

# Dechlorination ability of municipal waste incineration fly ash for polychlorinated phenols

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## Abstract

Pathways of pentachlorophenol dechlorination have been investigated on municipal waste incineration fly ash at 200 °C under nitrogen atmosphere. Thermodynamic calculations have been carried out for these dechlorination conditions using the method of total Gibbs energy minimization for the whole system consisting of gaseous components, i.e., chlorinated phenols, phenol, hydrogen chloride and the Cu<sub>3</sub>Cl<sub>3</sub> trimer and of solid Cu<sub>2</sub>O and CuCl<sub>2</sub> components. The effects of water, temperature and of the amounts of the reaction components on the thermodynamic equilibrium have been discussed and the experimental results compared with the calculated thermodynamic data.

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## 1. Introduction

Previous works of other authors as well as our studies (Stach et al., 2000; Pekárek et al., 2003) on dechlorination of polychlorinated dibenzo-*p*-dioxins (PCDD), dibenzofurans (PCDF), biphenyls (PCB) and benzenes (PCBz) in the presence of fly ash produced by municipal waste incineration (MWI) have clearly demonstrated that MWI fly ash can induce dehalogenation of these compounds, provided that the crystalline structure of the carbon present has been destroyed, copper is present in an appropriate form and the reaction occurs in an oxygen-deficient atmosphere. Dehalogenation reactions proceed at 250–350 °C and require the presence of a hydrogen donor in a sufficient amount. It should be

noted that the cyclic valence change from Cu<sup>0</sup> to Cu<sup>+</sup> or Cu<sup>2+</sup> and back is the primary condition for the occurrence of these dehalogenation reactions (Pekárek et al., 2003).

Another important factor is the formation of a reduction atmosphere due to gasification of the carbon component of fly ash that contains surface-adsorbed oxygen, yielding CO and CO<sub>2</sub>. Stieglitz (1998) has found that Cu(II) chloride apparently is the most active catalyst of carbon gasification. Our results (Bureš et al., 2003), obtained in the study of dehalogenation of hexachlorobenzene (HCBz), have led us to conclusion that copper actually acts as a reaction component rather than as a catalyst and, consequently, that HCBz dehalogenation reactions are thermodynamically controlled.

Fly ash from MWI plants contains significant amounts of basic PCDD/F precursors, polychlorinated benzenes and phenols in particular, at concentrations one order of magnitude higher than those of PCDD and PCDF. These precursors are strongly bound to fly ash.

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At 250–400 °C they become important components of de novo synthetic reactions yielding PCDD, PCDF, and PCB on solid particles contained in flue gases. When studying dehalogenations of PCBz (Stach et al., 1999; Bureš et al., 2003), the authors have found that, under the dehalogenation conditions used, the compounds mentioned above are not formed by de novo syntheses.

During the PCDD and PCDF formation, the reactivity of polychlorinated phenols is much higher than that of PCBz (Hell, 1999). Nevertheless, it has not yet been clarified whether chlorinated phenols (CP) can be dehalogenated under the conditions of the previous experiments, what dehalogenation pathways characterize the process and to what extent de novo synthetic reactions will be suppressed during dehalogenation experiments. In this respect it is of interest how the conclusions derived from the interpretation of the dehalogenation experiments by means of thermodynamic calculations (Bureš et al., 2003), can be applied to CP dechlorination. These points are discussed in the present work.

## 2. Experimental

### 2.1. Fly ash

Fly ash from fabric filters of the MWI Purotherm (Austria) installed at Klačterec was ground, Soxhlet-extracted with toluene for 24 h, air dried and sieved. The <0.1 mm particle size fraction was used in the experiments. The main chemical components of the fly ash sample were: Al 5.96, C 8.24, Ca 4.4, Fe 9.8, Mg 0.38, Si 33.96, Zn 0.2 and water of about 2.4 (all in wt.%), Cr 0.21, Ni 0.36, Cu 0.15 and Pb 0.45 (all in mg g<sup>-1</sup>). The fly ash apparent density and the calculated porosity were 1.03 g cm<sup>-3</sup> and 75%, respectively.

