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Mechanistic studies on the role of PAHs and related compounds in PCDD/F formation on model fly ashes

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Abstract

Model fly ashes containing Florisil ©, $CuCl_2 \cdot 2H_2O$ and PAHs with structures similar to dibenzo-*p*-dioxin or dibenzofuran were heated at 250°C in He/O_2 with regard to a supposed intramolecular reaction mechanism for oxygen incorporation. Highest reactivities in PCDF formation could be found for model compounds containing a biphenyl structure, while condensed π-systems lead to a decrease in reactivity for such compounds. Biphenyl is almost completely converted to dibenzofuran. PCDD formation from six-membered rings like xanthene/9,10-dihydroanthracene is of minor importance. ^{18}O-labeling of gaseous oxygen reveals no common reaction step for oxygen incorporation using 9-fluorenone, xanthene, diphenyl ether and diphenyl-2-carboxylic acid as model compounds. Pre-existing oxygen in reactants is a major source for ether groups in PCDD and PCDF. Determination of labeled and unlabeled CO and CO_2 besides He/O_2 reflects higher reactivities towards oxidation for model compounds containing ether groups than for compounds with carbonyl groups. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Model compounds; Intramolecular reaction; Heterogeneous reaction; Oxygen-18; De-novo-synthesis

1. Introduction

The PCDD/F formation on fly ashes can partly be ascribed to the de-novo-synthesis, which is a combination of transition metal catalyzed low-temperature oxidation and chlorination of the residual carbon and its inherent hydrocarbon structure. The role of PAHs and related compounds on fly ashes as precursors in PCDD/F formation by thermal treatment has been investigated by Jay and Stieglitz (1991), Schoonenboom and Olie (1995), Addink et al. (1995) and Iino et al. (1999). The detection of oxygen-containing related compounds on MSWI fly ashes has been described by Akimoto et al. (1997a,b). Olie et al. (1995) have described the role of gaseous oxygen in PCDD/F formation on fly ash, using gaseous $^{18}O_2$. Similar experiments with three different fly ashes were made by Wilhelm et al. (1999), who found a specific correlation between oxygen-16/18 released as CO/CO_2 and incorporated into PCDF. Still there is a lack of data comparing the tendencies of different reactant structures in PCDD/F-formation on model fly ashes, as well as formation studies of CO, CO_2, PCDD, PCDF and chlorinated phenols from model compounds using labeled gaseous oxygen.

The selected compounds are phenanthrene (I), anthracene (II), 9,10-dihydroanthracene (III), xanthene (IV), fluoranthene (V), 9-methylfluorene (VI), fluorene (VII), 9-fluorenone (VIII), diphenylmethane (IX), diphenyl ether (X), biphenyl-2-carboxylic acid (XI) and biphenyl (XII). CO/CO_2 production was supposed to be referred to an equal carbon content. Differences in molar weights of the reactants (154 (XII)−202 amu (V)) can be neglected, when conclusions are mainly drawn from differences of PCDD/F yields varying in order of magnitude. The selection was made due to the following considerations: (II)–(IV) serve as model compounds with a structure leading to dibenzo-*p*-dioxin by substitution of either CH or CH_2. (V)–(VIII) can be converted

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to dibenzofuran bodies by substitution of either CH_2, CHR as saturated groups or by C=O and CR_2 in a condensed π-system. (IX) and (X) may reveal similarities or differences between open- and closed-ring systems like (I)–(IV). (XI) and (XII) are related open-ring structures to (I) and (V)–(VIII). (XI) is related to supposed intermediates in the oxidation of (VI)–(VIII). The selected model compounds are also considered as carbon model compounds. Their potential to form PCDD/F may also support the hypothesis of their direct release by oxidative breakdown of the fly ash carbon, which is a basic reaction step in the concept of the de-novo-synthesis. Additionally, the influence of oxygen containing functional groups and their potential to serve as oxygen source for the ether bonds of PCDD/F shall be investigated by thermal treatment of (IV), (VIII), (X) and (XI) under a helium/$^{18}O_2$-atmosphere. Measuring the oxygen isotope contents in both the PCDD/F using GC–MS and in CO/CO_2 using online-MS helps to understand more about the oxygen transfer from the gas phase to organic precursors and the charcoal surface.

