

Formation of Chlorinated Compounds from Toluene in the Gas Phase and Particulate Carbon on a Model Fly Ash

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1. Introduction

The formation of polychlorinated dibenzo-p-dioxins (PCDD) and -furans (PCDF) in the colder zones of the MWI-plants involves heterogeneous reactions on the fly ash surface. Two different pathways have been postulated for PCDD/PCDF formation on fly ash:

- specific gas phase organic precursors such chlorobiphenyls, -benzenes^{1,2,3)}, -phenols^{2,4,5,6)} and toluene^{2,7,8)} react on the fly ash surface forming PCDD/F.
- de-novo synthesis^{9,10,11)}: formation of chlorinated compounds from macromolecular residual carbon and inorganic chloride. This reaction is catalyzed by Cu and Fe ions.

By experiments with ¹³C-carbon as particulate carbon and an organic precursor (¹²C-compound) it is possible to compare the formation of chlorinated compounds from particulate carbon (¹³C-enriched) with the formation from the organic precursor (¹²C-compounds). If these two formation routes proceed separately only ¹²C- and ¹³C-compounds will be formed. Mixed PCDD/PCDF with both kinds of C-atoms, however, have to be formed if these two pathways share some steps. The results from experiments using ¹³C-carbon as particulate carbon and ¹²C-toluene as a gas phase organic precursor are presented here.

2. Experimental

Materials

Magnesium silicate (60-100 mesh; Roth) was heated at 600°C for 24h.

A model fly ash mixture was prepared by addition of 4% ¹³C-enriched carbon (amorphous, 99%, Cambridge Isotope Laboratories), 0,4% Cu as CuCl₂·2H₂O (Merck) and 7% Cl as KCl (Merck) to pretreated magnesium silicate. The mixture was homogenized.

Thermal treatment and sampling

The model mixture (1g) was heated in an apparatus described earlier⁸⁾ at 275°C, 300 °C and 350°C for 2 hrs respectively with an synthetic air stream (50 ml/min) containing gaseous toluene (86,7 µg/ml air). Volatile compounds were collected using a cold trap consisting toluene cooled with ethanol/CO₂. After the thermal treatment the annealed sample was extracted by toluene. The toluene extract and the cold trap contents were analyzed separately. Clean-up was carried out according to standard procedures¹¹⁾.

Analysis

A solution of 1,3-dichloro-4-fluorobenzene, 1,3,5-trichloro-2,4,6-trifluorobenzene and 2,6-dichloro-4-fluorophenol in toluene was used as internal standard for the quantification of chlorobenzenes and chlorophenols. PCDD and PCDF are quantified using a solution of 1-bromo-2,3,7,8-tetraCDF as standard, added to the samples before the GC analysis.

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The samples containing chlorobenzenes and chlorophenols were measured by HRGC-LRMS with a DB-5 column. The PCDD/PCDF fraction was measured by HRGC-HRMS as described before¹¹.

3. Results and Discussion

Results of the experiments are reported in table 1. Significant amounts of PCBz, PCPh, PCDD and PCDF were formed either from ¹²C-toluene or ¹³C-enriched carbon. Dioxins and furans in which one phenyl ring is ¹²C (from toluene), the other one ¹³C-labeled (from ¹³C-carbon) were also found. ¹²C-chlorobenzenes are the main products with 92-99% of the total molar amounts of products (¹²C und ¹³C).

