CATALYTIC OXIDATION OF CHLOROAROMATIC TRACE CONTAMINANTS ADSORBED ON WESSALITH DAY BY OZONE

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ABSTRACT
Oxidation of several chloroaromatic compounds (polychlorinated benzenes Cl Bz, biphenyls PCB and dibenzo-p-dioxins and dibenzofurans PCDD/F) adsorbed on Wessalith DAY, a hydrophobic zeolite, by ozone was investigated. Laboratory-scale experiments were performed, investigating reaction products and kinetic parameters to elucidate the mechanism for some PCDD/F model compounds. In the presence of water, OH radicals were found to be the reactive species. The reaction rate (pseudo-first order law) of Cl Bz, PCB, and PCDD/F was investigated at several reaction temperatures (50, 70, and 90 °C). A zeolite sample from a hazardous waste incinerator (HWI) was treated with ozone and gave similar results. Copyright © 1996 Published by Elsevier Science Ltd

INTRODUCTION
In 1990, a limit concentration for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) of 0.1 ng TE/m³ was stipulated for the flue gas emissions of waste incinerators in Germany [1]. The MEDISORBON process is a new method to meet this limit [2]. It uses Wessalith DAY, a hydrophobic zeolite [3], to adsorb PCDD/F (and other trace contaminants) from the flue gas downstream of dust filters and scrubbers. Thus, the prescribed emission limit can be ensured over long operating periods ranging from 10 000 to 20 000 hours [4].

A disadvantage of all adsorption methods for flue gas cleaning is the necessity for either land disposal or burning (if possible) of the contaminated adsorbents. Therefore, it would be favorable to decontaminate the adsorbent (e.g. Wessalith) by destroying the adsorbed compounds. This could be done using a potent oxidant like ozone [5] which is easy to generate and not too expensive. Ozone lends itself well to in-situ decontamination of Wessalith.
EXPERIMENTAL

Wessalith pellets (cylinders, about 5 x 2 mm) were heated to 600 °C in a muffle furnace to remove any organic trace compounds present. Then, the pre-cleaned zeolite was loaded with chloroaromatic model compounds by addition and careful evaporation of dichloromethane solutions of these compounds. In general, about 100 µg of the model compound were added to 60 g of Wessalith. These loaded Wessalith samples were treated with ozone at 50-90 °C in a laboratory glass apparatus shown in Fig. 1.

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**Fig. 1:** Laboratory glass apparatus for ozone treatment of zeolite loaded with chloroaromatic compounds.

A stream of synthetic air (150 l/h) was passed through the ozone generator (Sander). Thus, an amount of 2.5 g O₃/h was generated, leading to a concentration in the gas of 50 mg O₃/m³. This gas mixture was passed through a tube furnace which heated the mixture to reaction temperature (50, 70, or 90 °C). The pre-heated gas mixture then entered the reactor packed with 60 g of loaded Wessalith. This reactor was a glass tube (30 mm i.d.) with a heating jacket, similar to a Liebig condenser. Both, tube and zeolite, were heated to reaction temperature by circulating hot water of constant temperature through the heating jacket of the glass tube.

Wessalith samples were taken at defined intervals. Internal standards were used for quantification, because the recovery rate was not constant. The standards used have chemical and physical properties similar to the analyte and are shown in Tab. 1.