2. Experiment

Materials. Mixtures with fairly high carbon contents corresponding to real fly ashes as discussed in the Sections 3.1 and 3.3: 88.5 wt% Florisil (85% SiO_2, 15% MgO); 3.3 wt% Cu as $CuCl_2 \cdot 2H_2O$; 2.6 wt% PAH/charcoal. Mixtures with lower concentrations as discussed in Section 3.2: 89.9 wt% Florisil; 3.7 wt% Cu as $CuCl_2 \cdot 2H_2O$; 0.2 wt% PAH. Materials used are listed in order of purity (%): (I), (II), (VIII) >99% (Merck); (VI), (VII), (IX), (X): 99% (Aldrich); (IV), (XII): 98% (Fluka); (V), (XI): 98% (Aldrich); (III): 97% (Aldrich). The experiments were performed in a tubular glass reactor (15 mm diameter, 500 mm length) which was mounted vertically in an oven. The model fly ashes were heated for 60 min at 250°C in a gas stream of 5% O_2 in helium and a flow rate of 30 ml/min. Oxygen-18 was added with a constant ^{18}O content of 92% ± 2% and a ^{16}O content of 8% ± 2%. The isotopic content of the gas feed before heating and the gas phase composition during the reaction was measured online by mass spectroscopy (Leybold quadrupole-MS, mass range 1–100 amu). The fly ashes were soxhlet extracted with toluene. After clean-up, the samples were analyzed by HRGC–MS in SIM mode.

3. Results and discussion

3.1. Molecular structure and reactivity

The yields of PCDD/F, PCBz and PCPhOH for each compound are listed in Table 1. The contribution of condensation products from PCBz and PCPhOH to PCDD/F-formation can obviously be neglected, considering the low PCDD yields from (VIII) and (XII). (I) and (II) produce almost equal amounts of PCDD, PCBz and PCPhOH, while the bent shape of (I) obviously seems to be more favorable for a conversion to PCDF. Iino et al. (1999) postulated, that phenanthrene-like segments of larger PAHs like coronene are responsible for the release of PCDF by oxidative breakdown and chlorination of the parent molecule at 400°C. Phenanthrene itself is much less reactive than most of the other compounds investigated by thermal treatment at 250°C. With the low reaction temperature in this study, preferably those reactions are favored, that occur most readily even under mild conditions: The PCDF-formation from (V)–(VIII) is strongly dependent on the hybridization of the carbon in 9-position. Condensed systems (V), (VIII) show little reactivity in PCDF formation compared to those containing saturated carbon atoms (VI), (VII). The analog reaction of this substitu-

Table 1
Yields of PCDD/F, PCPhOH and PCBz produced by thermal treatment (1 h, 250°C) of model fly ashes in (ng/g), reactant concentration 2.6 wt%

Reactant	PCDD	PCDF	PCBz	PCPhOH
Phenanthrene	20	3170	31790	2220
Anthracene	20	140	29070	2410
9,10-Dihydroanthracene	530	2760	79140	8560
Xanthene	2670	1310	2510	70420
Fluoranthene	460	2640	18000	3340
9-Methylfluorene	490	84820	21210	2580
Fluorene	20	58410	32590	1870
9-Fluorenone	0	2670	282480	3670
Diphenylmethane	2160	23400	308460	52000
Diphenyl ether	10850	127290	40980	116560
Biphenyl-2-carboxylic acid	40	36970	78950	10320
Biphenyl	0	1419690	301950	5420
Blank	0	70	10	0

tion (CH_2/CHR→ –O–) is the formation of dibenzo-*p*-dioxin and its chlorinated homologs from either (III) or (IV), but the yields of these reactions can almost be neglected. A competitive reaction for (IV) seems to be CH_2-elimination followed by intramolecular condensation of the aromatic rings, leading to PCDF. The high PCDF yields from (X) exceed the PCDD yields by a factor of 10 and may be explained by such a mechanism. Cleavage of C–C-bonds is favored compared to cleavage of C–O-bonds by more than 100 kJ/mol. If formation of free phenyl- or phenoxy-radicals was a major reaction step, PCDD/F concentrations formed from (III), (IV), (IX) should be in the same magnitude as those formed from (X). (XII) shows extremely high PCDF yields and no PCDD formation at all. This result provides strong evidence for the intramolecular formation of the ether bond without further destruction of the reactant skeleton. The functional group (–COOH) in (XI) leads to a decrease in reactivity.

3.2. *Investigation of biphenyl as PCDF precursor*

The high reactivity of biphenyl in PCDF formation has furthermore been investigated in comparison with dibenzofuran as reactant under the same reaction conditions.

Table 2 shows the PCDD/F yields of low concentrated model mixtures containing biphenyl and dibenzofuran.