Toluene has a higher reactivity than ¹³C-carbon. At 275°C the conversion of toluene related to the molar amounts of ¹²C-carbon contained in the toluene added and ¹³C-carbon are 0,04 and 0,02% respectively. At higher temperature higher yields are obtained. At 350°C 0,45% of the toluene and 0,07% of the ¹³C-carbon are converted to the products.

reactants	products	amount (ng/g of model mixture)		
		275°C	300°C	350°C
¹² C-toluene *	PCBz	354600	1447210	4423630
	PCPh	33740	41790	5730
	PCDD	1040	3540	585
	PCDF	540	3288	930
¹³ C-carbon *	PCBz	26350	29280	89560
	PCPh	925	1910	300
	PCDD	160	340	40
	PCDF	1265	3400	320
¹² C-toluene and ¹³ C-carbon	PCDD	560	1370	235
	PCDF	100	430	200

Table 1. Formation of PCBz, PCPhOH, PCDD and PCDF from ¹²C-toluene and ¹³C-carbon.

Reaction time : 2 hrs

* Amounts of reactants:

¹³C-carbon: 40 mg

¹²C-toluene: 520 mg ; 520mg toluene contains 407 mg of ¹²C-carbon
(methyl group was not considered)

3.1. Formation of chlorinated compounds as a function of the temperature

The formation of chlorinated compounds from ¹²C-toluene shows the same temperature dependency as the formation from ¹³C-carbon. The amount of PCBz increases continually with the temperature, whereas the formation of PCPh, PCDD and PCDF shows an optimum at 300°C (Figure 1). This temperature peak results from the competition between destruction and formation reactions. PCBz destruction does not take place because immediately after its formation these compounds are desorbed and transferred to the cold trap. At any temperature no amount of PCBz was found adsorbed on the model fly ash, whereas chlorophenols are only found on the model fly ash. Probably these compounds are strongly bound at the alkaline surface (magnesium silicate). At low temperatures dioxins and furans are also adsorbed on the reaction surface but at 350°C desorption takes place, so that the main part of PCDD/F goes in to the gas-phase. Dioxins and furans which are not desorbed at this temperature are probably destroyed.

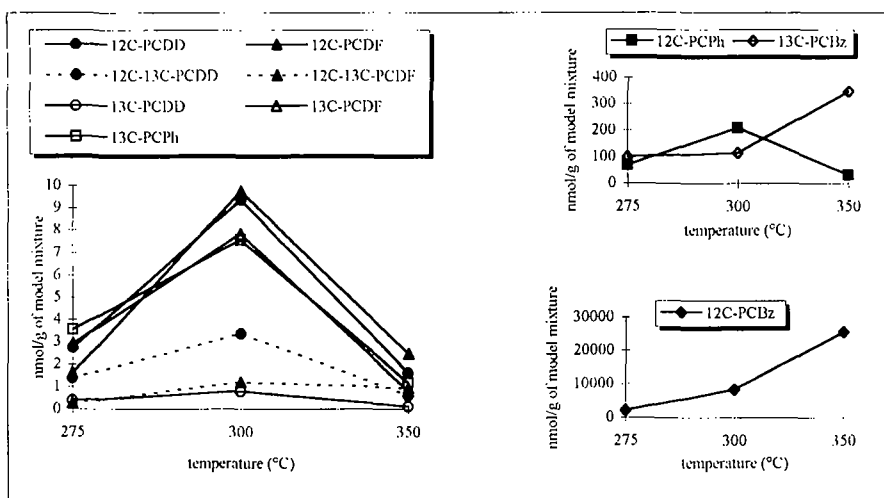


Figure 1.: Formation of chlorinated compounds from ^{12}C -toluene and ^{13}C -carbon on a model mixture as a function of the temperature. Reaction time : 2 hrs

3.2. Comparison between the products from toluene and ^{13}C -carbon.

Chlorobenzenes are the main products from toluene (96-99% of the total molar amount of toluene products). Significant amounts of chlorophenols are also formed. PCDDs and PCDFs are the minor products. At 275°C the PCDD formation dominates, whereas at higher temperatures the PCDF formation is favoured.

Chlorobenzenes are also the main products from ^{13}C -carbon (85-99%). The amounts of chlorophenols and PCDF are similar. Only little PCDD amounts were detected. The preference of the PCDF formation from particulate carbon ("de-novo synthesis") is already known⁹⁾.