### 2.2. Chemicals

HCl p.a., Na<sub>2</sub>SO<sub>4</sub> p.a. (Lachema), nitrogen N5 (Linde), monochlorophenols, dichlorophenols, 2,4,6-, 2,3,6-, 2,4,5-, 2,3,4-trichlorophenols (Aldrich), 3,4,5-trichlorophenol, 2,3,5,6- and 2,3,4,6-tetrachlorophenols (Supelco), 2,3,5-trichlorophenol, 2,3,4,6-tetrachlorophenol and the standard solution of chlorophenols Phenol-Mix 10, 50 ng μl<sup>-1</sup> all in acetonitrile (Dr. Ehrenstorfer), toluene 99.5% ACS spectrophotometric grade, 1-bromonaphthalene (Aldrich), ethyl acetate (SupraSolv), 2-butanone (p.a.), pyridine (Merck), and acetic anhydride (Supelco) were used as obtained.

### 2.3. Dechlorination experiments

A sample of fly ash (0.3 g) and a given isomer of chlorophenols (100 μg) were homogenized by grinding

in a mortar and transferred to a glass ampoule (volume = 6.4 ml). The ampoule was then sealed under nitrogen (N5) atmosphere and heated at 200 °C for 30 min, or for 1 h in the case of the very stable 3,5-dichlorophenol. We have found that the amount of hydrogen donors and of copper in the system (0.045 mg) originating from the matrix of the fly ash are in sufficient concentrations for dechlorination reactions to proceed.

### 2.4. Chlorophenol analysis

The sample was treated with conc. HCl (1 ml) for 1 h, filtered, the sediment was washed with water, air dried, Soxhlet extracted with 2-butanone for 8 h and the filtrate extracted with ethyl acetate (5 × 10 ml). The combined 2-butanone and ethyl acetate extracts were dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated to ca. 1 ml under reduced pressure and redissolved in 10 ml of toluene. A total of 50 μl of acetic anhydride and 50 μl of pyridine were added to a 1 ml aliquot of the toluene solution which was then set aside at room temperature in a capped vial overnight in order to acetylate chlorophenols. The solution of acetylated chlorophenols was then analyzed on a DB-5MS column (30 m × 0.25 mm × 0.25 μm, J&W Scientific), using HP 6890 gas chromatograph and HP 5973 mass selective detector in the selected ion monitoring mode. 1-Bromonaphthalene, 2,4-dichloro[<sup>13</sup>C]phenol and 4-chloro[<sup>13</sup>C]phenol were used as internal standards. The temperature programme: initial temperature 50 °C for 3 min, ramp at 25 °C min<sup>-1</sup> to 120 °C and then 10 °C min<sup>-1</sup> to 290 °C. The average velocity of the helium carrier gas was 37 cm s<sup>-1</sup>. An eight-point calibration curve provided a linear concentration range of 5–2500 ng ml<sup>-1</sup>. The 2,4- and 2,5-dichlorophenol isomers were not separated by the GC-MS method used.

## 3. Results and discussion

### 3.1. Dechlorination experiments

The dechlorination of CP was carried out under the conditions of a single C–Cl bond cleavage as the predominating reaction. This was achieved by the use of a relatively low dehalogenation temperature (200 °C) compared to PCBz dechlorinations (Bureš et al., 2003) and of short reaction times. To determine the positions on the benzene ring at which C–Cl bonds are preferentially cleaved, we dechlorinated a complete series of penta (PCP), tetra (TeCP), tri (TCP) and dichlorophenol (DCP) isomers.

The results and experimental conditions of the dehalogenations up to monochlorophenols (MCP) are given in Table 1. All the chlorophenols determined experimentally after dehalogenations are given in

Table 1  
Products of the dechlorination of chlorophenols on municipal waste incineration fly ash