More than 7% of dibenzofuran are directly converted to PCDF by chlorination, while the main reaction remains the oxidation to CO and CO_2. The PCDF yields from biphenyl and dibenzofuran are in the same range. Calculating from the molar weights of reactants, more than 72% of biphenyl are converted to tetra- to octa-chloro-dibenzofurans. The highest PCDF yields produced from single PCB isomers under similar reaction conditions lie in the range of 50% (Scholz et al., 1997). Chlorination of the reactant rather seems to inhibit conversion to PCDF, although mono-chlorobiphenyl is known to serve as an efficient reactant in the preparation of dibenzofuran. Scholz (1997) found that $\alpha,\alpha,\alpha',\alpha'$-polychlorinated PCBs show little conversion to PCDF, while a decreased chlorination grade in this position leads to an enhanced reactivity in PCDF formation. The high similarity of the homolog patterns of PCDF produced from either biphenyl or dibenzofuran found in this study does not indicate the need for primary (poly-) chlorination of biphenyl.

Table 2
PCDD/F yields produced by thermal treatment of model fly ashes (1 h, 250°C) containing dibenzofuran and biphenyl in (ng/g), reactant concentration 0.2 wt%

Reactant	Biphenyl	Dibenzofuran
PCDD (sum)	1	24
T_4CDF	109	1050
P_5CDF	1444	1722
H_6CDF	14417	17072
H_7CDF	5142	6685
O_8CDF	2005	2509
PCDF (sum)	23119	29041

3.3. ^{18}O *labeling*

3.3.1. *Chlorinated organics*

The thermal treatment of the model fly ashes doped with the compounds (IV), (VIII), (X) and (XI) in a He/$^{18}O_2$ atmosphere allows to distinguish between gas phase and solid phase as oxygen sources for the ether groups of PCDD/F. The ^{16}O content of the chlorinated organics produced from the selected model compounds corresponds approximately to the fraction of oxygen containing molecules, that have been transformed directly to PCDD/F and chlorinated phenols by intra- or intermolecular conversions. The ^{18}O content on the other hand reflects roughly the fraction of molecules produced by incorporation of gaseous oxygen. As the values of the ^{16}O and ^{18}O contents, however, have been calculated on the basis of ratios between chromatograms of M-peak/M + 2-peak/M + 4-peak for each isomer, the average error increases with the chlorination grade, since the integrated M-peak is multiplied by a higher factor according to the ratios generated by the mole peak cluster of ^{35}Cl and ^{37}Cl. A relative small M-peak in combination with a high factor may therefore lead to values of isotopic contents higher than 100%. The values of the average ^{16}O content for all isomers of PCDD/F and chlorinated phenols found are given in Table 3.

The incorporation rate of gaseous oxygen to PCDD/F from model compounds is low, except for H_7CDF showing strong deviation. It depends on the chlorination grade for PCDF formed from model compounds (IV) and (X).

The incorporation rate of gaseous oxygen to form chlorinated phenols from model compounds with carbonyl group is in the range of 30–40%. The presumed main reaction pathway for phenol production is the cleavage of ether groups.

The incorporation of gaseous oxygen into chlorinated products from charcoal increases with the chlorination grade, except for O_8CDF. This result is in good agreement with the findings of Olie et al., for PCDD/F produced from fly ash doped with charcoal. PCDD produced from xanthene and diphenyl-2-carboxylic acid do hardly contain any oxygen from the gas phase. While gaseous oxygen is needed for the heterogeneous oxidation, oxygen of solid phase origin is the main source for PCDDs. H_2O, Si–OH and other reactant molecules are possible sources for ^{16}O. The differences in ^{18}O contents between PCPhOH and PCDD again indicate that

Table 3
^{16}O content (%) of PCDD/F and PCPhOH on model fly ashes thermally treated in a He/$^{18}O_2$ atmosphere (1 h, 250°C), reactant concentration 2.6 wt%[a]

^{16}O content	Xanthene	Diphenyl ether	9-Fluorenone	Biphenyl-2-carboxylic acid	Charcoal
D_2PhOH	98	77	75	62	100
T_3PhOH	105	89	69	58	89
T_4PhOH	104	76	70	61	57
P_5PhOH	85	82	77	70	47
T_4CDD	95	85	n.m.	88	n.m.
P_5CDD	98	86	n.m.	101	n.m.
H_6CDD	100	83	85	103	75
H_7CDD	106	89	89	105	60
O_8CDD	129	66	105	139	33
T_4CDF	101	99	82	85	100
P_5CDF	90	90	84	87	69
H_6CDF	101	109	91	93	78
H_7CDF	56	59	55	50	39
O_8CDF	127	136	79	129	82

[a] n.m.: not measurable.

phenol condensation cannot be an important reaction pathway to PCDD formation under the chosen conditions. PCDF formed from (VIII) and (XI) show a higher incorporation rate of up to 20% of gaseous ^{18}O, while the lower rates for (IV) and (X) can be ascribed to a higher degree of intramolecular condensation reactions.