**Tab. 1:** Investigated compounds, abbreviations, and internal standards used.

<table>
<thead>
<tr>
<th>Compound (Analyte)</th>
<th>Abbreviation</th>
<th>Internal Standard</th>
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<tbody>
<tr>
<td>3,3',4,4'-Tetrachlorobiphenyl</td>
<td>PCB 77</td>
<td>1,2,3,4-Tetrachlorodibenzo-p-dioxin</td>
</tr>
<tr>
<td>2,3,3',4,4'-Pentachlorobiphenyl</td>
<td>PCB 105</td>
<td>1,2,4,7,8-Pentachlorodibenzo-p-dioxin</td>
</tr>
<tr>
<td>2,3,4,4',5-Pentachlorobiphenyl</td>
<td>PCB 114</td>
<td>1,2,4,7,8-Pentachlorodibenzo-p-dioxin</td>
</tr>
<tr>
<td>2,3,3',4,4',5-Hexachlorobiphenyl</td>
<td>PCB 156</td>
<td>1,2,4,7,8-Pentachlorodibenzo-p-dioxin</td>
</tr>
<tr>
<td>Decachlorobiphenyl</td>
<td>PCB 209</td>
<td>Decachlorodiphenyl ether</td>
</tr>
<tr>
<td>2,4,8-Trichlorodibenzofuran</td>
<td>2,4,8-Cl₃DF</td>
<td>3,3',4,4'-Tetrachlorobiphenyl</td>
</tr>
<tr>
<td>1,2,3,4-Tetrachlorodibenzo-p-dioxin</td>
<td>1,2,3,4-Cl₃DD</td>
<td>3,3',4,4'-Tetrachlorobiphenyl</td>
</tr>
<tr>
<td>1,2,4,7,8-Pentachlorodibenzo-p-dioxin</td>
<td>1,2,4,7,8-Cl₄DD</td>
<td>3,3',4,4'-Tetrachlorobiphenyl</td>
</tr>
<tr>
<td>Decachlorodiphenyl ether</td>
<td>DCDE</td>
<td>Decachlorobiphenyl</td>
</tr>
<tr>
<td>1,2,3,5-Tetrachlorobenzene</td>
<td>1,2,3,5-Cl₃Bz</td>
<td>1,3,5-Tribromobenzene</td>
</tr>
<tr>
<td>1,2,3,4-Tetrachlorobenzene</td>
<td>1,2,3,4-Cl₄Bz</td>
<td>1,3,5-Tribromobenzene</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>Cl₃Bz</td>
<td>1,3,5-Tribromobenzene</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>Cl₄Bz</td>
<td>1,3,5-Tribromobenzene</td>
</tr>
</tbody>
</table>
After addition of internal standards, the samples were extracted with n-hexane for 3 hours in a soxhlet apparatus. Analysis was done using gas chromatography (Varian GC 3400, 30 m capillary column SE 54) with an electron capture detector (ECD, 280 °C) using suitable temperature programs (60 °C/3 min, 5 °C/min, 200 °C/0 min, 10 °C/min, 270 °C/0 min for Cl₂Bz, 60 °C/3 min, 10 °C/min, 270 °C/20 min for PCB and PCDD/F). For some experiments (see below), GC/MS with low resolution MS (Hewlett Packard 5890 Series II, 25 m capillary column HP 5, "Selected Ion Monitoring" mode of the MS, detecting the 2 most abundant masses for each compound) was used with a simple temperature program (50 °C/3 min, 10 °C/min, 280 °C/15 min). For the sample from the HWI, standard methods of PCDD/F analysis were used [6].

RESULTS

Reaction Products and Mechanism

A number of experiments was performed to determine the reaction products and the kinetics of the reaction. In these experiments four model compounds for PCDD/F were used: 2,4,8-Cl₃DF, 1,2,3,4-Cl₄DD, 1,2,4,7,8-Cl₄DD, and decachlorodiphenyl ether (DCDE). The perchlorinated ether was used as a model for the perchlorinated Cl₄DD and Cl₆DF. The less chlorinated compounds should show the influence of different degrees of chlorination.

Two impingers were filled with 200 ml n-hexane and dichloromethane respectively and connected to the exit of the glass tube (see Fig. 1). The solutions were concentrated separately to 10 ml each in a stream of nitrogen and analyzed by the method of GC/LRMS in SIM mode. This procedure allowed to determine the desorbed amount of educts. It showed that desorption was <4 % of the adsorbed educt mass. Therefore, desorption could be neglected.

On the other hand, analyzing the concentrated impinger solvents allowed to look for volatile organic reaction products. Analysis of the solutions was done with the GC/MS system described above. In this case the "Scan mode" (m/z=50-400) of the MS was chosen. However, organic reaction products could not be found at a detection limit of 30 ng/µl related to hexachlorobenzene (or 4 % of educt masses). Therefore, it was assumed that complete oxidation took place. In another experiment, two impingers were filled with 2 n KOH to absorb CO₂. Solutions were analyzed with a total carbon analyzer (Rosemount-Dohmann) which automatically added acid and measured evolving CO₂ by non-dispersive IR spectrometry. The yield of CO₂ was determined to be 68 % ± 9 %.

To investigate the effect of the zeolite surface, oxidation of PCDD/F model compounds adsorbed on the surface of Wessalith was compared with oxidation of PCDD/F model compounds adsorbed on glass rings. In one experiment, compounds were adsorbed on the surface of glass rings; in a second, they were adsorbed on Wessalith. In the experiment with glass rings, there was considerable desorption (9-76 %), which did not take place when using Wessalith. This desorption makes quantification of the oxidation difficult. However, oxidation was much slower than in the experiments with Wessalith (Tab. 2). This result is evidence for catalytic effects of the zeolite.