Reactant	Relative percentages of products after dechlorination																	
	PCP	TeCP			TCP						DCP				MCP			
		2,3,4,5-	2,3,4,6-	2,3,5,6-	2,3,4-	2,3,5-	2,3,6-	2,4,5-	2,4,6-	3,4,5-	2,3-	2,4(+2,5)-	2,6-	3,4-	3,5-	2-	3-	4-
PCP	59	13	3	21	–	2	–	1	–	1	–	–	–	–	–	–	–	
2,3,4,5-TeCP	1	33	–	–	–	9	–	6	–	16	–	2	–	6	18	–	7	2
2,3,4,6-TeCP	2	3	42	1	5	1	3	31	4	1	–	4	–	3	–	–	–	
2,3,5,6-TeCP	–	–	–	34	–	23	1	–	–	–	1	6	–	–	26	1	8	–
2,3,4-TCP	–	–	–	–	66	–	–	–	–	–	4	6	–	22	–	–	1	1
2,3,5-TCP	–	–	–	–	–	63	–	–	–	–	–	3	–	–	33	–	1	–
2,3,6-TCP	–	–	–	–	–	–	68	–	–	–	5	24	1	–	–	–	2	–
2,4,5-TCP	–	–	–	–	–	–	–	81	–	–	–	9	–	8	–	–	1	1
2,4,6-TCP	–	–	–	–	–	–	–	–	73	–	–	24	2	–	–	–	–	1
3,4,5-TCP	–	–	–	–	–	–	–	–	–	67	–	–	–	9	22	–	2	–
2,3-DCP	–	–	–	–	–	–	–	–	–	–	68	–	–	–	–	2	30	–
2,4-DCP	–	–	–	–	–	–	–	–	–	–	–	86	–	–	–	2	–	12
2,5-DCP	–	–	–	–	–	–	–	–	–	–	–	82	–	–	–	1	17	–
2,6-DCP	–	–	–	–	–	–	–	–	–	–	–	–	94	–	–	6	–	–
3,4-DCP	–	–	–	–	–	–	–	–	–	–	–	–	–	99	–	–	1	–
3,5-DCP <sup>a</sup>	–	–	–	–	–	–	–	–	–	–	–	–	–	–	91	–	9	–

Experimental system: 0.3 g fly ash+100 µg of a given chlorophenol, 200 °C, reaction time 30 min (<sup>a</sup>one hour), atmosphere of 99.999% nitrogen.

relative percentages. The values given in Table 1 are the averages of five parallel determinations. The standard deviations of the average value for the 95% confidence limits ranged from  $\pm 0.91$  to  $\pm 9.63\%$ . The phenol was not analytically determined, and so the relative proportions were calculated only from the sum of the chlorinated isomers. The results indicate that a small amount (1–2%) of pentachlorophenol is detected among the chlorophenol isomers only during the dehalogenations of 2,3,4,6- and 2,3,4,5-TeCP. Therefore, we analysed, using the GC/MS method, the purity of corresponding TeCP commercial compounds and have found that 2,3,4,6- and 2,3,4,5-TeCP are contaminated by 7% and 1% of PCP, resp. This is the main reason for the PCP presence in the dehalogenation products. The possibility of TeCP chlorination to PCP under the studied conditions is highly improbable. The recovery expressed as the molar ratio of the total amount of the determined chlorophenols to the amount of the initial isomer to be dehalogenated varied from 28% to 86%. It should be pointed out, that, despite these large differences, the relative molar ratios of the dechlorination products did not change significantly with the recovery, so that these differences were unimportant in the analysis of the dehalogenation pathways and the parameters of the dehalogenation process.

As very reactive phenols can also be transformed into PCDF and PCDD via their condensation reactions (Grabic et al., 2002), in contrast to PCBz dehalogenations (Hell, 1999; Bureš et al., 2003) in which the condensation products have not been detected, we have also evaluated the formation of PCDD and PCDF by dehalogenation of 2,3,4,5-TeCP, i.e. for the reaction with the lowest recovery (28%) with respect to the dehalogenation products. We have found that the condensation reactions do take place and that the PCDD formation ( $110 \text{ ng g}^{-1}$ ) predominate over PCDF ( $31.5 \text{ ng g}^{-1}$ ), in agreement with our previous work (Grabic et al., 2002). The predominant products are HpCDD, HxCDD, HpCDF and HxCDF, the main toxic substances being 1,2,3,7,8-PeCDD; 2,3,4,7,8-PeCDF, and 2,3,4,6,7,8-HxCDF. However, these compounds have been detected in concentrations approximately by ca. three orders of magnitude lower compared to the extracted chlorophenols, and thus their formation cannot account for the low recovery observed for 2,3,4,5-TeCP dehalogenation.