3.3.2. *CO/CO$_2$ in the gas phase*

The gas phase composition for each run is shown in Figs. 1–3, the total values for 1 h of reaction are listed in Table 4.

The following results can be concluded from the data received: all compounds show desorption of formerly chemisorbed $C^{16}O_2$ in the first period of reaction and a strong correlation between concentrations of ^{18}O-labeled CO/CO$_2$ can be observed (Figs. 1–3). The maximum concentrations are achieved with a time delay compared to $C^{16}O$/$C^{16}O_2$. This result suggests different CO/CO$_2$ formation pathways from gaseous and solid phase oxygen. Charcoal shows the highest CO/CO$_2$ production with the highest ^{18}O content (Fig. 3). The oxidation is fast compared to the fly ashes with model compounds. Only 40% of the oxygen in CO/CO$_2$ produced from charcoal is of gaseous origin (Table 4). The ^{18}O content of CO/CO$_2$ follows the order (VIII):22% < (XI):26% < (X):29% < (IV):37%. Solid phase oxygen is the major source for gaseous oxidation products, still ^{18}O contents are remarkably high compared to those of PCDD/F (Tables 3 and 4). Similar reactivities can be found for model compounds with ether groups. The formation pathways of $C^{16}O$ and $C^{16}O^{18}O$ released from (IV) and (X) appear to be

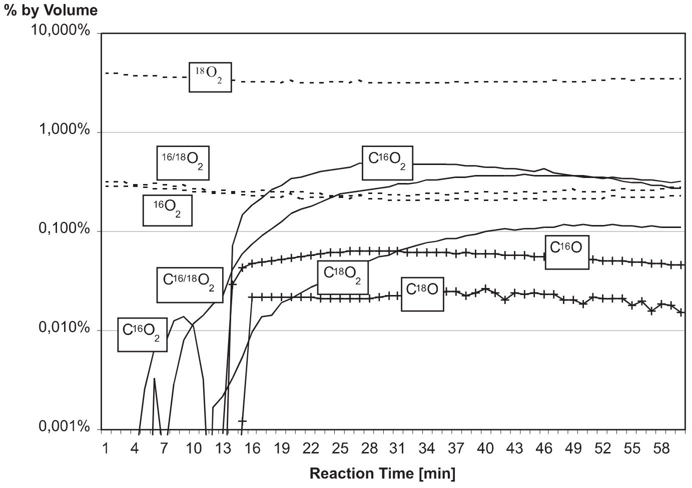

Fig. 1. Gas phase composition: model fly ash containing diphenyl ether.

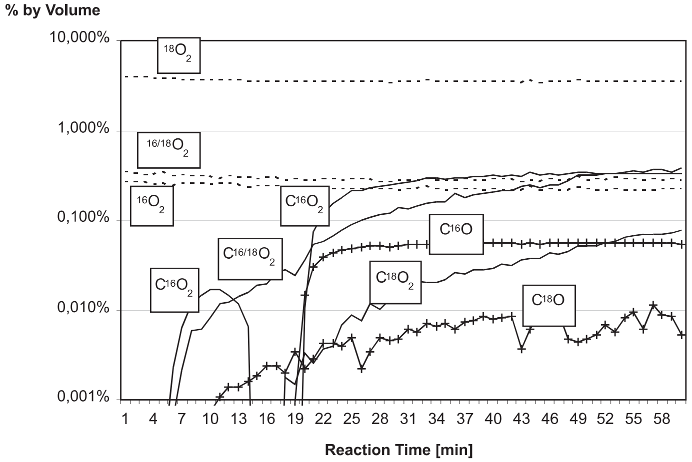

Fig. 2. Gas phase composition: model fly ash containing diphenyl-2-carboxylic acid.