Significant amounts of $^{12}\text{C}_6/^{13}\text{C}_6$ -PCDD were also found. For the formation of this mixed PCDD it is necessary that a $^{12}\text{C}_6$ -ring (from toluene), e.g. chlorophenols and chlorobenzenes, reacts with another one from ^{13}C -carbon. The formation of mixed PCDD is more favoured than the formation of $^{13}\text{C}_{12}$ -PCDD. This is not surprising since the concentration of toluene products is higher than the products from ^{13}C -carbon.

Minor amounts of $^{12}\text{C}_6/^{13}\text{C}_6$ -PCDF are found. This fact indicates that precursor phenyl rings, e.g. chlorophenols and chlorobenzenes, are less involved in the formation of PCDF from ^{13}C -carbon and toluene.

Chlorination degree of the products from toluene and ^{13}C -carbon

At the whole temperature range studied products from toluene have lower chlorination degrees than those from ^{13}C -carbon ones (table 2). The distribution of toluene and ^{13}C -carbon products between the different chlorinated congeners is reported in table 2.

At 275°C dichlorobenzenes are the main component of the ^{12}C -chlorobenzenes. At higher temperatures the formation of trichlorobenzenes from toluene is favoured.

With increasing temperature the chlorination degree of PCDD, PCDF and PCPh decreases. This finding is an experimental proof that at higher temperatures these compounds are dechlorinated. So it is understandable why the formation of this products showed an optimum at 300°C (s. above).

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compound	chlorination degree						
	Cl ₂	Cl ₃	Cl ₄	Cl ₅	Cl ₆	Cl ₇	Cl ₈
¹² C ₁₂ -PCDD	n. i.	n. i.	12	33	34	14	7
¹³ C ₁₂ -PCDD	n. i.	n. i.	1	4	23	47	26
¹² C ₁₂ -PCDF	n. i.	n. i.	36	37	23	4	1
¹³ C ₁₂ -PCDF	n. i.	n. i.	1	2	11	25	61
¹² C ₆ / ¹³ C ₆ -PCDD	n. i.	n. i.	4	18	40	15	22
¹² C ₆ / ¹³ C ₆ -PCDF	n. i.	n. i.	19	30	35	13	3
¹³ C ₆ -PCBz	38	56	5	0	1		
¹³ C ₆ -PCBz	1	4	19	44	32		
¹² C ₆ -PCPh	19	61	14	6			
¹³ C ₆ -PCPh	1	2	21	76			

Table 2.: Percentage (molar) distribution of PCDD, PCDF, PCBz and PCPh formed from ¹²C- toluene and ¹³C-carbon between the different chlorination degrees at 300°C.
n.i. : not investigated

3.3. Isomer distributions; mechanistic aspects

Formation of chlorinated benzenes

The PCBz formation from toluene is very necessary. The main component of dichlorobenzenes is the 1,3-isomer (90%). The 1,2,3-isomer (95%) and the 1,2,3,4-isomer are the main tri- and tetrachlorobenzenes found. This shows that tri- and tetrachlorobenzenes are formed by an ortho-directed chlorination. A surface catalyzed radical mechanism has been proposed earlier^{11,12)} to explain the preferred formation of 1,2,3-trichlorobenzene in the CuCl₂ catalyzed (oxy)-chlorination of benzene at 300°C.

The formation of chlorobenzenes from ¹³C-carbon has lower selectivity than the formation from toluene and involves other chlorobenzene isomers. The mechanism forming chlorobenzenes from particulate carbon is apparently a different one.

Formation of chlorinated phenols

At 275 und 300°C the 2,6-isomer is the main dichlorophenol (40%) formed from toluene. Since the 2,4- and 2,5-isomers are not separated by GC conditions applied, it is not possible to determinate the exact amounts of this two isomers. But both isomers together represent 45% of the total amount of dichlorophenols that are formed from toluene. At 350°C the 2,3-isomer is also found.