Isomerization reactions have not been detected under the dehalogenation conditions used. The low concentrations of 2,3,4,5- and 2,3,5,6-TeCP, 3,4,5- and 2,3,5-TCP that have been found for 2,3,4,6-TeCP dehalogenation are very likely to come from the dehalogenation of pentachlorophenol that is an impurity (ca. 7% by GC/MS) in the initial 2,3,4,6-TeCP.

From Table 1 it is clear that the preferred pathway of PCP dechlorination on MWI fly ash under the

given experimental conditions consists of the following steps: pentachlorophenol  $\rightarrow$  2,3,5,6- and 2,3,4,5-tetrachlorophenol  $\rightarrow$  2,3,5- and 3,4,5-trichlorophenol  $\rightarrow$  3,5-dichlorophenol  $\rightarrow$  3-chlorophenol. The formation of 2,3,4,6-tetrachlorophenol, 2,3,4-, 2,3,6-, 2,4,6-trichlorophenols and 2,3-, 2,6-dichlorophenols is insignificant.

The results of the dehalogenation experiments have demonstrated that the reactivity of the C–Cl bonds in chlorophenols mainly decreases along the sequence *ortho* > *para* > *meta* with respect to the OH group. The chlorine in the *meta* position seems to have the lowest reactivity and thus to be the most resistant to its splitting off by dehalogenation. The dechlorination pathways presented in Table 1 demonstrate that if both chlorine atoms are in the *ortho* position with respect to the phenol OH group and one of them is adjacent to the *meta* chlorine, then such *ortho*-chlorine is more reactive. Under the experimental conditions used, the most stable isomers in their individual level of chlorination are 2,3,5,6- and 2,3,4,5-tetrachlorophenol, 2,3,5- and 3,4,5-trichlorophenol, 3,5-dichlorophenol and 3-chlorophenol.

It is worthy of noting that the chlorophenols with the chlorine in the *meta* position are more resistant toward biodegradation than the corresponding *ortho*-isomers in agreement with Devillers and Chambon (1986). With respect to the degree of chlorination, the most toxic chlorophenols (not considering the undoubtedly most toxic pentachlorophenol whose benzene ring is fully substituted by chlorine atoms) are 2,3,4,5-TeCP, 2,3,5,6-TeCP, 3,4,5-TCP, and 3,5-DCP, in good agreement with the most stable chlorophenol isomers found experimentally.

### 3.2. Chemical equilibrium calculations

In order to interpret the pathways of pentachlorophenol dechlorination thermodynamically we have performed chemical equilibrium calculations for the individual dechlorination steps, from pentachlorophenol up to phenol.

In the case of polychlorinated phenols, the complete thermochemical data are only available for several compounds. The thermodynamic data have been tabulated (Frenkel et al., 1994) for 2,3-, 2,4-, 2,5-, and 3,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol. The entropies and molar heat capacities for dichlorophenols have been taken in these tables from Shaub (1982) and calculated from estimated vibration frequencies. The enthalpy of formation of 2,4,6-trichlorophenol taken from the same source has also been estimated. The thermochemical data for the other polychlorinated phenols are either incomplete or not available at all. Therefore, most of the required data had to be estimated.

Shaub (1983) calculated the enthalpies of formation of polychlorophenols using Benson's contribution method (Benson et al., 1969; Benson, 1976), but, unfortunately, only for the temperature of 298 K. Dolfin and Harrison (1992) used Benson's method (Benson, 1976) to calculate  $\Delta G_f^\circ$  from the elements for chlorinated phenols in the ideal gas phase and 298 K.

Saito and Fuwa (2000) obtained thermochemical quantities for polychlorinated phenols by using statistical thermodynamics. The enthalpies of formation, molecular geometries and vibration frequencies have been determined by Stewart's semiempirical quantum chemical method PM3 (Stewart, 1989a,b). However, semiempirical methods, including the PM3, mostly provide vibration frequencies that are subject to considerable errors. When compared to the procedure used by Saito and Fuwa (2000), the Benson method yields better results, especially for enthalpies of formation and the molar heat capacities.