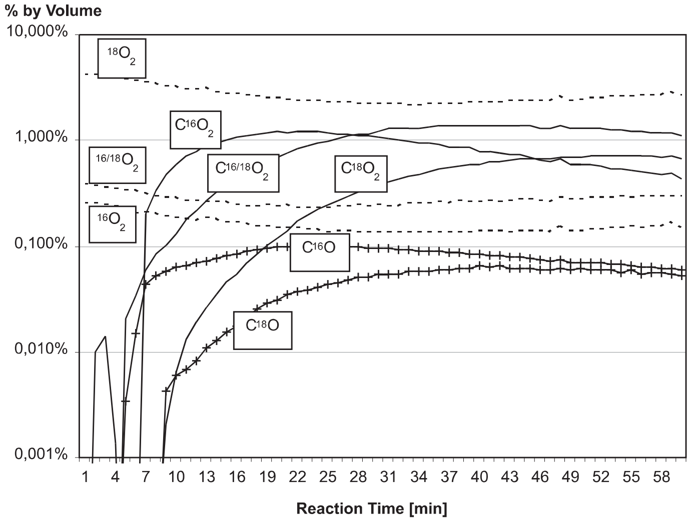

Fig. 3. Gas phase composition: model fly ash containing charcoal.

coupled, suggesting CO-elimination and further oxidation to CO_2 from the intermediates (Fig. 1). The total CO/CO_2 amounts produced from (IV) and (X) exceed those formed from (VIII) and (XI) and follows the same order as their ^{18}O content (Table 4).

4. Conclusions

The following conclusions can be made for the investigated model compounds under the chosen reaction conditions and the concentrations used in these experiments:

The substitution of α-hydrogen atoms of biphenyl and related compounds by an ether group is the most efficient reaction for PCDF production from the selected compounds. Lower chlorinated PCB may be intermediates in substitution reactions of HCl by ether groups, but direct conversion of biphenyl to dibenzofuran could rather explain the great similarities of the homolog patterns and yields of PCDF produced from both dibenzofuran and biphenyl. The facile formation of an ether bond resulting in a dibenzofuran body supports the model of similar processes occuring on the fly ash carbon surface. The hypothesis of phenyl- or phenoxy-radicals as important intermediates can hardly explain the obvious influence of the reactants' structure on the molar ratio of PCDD to PCDF formed from the different model compounds. Condensation of (poly-) chlorinated phenols or –benzenes as a major reaction

Table 4
Formation of CO/CO_2 and mass balance calculated for oxygen (μmol) by thermal treatment of model fly ashes (1 h, 250°C) doped with model compounds (2.6 wt%)

Reactant:	Xanthene	Diphenyl ether	9-Fluorenone	Biphenyl-2-carboxylic acid	Charcoal
Release by oxidation					
$C^{16}O$	24	32	9	26	54
$C^{18}O$	0	12	1	3	30
$C^{16}O_2$	207	219	58	142	549
$C^{16}O^{18}O$	270	166	36	110	661
$C^{18}O_2$	76	43	4	17	272
^{16}O	708	636	161	420	1813
^{18}O	422	266	46	147	1235
Absorption					
$^{16}O_2$	37	45	22	30	74
$^{16}O^{18}O$	34	46	31	44	66
$^{18}O_2$	425	454	156	284	1156
^{16}O	108	136	75	104	214
^{18}O	884	954	343	612	2378
Balance					
^{16}O	+600	+500	+86	+316	+1599
^{18}O	−462	−688	−297	−465	−1134

pathway can be excluded as well, since they appear as byproducts in high concentrations (Table 1, see reactants: (XI), (XII)), where highest PCDF yields are obtained besides lowest PCDD concentrations. In general, PCDF formation by a supposed intramolecular conversion seems to occur rather than PCDD formation. The mechanism of conversion is still unknown, but a participation of copper-(II)-ions seems plausible, as it is also known to catalyze carbon gasification.

Model compounds with inherent ether groups are rather likely to be attacked by gaseous oxygen than carbonyl groups. Incorporation of gaseous oxygen to model compounds is low compared to charcoal. Chemically bonded oxygen of charcoal and model compounds are a very efficient source in PCDD/F formation. PCDF formed from compounds containing carbonyl functions rather tend to incorporate gas phase oxygen than (IV) and (X). Higher chlorinated organics produced from charcoal are rather likely to be formed by heterogeneous oxidation than lower chlorinated organics, which may be formed by direct release of precursor structures from the coal matrix.

5. Summary

Biphenyl-like structure elements of amorphous carbon may easily be converted to PCDF precursors. Ether groups show high reactivity in the Cu (II)-catalyzed low-temperature oxidation at 250°C. Chemically bonded oxygen of the carbon matrix is supposed to be an important source for PCDD/F formed by de-novo-synthesis.

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