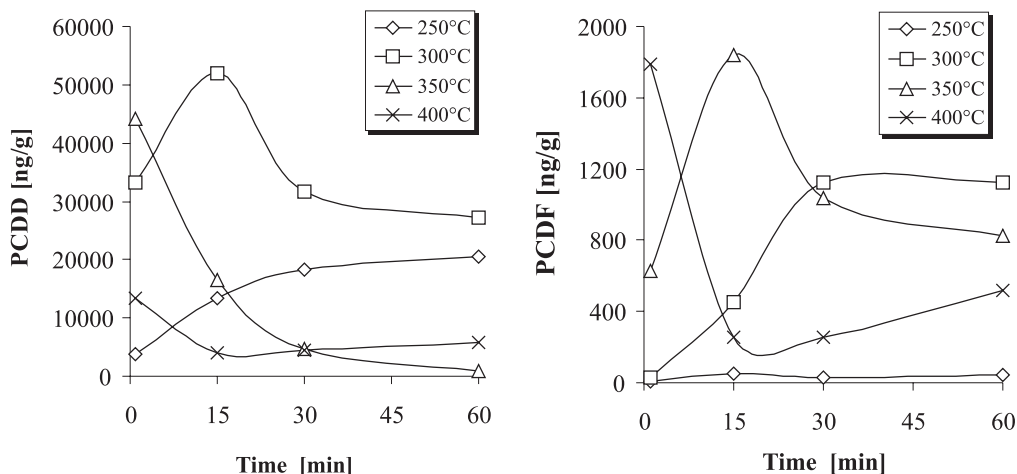
Fig. 1. Formation of PCDD and PCDF (ng/g) on model fly ash from 2,4,6-Cl₃Ph as a function of reaction temperature and time.

Table 2
Fraction of 2,4,6-Cl₃Ph (%) which is oxidized to CO and CO₂

Temperature	250°C				300°C				350°C				400°C			
Time (min)	1	15	30	60	1	15	30	60	1	15	30	60	1	15	30	60
CO	0	0	0	0	0	2.6	2.9	4.6	4.8	9.5	10.4	15.2	10.6	11.5	11.2	16.6
CO₂	2.6	6.1	10.6	11.6	5.9	11.0	14.6	27.5	25.5	44.1	56.1	69.5	38.8	51.3	52.6	58.5
CO₂/CO	∞	∞	∞	∞	∞	4.2	5.0	6.0	5.3	4.6	5.4	4.6	3.7	4.5	4.7	3.5

For the calculation of the reaction order, we assume that the decrease of the chlorophenol concentration, based on the formation of PCDD, is given by

$$-\frac{d[Ph]}{dt} = k[Ph]^n, \qquad (1)$$

with Ph = 2,4,6-Cl₃Ph or 2,3,4,6-Cl₄Ph, respectively.

Taking logarithms on both sides leads to

$$\ln\left(-\frac{d[Ph]}{dt}\right) = \ln k + n\ln[Ph]. \qquad (2)$$

Taking into account that only a fraction of the chlorophenol is converted into PCDD (6% on EPA fly ash, 2.2% on model fly ash and 25% on Ontario fly ash), the chlorophenol concentration for this pathway has to be corrected

$$[Ph]_{corr.} = f[Ph]. \qquad (3)$$

With the assumption that the increase of the PCDD concentration (formation of PCDD) is linearly correlated to the decrease of the chlorophenol concentration, the following equation results:
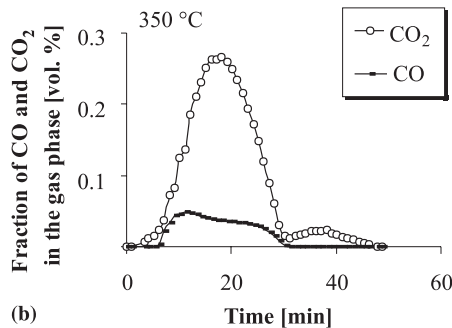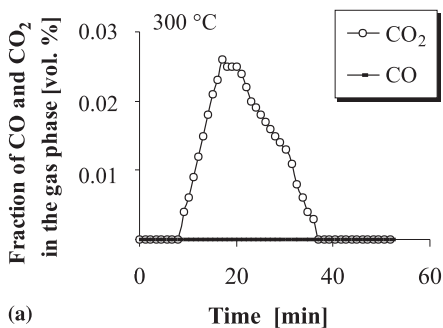

(a)   (b)

Fig. 2. Online volume percentages of CO and CO₂ formed by oxidation of 2,4,6-Cl₃Ph on model fly ash. The values are normalized to 1 g model fly ash: (a) heating time: 1 min (at 300°C); (b) heating time: 30 min (at 350°C).