For this reason we have based our estimation of the thermochemical data for a wide temperature range on Benson's contribution method. The  $G$ -functions ( $G^\circ - H_{298}^\circ)/T$  used in the chemical equilibrium calculations have been obtained by a modified Benson method developed for direct estimation of the  $G$ -functions (Bureš, 1989).

Benson's contribution method provides a very good estimate of the enthalpy of formation of dichlorophenols, since the tabulated values (Ribeiro da Silva et al., 1994) differ from the calculated ones only by ca. 5 kJ mol<sup>-1</sup>. The enthalpies of formation calculated for monochlorophenols and pentachlorophenol significantly differ from the tabulated data (Sinke and Stull, 1958; Spieksma et al., 1994) and the difference amounts to 27 kJ mol<sup>-1</sup>. The difference between the estimate of the enthalpy of formation for 2,4,6-trichlorophenol obtained by Benson's method and the data reported by Shaub (1982) amounts to 34 kJ mol<sup>-1</sup>.

A comparison of the estimated entropies of dichlorophenols at 298 K with the reported data (Shaub, 1982) is satisfactory (a positive deviation of ca. 16 J K<sup>-1</sup> mol<sup>-1</sup>), whereas the difference for 2,4,6-trichlorophenol is +24 J K<sup>-1</sup> mol<sup>-1</sup>. The estimated entropy of pentachlorophenol is identical with the values reported by Spieksma et al. (1994) and Hildebrand et al. (1958), but differs by +31 J K<sup>-1</sup> mol<sup>-1</sup> from those reported by Faniran (1979).

A comparison of the molar heat capacities for 300 and 1000 K calculated for the above chlorophenols by Benson's method with the reported data (Faniran, 1979; Shaub, 1982) demonstrates a very good agreement, the average deviation being 4 J K<sup>-1</sup> mol<sup>-1</sup>.

Our thermodynamic calculations have been aimed at determination of the relative stabilities of the individual isomers for a given degree of substitution of the phenol ring by chlorine atoms (chlorination degree). To ensure consistency of the data, the estimates for all the chloro-

phenols have been obtained by Benson's method, except for pentachlorophenol for which the experimentally determined enthalpy of formation (Cox and Pilcher, 1970) have been used.

The chemical equilibria in the systems under study have been calculated by analogy with our previous work dealing with dehalogenation of chlorobenzenes (Bureš et al., 2003). The equilibrium compositions have been determined by minimizing the total Gibbs energy of a given system, maintaining the material balance for individual elements constant. The input components in the calculations have been the individual polychlorinated phenols, water vapour and copper metal. The amount of water vapour was changed from 0.2 to 3 mol and the amount of copper from 0.01 to 3 mol per one mol of polychlorinated phenol. The reaction products considered involved all the chlorinated phenol derivatives having the lower number of chlorine atoms than the dehalogenated compound, phenol, hydrogen chloride, Cu<sub>3</sub>Cl<sub>3</sub>, and solid Cu<sub>2</sub>O and CuCl<sub>2</sub>. The calculations have been carried out for atmospheric pressure and 473 K, which corresponded to the experimental dehalogenation conditions. To evaluate the effect of the temperature, the chemical equilibrium calculations have been done also for temperatures of 500–750 K.

The equilibrium compositions calculated for the above system were first used to evaluate the relative distribution of the dehalogenation products containing one chlorine less than the starting compound. It has been found that the equilibrium compositions depend on the temperature, but not on the components of the system and the type of the starting chlorophenol isomer. For comparative purposes we have also studied the chemical equilibrium in the isomerization of di- to tetrachlorosubstituted phenols in the gas phase. The molar ratios obtained from the equilibrium data for heterogeneous dechlorinations are identical with the distribution of individual isomers in the systems in which isomerization is the only reaction taking place. We encountered the same situation by us earlier in the study of dehalogenation of polychlorinated benzenes (Bureš et al., 2003).

The relative distribution of the dehalogenation products expressed in terms of molar percentage and the Gibbs energies of formation ( $\Delta G_f^\circ$ ) calculated for 473 and 298 K are listed in Table 2 and compared with the data reported by Dolfin and Harrison (1992) for ideal gas phase.