Tab. 2: Oxidation of four chloroaromatic model compounds on the surface of glass and Wessalith. The table shows the oxidized portion [%] after 3 h treatment with ozone at 90 °C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>2,4,8-Cl₃DF</th>
<th>1,2,3,4-Cl₄DD</th>
<th>1,2,4,7,8-Cl₄DD</th>
<th>DCDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass rings</td>
<td>15 %</td>
<td>20 %</td>
<td>12 %</td>
<td>0 %</td>
</tr>
<tr>
<td>Wessalith pellets</td>
<td>&gt; 89 %</td>
<td>&gt; 91 %</td>
<td>&gt; 84 %</td>
<td>98 %</td>
</tr>
</tbody>
</table>
In another set of experiments, oxidation by ozone in the presence of water was compared with oxidation in the absence of water. In the first experiment, water was added by passing the air/ozone mixture through an impinger filled with water. Thus, the gas mixture was approximately saturated with water. In the second experiment, the presence of water was approximately excluded from the apparatus. Results for a typical model compound, 1,2,3,4-Cl₄DD (Fig. 2) show that oxidation was faster in the presence of water than in the absence of water.

![Graph showing oxidation of 1,2,3,4-Cl₄DD by ozone in presence and absence of water.]

Fig. 2: Oxidation of 1,2,3,4-Cl₄DD by ozone in presence and in absence of water (DL = detection limit).

Therefore, it was assumed that in the presence of water, reactive OH radicals are formed which react faster than ozone. To confirm this assumption, experiments were performed using cyclohexane as a scavenger for OH radicals. Cyclohexane does not react with ozone at room temperature, but it does react with OH radicals [7]. Therefore, cyclohexane was added slowly before the reactor tube (see Fig. 1), using a titrator (Metrohm) at a rate of 150 µL/min. In a set of two experiments, cyclohexane was allowed to react with ozone in the presence and absence of water, respectively. Products were trapped in an ice-cooled vessel connected to the exit of the reactor (see Fig. 1). It was found that in the presence of water, the cyclohexanol yield was about twice as high as in the absence of water. This result is evidence for the presence of OH radicals.

**Reaction Rates at Different Temperatures**

Reaction rates were determined at three different reaction temperatures (50, 70, and 90 °C) in the presence of water. The results for oxidation of chlorinated benzenes (Fig. 3), PCBs (Fig. 4), and PCDD/F (Fig. 5), at 50 and 70 °C, are shown in the subsequent figures. For PCDD/F, a further experiment was performed at 90 °C (Fig. 6).

Polycondensed aromatic hydrocarbons (PAH) and polychlorinated phenols were investigated as well. The results at a reaction temperature of 50 °C showed a very fast degradation of these compounds. The concentrations of all substances were below the detection limit (DL) or near DL after 30 min. DL was about 2 % of the original concentration. Thus, almost no difference in the reactivity of the compounds could be observed because of the high reaction rate.

**Sample from a Hazardous Waste Incinerator (HWI)**

At a HWI, a 130 m³/h branch stream of the flue gas (downstream of dust filters and scrubbers) was passed through two successive layers (10 and 20 cm thick) of Wessalith. The apparatus will be described in detail in a publication
Fig. 3: Oxidation of some polychlorinated benzenes by ozone at 50 °C (left) and 70 °C (right).

Fig. 4: Oxidation of some polychlorinated biphenyls by ozone at 70 °C (left) and 90 °C (right).
Fig. 5: Oxidation of some polychlorinated dibenzodioxins (DD) and dibenzofurans (DF) by ozone at 50 °C (left) and 70 °C (right).

Fig. 6: Oxidation of some polychlorinated dibenzodioxins (DD) and dibenzofurans (DF) by ozone at 90 °C. (DL = Detection limit)
Fig. 7: Oxidation of polychlorinated dibenzodioxins (DD) and dibenzofurans (DF) by ozone at 90 °C.
following soon [4]. A Wessalith sample was taken after 8 900 h of adsorption and treated with ozone in the laboratory apparatus as described above. At defined intervals, Wessalith samples were taken and analyzed using state-of-the-art PCDD/F analysis methods [6]. Oxidation was investigated at a reaction temperature of 90 °C. Results are shown in Fig. 7.