The formation of tri- and tetrachlorophenols from toluene is more selective. The 2,4,6- and 2,3,4,6-isomers are the main components, with a percentage of 96-50% and 96-80% respectively.

Probably at 275°C only 2,6- and 2,4-dichlorophenols, but not the 2,5-isomer, are formed. The higher chlorinated phenols are formed via chlorination at p-position (to OH-group referred). Probably electrophilic substitution, in which the hydroxyl directs to the ortho- and para-positions, takes place. At 350°C 2,3,6- and 2,3,4-trichlorophenols are also found. These isomers are probably formed from 2,3-dichlorophenol by chlorination at the para- and ortho-position respectively.

From ¹³C-carbon only the highly chlorinated chlorophenols are formed. The mechanism forming these compounds from particulate carbon ist not clear. With a ratio of 66/30 are the 2,3,4,6- and 2,3,4,5-isomers the main tetrachlorophenols formed.

Formation of chlorinated dioxins

The ¹²C₁₂-PCDD formation just as the formation of ¹²C₆/¹³C₆-PCDD is very selective and the main isomers are the same: 1,3,6,8- and 1,3,7,9-tetraCDD; 1,2,4,7,9-, 1,2,4,6,8- and 1,2,3,7,9-pentaCDD; 1,2,4,6,7,9-, 1,2,4,6,8,9- and 1,2,3,4,6,8-hexaCDD (these isomers could not be separated). These tetraCDD isomers are the products of the condensation of two 2,4,6-trichlorophenols. PentaCDDs are formed via condensation of 2,3,4,6-tetrachlorophenol with 2,4,6-trichlorophenol. 1,2,3,4,6,8-hexaCDD

is the only product of the condensation of 2,4,6-trichlorophenol with pentachlorophenol. Only small amounts of higher chlorinated dioxins are formed since toluene only forms low chlorinated chlorophenols.

Mixed dioxins, $^{12}\text{C}_6/^{13}\text{C}_6$ -PCDDs, are formed via condensation of a chlorophenol from toluene with a chlorophenol from ^{13}C -carbon. HexaCDD, the main mixed dioxin, can be formed via condensation of 2,4,6- ^{12}C -trichlorophenol with ^{13}C -pentachlorophenol.

The dioxins that are formed from ^{13}C -carbon are highly chlorinated just like ^{13}C -chlorophenols. Probably ^{13}C -PCDDs are also formed at least partly by condensation of chlorophenols.

Formation of chlorinated furans

The mechanism forming PCDFs from ^{13}C -carbon and toluene could not be understood. From ^{13}C -carbon no main ^{13}C -PCDF isomers are formed. In strong contrast some congeners of ^{12}C - and $^{12}\text{C}_6/^{13}\text{C}_6$ -PCDF are preferred. The main isomers of ^{12}C -PCDFs are generally not the same like the mixed furans.

4. Conclusions

Using ^{12}C -toluene and ^{13}C -carbon on a model mixture the reactions forming chlorinated compounds from toluene in the gas-phase and particulate carbon were investigated. The following conclusions may be arrived at:

- Toluene is more reactive and selective than particulate carbon.
- Toluene products are higher chlorinated than ^{13}C -carbon products.
- The mechanism forming chlorobenzenes from toluene and ^{13}C -carbon are probably different. The formation from toluene involves chlorination in ortho-position.
- Chlorophenols are formed from toluene via oxychlorination.
- The formation of characteristic PCDD isomers and mixed ($^{12}\text{C}_6/^{13}\text{C}_6$) PCDDs indicate that they are probably formed partly via condensation of chlorophenols.
- Since only small amounts of mixed PCDFs are formed condensation of intermediate phenyl compounds (chlorophenols and chlorobenzenes) plays no significant role in the formation of PCDFs from toluene or from particulate carbon.

5. References

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