It is evident that the  $\Delta G_f^\circ$  values calculated for 298 K by us differ from those of Dolfin and Harrison (1992) by max. 4 kJ mol<sup>-1</sup>, which does not exceed the declared error of Benson's method. However, the latter authors give identical  $\Delta G_f^\circ$  values for 2- and 3-chlorophenol. This is rather unexpected, since Benson's method contains a contribution that makes it possible to include also into the calculation the effect of the pair of *ortho*-substituents

Table 2

Gibbs energies of formation ( $\text{kJ mol}^{-1}$ ) and relative percentages of dehalogenated products for individual chlorophenol isomers at 473 K and comparison of the calculated energies for 298 K with data of Dolfig and Harrison (1992)

Compound	$(\Delta G_f^\circ)_{473}$	Mol. %	$(\Delta G_f^\circ)_{298}$	$(\Delta G_f^\circ)_{298}$ Dolfig and Harrison (1992)
2-Chlorophenol	-17.1	28.5	-57.3	-56.4
3-Chlorophenol	-19.1	47.7	-60.0	-56.4
4-Chlorophenol	-16.4	23.8	-58.2	-54.7
2,3-Dichlorophenol	-31.0	2.8	-73.2	-72.3
2,4-Dichlorophenol	-40.2	29.5	-82.4	-81.5
2,5-Dichlorophenol	-40.2	29.5	-82.4	-81.5
2,6-Dichlorophenol	-35.4	8.8	-78.0	-79.8
3,4-Dichlorophenol	-33.0	4.8	-75.9	-72.3
3,5-Dichlorophenol	-39.5	24.7	-83.4	-79.8
2,3,4-Trichlorophenol	-44.9	1.6	-89.1	-87.9
2,3,5-Trichlorophenol	-54.1	17.0	-98.3	-97.1
2,3,6-Trichlorophenol	-52.1	10.2	-95.7	-97.1
2,4,5-Trichlorophenol	-54.1	17.0	-98.3	-97.1
2,4,6-Trichlorophenol	-58.5	52.8	-103.1	-104.5
3,4,5-Trichlorophenol	-44.2	1.4	-90.1	-86.1
2,3,4,5-Tetrachlorophenol	-58.8	32.6	-105.1	-103.7
2,3,4,6-Tetrachlorophenol	-66.0	20.4	-111.6	-112.9
2,3,5,6-Tetrachlorophenol	-63.2	46.9	-109.9	-111.3

on the enthalpy of formation, so that the Gibbs energies of the two compounds mentioned above should differ from one another. A similar situation also occurs for 2,6- and 3,5-dichlorophenol, as well as for 2,3,5-, 2,3,6-, and 2,4,5-trichlorophenol. The results listed in Table 2 demonstrate that the higher *ortho*-chlorinated isomers are less stable.

The calculation of the Gibbs energies of formation makes it possible to conclude that, for a given degree of chlorination, the most thermodynamically stable are the isomers: 2,3,4,6-tetrachlorophenol (-66.0); 2,4,6-trichlorophenol (-58.5); 2,4- and 2,5-dichlorophenol (both -40.2, in agreement with the fact that this pair of isomers is difficult to differentiate analytically), and 3-chlorophenol (-19.1  $\text{kJ mol}^{-1}$ ). An agreement of the experimental results with the thermodynamic calculations has been obtained for the tetra- and monochlorophenol isomers. With dichlorophenols, the difference between 2,4-, 2,5-DCP and 3,5-DCP lies within the experimental error (0.7  $\text{kJ mol}^{-1}$ ).

A fundamental difference between the experimental and the calculated data has been found for the trichlorophenol isomers. The dechlorination experiments point to the both trichlorophenols having two chlorine atoms in the *meta* position with respect to OH as the most stable isomers, whereas the calculations predict that the most stable isomer is 2,4,6-trichlorophenol, i.e. the isomer with the unoccupied *meta* positions. In contradiction to similar equilibrium calculations performed in the previous work (Bureš et al., 2003) for the dechlorination of polychlorinated benzenes the accuracy of the equilibrium data obtained for chlorinated phenols suffers

from the absence of reliable input data, especially the enthalpies of formation of these compounds.

For example, if the value of the enthalpy of formation -160.6  $\text{kJ mol}^{-1}$ , which is the average of the result of Benson's method and the value reported by Shaub (1982), is taken for 2,4,6-trichlorophenol in the calculation of the isomerization equilibrium of trichlorophenols, then the proportion of this compound in the equilibrium mixture decreases to the mere 1.4 mol%.