DISCUSSION

On treatment with ozone, concentrations of all investigated compounds decreased exponentially (Figs. 3-6). As one reactant (ozone) was used in great abundance, this decrease can be attributed to a reaction following a rate law of pseudo-first order.

The same was true for the experiment with the sample from the HWI. PCDD/F concentrations (tetra- to octachloro-DD/DF) decreased exponentially (Fig. 7). Furthermore, the oxidation rate of the perchlorinated compounds (OCDD and OCDF) was lower than for the rest of the compounds. However, in contrast to the model experiments, a residual concentration of ~10 % was observed. Further degradation of PCDD/F could not be achieved. The reason for the residual concentration cannot be identified from the results. One possible cause could be the presence of other substances or fly ash. These substances may have prevented the ozone or OH radicals from reaching all of the adsorbed PCDD/F.

Perchlorinated compounds were oxidized at a much slower rate than compounds which possess at least one aromatic C-H position. This can be recognized by plotting \( \ln(c/c_0) \) against reaction time for some compounds (Figs. 8, 9). In these diagrams, a steeper line corresponds to a faster degradation by ozone. Viewing Fig. 8, the steeper line for \( \text{Cl}_2\text{Bz} \) (which possesses an aromatic C-H-position) compared with the lines for the perchlorinated compounds is obvious. The reaction rate constants \( k \) were calculated from the line parameters and are one magnitude higher for \( \text{Cl}_2\text{Bz} \) (\( k = 0.102 \text{ min}^{-1} \)) than for the perchlorinated compounds (\( k \text{ [min}^{-1}] = 0.014 \) (DCDE), 0.007 (PCB 209), and 0.008 (\( \text{Cl}_6\text{Bz} \)).

![Figure 8: Logarithmic plot of the concentration (reaction with O\textsubscript{3} at 70 °C) of Cl\textsubscript{2}Bz (crosses/pointed-dotted line), DCDE (triangles/full line), Cl\textsubscript{6}Bz (rhombs/dotted line), and PCB 209 (squares/pointed line).](image_url)
From Fig. 9 it can be seen that the reaction rate of non-perchlorinated PCBs decreases slightly with increasing chlorine content. PCB 77 contains four, PCB 105 and 114 five, PCB 156 six, and PCB 209 ten chlorine atoms per molecule. Again, the reaction is much slower for the perchlorinated PCB 209.

Fig. 9: Logarithmic plot of the concentration (reaction with O$_3$ at 70 °C) of PCB 77 (crosses/fat line), 114 (squares/pointed-dotted), 105 (circles/full line), 156 (squares/dotted-pointed) and 209 (rhombs/pointed line).

These results are consistent with the presence of OH radicals as the reactive species. Benzene and other aromatic compounds are known to react with OH radicals

- either by addition of the OH radical to the aromatic π system (at low temperatures, T<50 °C)
- or by abstraction of hydrogen atoms from the aromatic ring (at higher temperatures, T>100 °C) [8].

For chloroaromatic compounds (including PCDD/F and PCB), OH addition is the predominant pathway at room temperature and below [9]. The reaction mechanism at elevated temperature (50-90 °C) is not known for chloroaromatic compounds.

Abstraction of a hydrogen atom is not possible for perchlorinated compounds. On the other hand, abstraction of a chlorine atom by OH radicals is endothermic [10] and can therefore be ruled out. This could explain the low reactivity of perchlorinated compounds observed.

H abstraction is possible for compounds with aromatic C-H-positions and can be assumed to be the main reaction pathway for these compounds. The slight decrease in reactivity of non-perchlorinated compounds with increasing chlorine content can be explained by the electrophilic properties of the OH radical [11]. Electron density of aromatic compounds decreases with chlorine content because of the -I effect of the chlorine substituents. Therefore, the reactivity of chloroaromatic compounds with many chlorine substituents decreases. This result is similar to the findings for 'true' electrophilic reagents (e.g. Br$_2$).
Besides mechanistic results it can be concluded, that PCDD/F (and other trace contaminants present in flue gas) adsorbed on Wessalith DAY can be oxidized by ozone in the presence of water. The reaction takes place at low temperature (< 100 °C) and proceeds to CO₂. For a commercial use of the oxidation method, experiments on a larger scale (experimental plant) have been performed and will be published soon [4].

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**REFERENCES**