Table 3
PCDD concentration (µg/g) after thermal treatment of EPA and model fly ash (0.2 g fly ash and 1.8 g glass beads) as a function of [2,4,6-Cl$_3$Ph] (300°C, 30 min), and Ontario fly ash (0.1 g fly ash and 0.9 g glass beads) as a function of [2,3,4,6-Cl$_4$Ph] (300°C, 15 min), 10% O$_2$ in N$_2$, 80 ml/min; x = #of Cl-atoms/phenol

	EPA fly ash (x = 3)						Model fly ash (x = 3)						Ontario fly ash (x = 4)		
Cl$_x$Ph (ng/ml)	0	18	55	186	400	467	2.6	3.9	6.2	166	316	410	150	350	700
PCDD (µg/g)	1.8	5.2	11.4	40.6	207	232	–	–	–	–	–	–	–	–	–
PCDD (µg/g)	–	–	–	–	–	–	0.2	0.9	0.6	21.4	76.0	79.4	–	–	–
PCDD (µg/g)	–	–	–	–	–	–	–	–	–	–	–	–	20	77	110

$$\ln\left(\frac{d[PCDD]}{dt}\right) = \ln(kf^n) + n\ln[Ph]. \qquad (4)$$

The calculation of f is based on the yield of PCDD. The PCDD concentrations were converted in µmol/g s and those of the chlorophenol concentrations in µmol/g fly ash.

The reaction order and the rate coefficient can be determined by plotting $\ln(d[PCDD]/dt)$ versus $\ln[Ph]$ (Fig. 3(a)–(c)). Thus, from the slope of the straight line, the reaction order and from the intercept, the rate coefficient for the reaction of 2,4,6-Cl$_3$Ph and 2,3,4,6-Cl$_4$Ph, respectively, to PCDD can be obtained. From Eq. (4), the following values resulted for the reaction orders (n): 1.23 for EPA, 1.08 for model and 1.12 for Ontario fly ash, and for the rate coefficients (k): 1.7×10^{-4} for EPA, 2.4×10^{-4} for model and 3.1×10^{-5}

for Ontario fly ash. The formation of PCDD from both chlorophenols follows approximately a first-order reaction independent on the matrix.

4. Conclusions

In a series of thermal experiments, the formation of PCDD/F and related compounds from 2,4,6-trichlorophenol as a precursor were studied on model fly ash. Chlorinated benzenes are the major products among the chlorinated organic compounds derived from the 2,4,6-trichlorophenol, with lesser quantities of PCDD, PCDF and higher chlorinated phenols. The PCBz are formed from the 2,4,6-Cl$_3$Ph by ipso-substitution of the hydroxyl group with chlorine. Dechlorination of the 2,4,6-Cl$_3$Ph and isomerization reactions of the chlorophenols formed are negligible. The concentration profile of the PCDD and PCDF as a function of the reaction time shows a maximum at 300°C and 350°C (15 min), respectively; this could be due to a competition between condensation reactions of the precursor and dechlorination and oxidation reactions of PCDD/F. The main reaction of the 2,4,6-Cl$_3$Ph is oxidation to carbon monoxide and carbon dioxide. In the concentration profile of carbon dioxide, a time-delayed second maximum is observed, which might be due to the oxidation of the PCDD/F formed or oligomerization products.

The condensation reactions of gaseous 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol to PCDD are approximately first-order on both fly ash as well as the model fly ash.
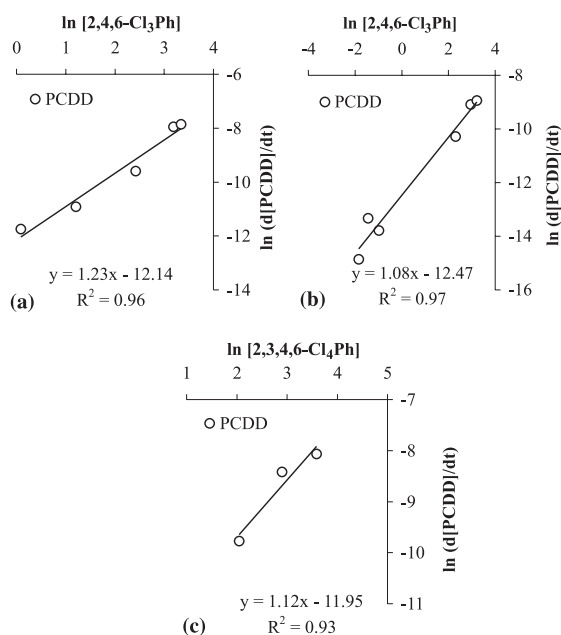

Fig. 3. PCDD formation from gaseous chlorophenols on: (a) EPA fly ash; (b) model fly ash; (c) Ontario fly ash.

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