These findings clearly show that the results of the experiments and their comparison with the thermodynamic chemical equilibrium calculations are less consistent than those in the previous study (Bureš et al., 2003) dealing with dehalogenation of benzenes. Therefore, our results do not permit conclusion that the dechlorination reactions proceed to a near equilibrium. However, it should be emphasized that the values calculated for the dechlorination reaction from  $\Delta G_{\text{reaction}}^\circ$  can directly be correlated only with the equilibrium constants of these reactions. Thus they do not provide information on the reaction rates and the ease with which the dechlorination reaction takes place.

The equilibrium compositions thus obtained have further been used to calculate the ratios of the amounts of  $\text{Cu}_3\text{Cl}_3$  to HCl in the equilibrium state of the dechlorination of pentachlorophenol at 473 K, in dependence on the initial amounts of Cu and water vapour (Table 3). It has been found that the above ratio steeply increases with increasing amount of metallic copper. A similar trend has already been observed by us in the dehalogenation of polychlorinated benzenes

Table 3

The ratio of the amount of  $\text{Cu}_3\text{Cl}_3$  to HCl in the dechlorination equilibrium of pentachlorophenol at 473 K in the dependence on the initial amounts of copper and water vapour

$N^\circ$ ( $\text{H}_2\text{O}$ )/mol	$n^\circ$ (Cu)/mol				
	0.01	0.2	1.0	2.05	3.0
0.2	1.2	$1.0 \times 10^1$	$1.5 \times 10^9$	$1.5 \times 10^9$	$1.5 \times 10^9$
0.5	$7.1 \times 10^{-1}$	5.6	$2.2 \times 10^1$	$6.4 \times 10^8$	$6.4 \times 10^8$
1	$4.8 \times 10^{-1}$	3.6	$1.2 \times 10^1$	$2.5 \times 10^1$	$4.5 \times 10^1$
1.5	$3.8 \times 10^{-1}$	2.8	9.2	$1.6 \times 10^1$	$2.5 \times 10^1$
2	$3.3 \times 10^{-1}$	2.5	7.5	$1.3 \times 10^1$	$1.8 \times 10^1$
3	$2.5 \times 10^{-1}$	1.9	5.7	9.4	$1.3 \times 10^1$

(Bureš et al., 2003). The two findings thus strongly support the idea that metallic copper acts in the dehalogenation process as an active component of the reaction system rather than as a catalyst.

#### 4. Conclusions

Several more conclusions can be drawn from the results obtained:

The preferred pathway of the PCP dechlorination on MWI fly ash involves the following steps: pentachlorophenol  $\rightarrow$  2,3,5,6- and 2,3,4,5-tetrachlorophenol  $\rightarrow$  2, 3,5- and 3,4,5-trichlorophenol  $\rightarrow$  3,5-dichlorophenol  $\rightarrow$  3-chlorophenol.

The reactivity of the C–Cl bonds mostly follows the order,  $o > p > m$  with respect to the OH group.

Under the dehalogenation conditions used, isomerization reactions do not occur to an appreciable extent.

In contrast to the PCBz dehalogenation, the possibility of chlorinated phenols coupling to PCDD and PCDF was proved in ng concentrations even under dechlorination experimental conditions.

A comparison of the experimental results with the thermodynamic equilibrium calculations suffers to a certain extent from the lack of reliable input data, but certain conclusions can still be drawn. The higher *ortho*-chlorinated isomers are less stable.

There is a discrepancy between the prediction of the stability of trichlorophenol isomers by the experiment and by the thermodynamic calculation; the former predicts that the most stable isomers contain chlorine atoms in the *meta* position with respect to the OH group, whereas the latter assumes that the most stable isomer has the *meta* positions unoccupied.

It has been demonstrated that the equilibrium ratio of gaseous  $\text{Cu}_3\text{Cl}_3$  vs. HCl rapidly increases with increasing amount of copper metal present. The fact that the initial amount of copper influences strongly the equilibrium composition, supports the assumption that copper acts as a regular reactant in the dehalogenation process and not as a catalyst.

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