

## Reaction Of Some Chlorinated Dibenzo-p-Dioxins and Dibenzofurans

### With Copper(II)-Montmorillonite

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#### Abstract

Copper(II)-montmorillonite reacts with some chlorinated dibenzo-p-dioxins and furans to dimeric and oligomeric species by radical reaction. The products were identified by mass spectrometry.

#### Introduction

The reaction between Cu(II)-smectite (montmorillonite) and unsaturated hydrocarbons like benzene, toluene, anisole (see ref. 1-7 in ref. 1), chloranisole (12), chlorophenols (2), chloroethenes (3), dibenzo-p-dioxin and chlorodibenzo-p-dioxin (4) to form radical cations and in addition polymeric substances is well documented. The formation of polymeric species from the chlorinated hydrocarbons has been proposed as a way to form less toxic products in an inexpensive and easy way by reaction with a simple mineral material, especially in the case of chlorinated dioxins and other highly toxic substances (1,3,4).

Because there are only two chlorinated dibenzo-p-dioxins investigated (4), we repeated the experiments between Cu(II)-montmorillonite and some selected chlorinated dibenzo-p-dioxins and dibenzofurans.

#### Experimental

30 g montmorillonite K10 (Aldrich) was stirred with 300 ml 0.3 M NaCl-solution at room temperature for 18 h, filtered and washed twice with distilled water. The Na-ion exchanged mineral was then again stirred for 18 h with 150 ml 1 M CuCl<sub>2</sub>·2H<sub>2</sub>O-solution, filtrated and washed with distilled water, until no chlorid could be detected with AgNO<sub>3</sub> in the washwater. The mineral was dried and stored in vacuum over P<sub>2</sub>O<sub>5</sub>.

The organo-chlorine complexes were prepared as described in (ref. 4, Fig. 4) with the quantities shown in table I. Isolation of the reaction products was done by extraction with methanol or n-hexane. The description of the experimental details is given in table I. For the GC-MS measurements an aliquot of 1  $\mu$ l was injected. For the solid probe MS about 5 to 10  $\mu$ l of the solution were taken into a small gold crucible and the liquid allowed to evaporate.

Table I

No.	Hydrocarbon	Cu(II) Mineral	Solvent	Extraction solvent	Extr. method	Identifi. cation	Color of complex	oligomeric species
1	43 mg Dachlor DD	2 g	20 ml n-Hexane	30 ml Methanol	A	C, D	blue	yes
2	43 mg Dachlor DD	0.084 g	15 ml n-Hexane	8 ml Methanol	B	D	blue	no (see rem. I:)
3	53 mg Dachlor DD	2 g	20 ml n-Hexane	20 ml Methanol 10 ml Toluene	A	C, D	green-blue	yes
4	53 mg Dachlor DD	2 g	20 ml Isoclane	10 ml Methanol 20 ml Toluene	A	D	medium-brown	no
5	53 mg Dibenzofuran	2 g	20 ml n-Hexane	30 ml Methanol	A	C, D	brown	yes
6	53 mg Dachlor DF	2 g	20 ml n-Hexane	20 ml Methanol 10 ml Toluene	A	C, D	gray-brown	yes
7	53 mg Dachlor DF	2 g	20 ml Isoclane	10 ml Methanol 20 ml Toluene	A	D	medium-brown	no

- A: Evaporating the solvent. Rotating the mineral with the extraction-solvent with a evaporator (60° C waterbath) for 30 min, filtering the suspension and concentration of the extract to 4-5 ml, filtering the muddy liquid and concentrating to 200-300  $\mu$ l with a gentle stream of pure nitrogen.
- B: Decanting the solvent, shaking the mineral with the extraction-solvent for about 5 min, filtering the suspension and evaporating the extract to dryness with a gentle stream of pure nitrogen.
- C: Mass selective detector, Mod. 5970 (Hewlett Packard), in combination with a Mod. 5890 gas chromatograph and a data workstation.
- D: 53 m column (J&W) 30 m length, 0.25 mm i.d., J&W-On-Column injector, carrier gas He, pressure 1 bar, injection volume 1  $\mu$ l, temperature program 105° for 3 min, then 10°/min to 325°, hold for 40 min.
- E: Solid probe mass spectrometry with a Finnigan 4500 quadrupole mass spectrometer and an Incoos datasystem, solid probe inlet, temperature programmed evaporation (manually controlled) from 50° C to 350° C.
- F: Two other experiments with separately prepared and different quantities of Cu(II) nonchlorinated, isoclane as solvent, modified experimental conditions also gave no dimeric or oligomeric chlorinated species.

### Results and Discussion

In all experiments, except experiment 2, dimeric dioxins and furans could be detected with GC-MS, also substituted dimeric dioxins and furans (mostly methyl-substituted species). Other substituted substances could be identified only tentatively, the mass spectra indicating the presence of reaction products possibly from humic acids of the montmorillonite.

The dimeric species of the dioxins and furans were identified by correct molecular-weight and the ratio of the isotope peaks corresponding to the number of the chlorine atoms. In Fig. 1 sections of the total ion chromatograms and the mass spectra of dimeric dibenzofuran (left) and dimeric 3,6-dichlorodibenzofuran (right) are shown

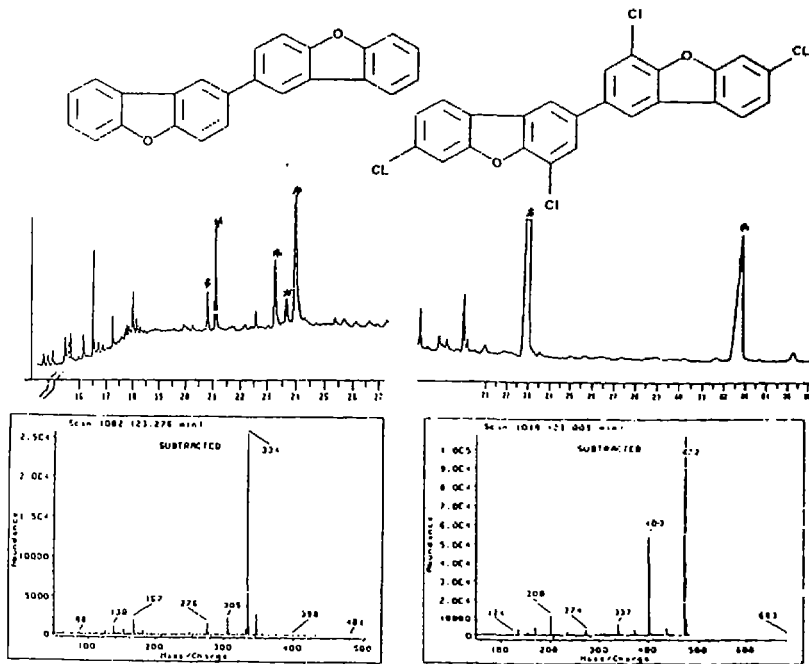


Fig. 1: One of the possible structure formulas, total ion chromatogram and mass spectra of the dimeric dibenzofuran (left) and 3,6-dichlorodibenzofuran (right). The \* -signed peaks belongs to the dimeric species

As shown in Fig. 1 five dimeric dibenzofurans and two dimeric dichlorodibenzofurans could be identified in experiment no. 5 and 6 (see table I) using solid probe insertion with programmed evaporation. Even *in and for monoic species* were identified. No dimeric reaction product of the 2,7-dichlorodibenzop-dioxin was obtained. This could be explained by steric hindrance. The place in the interlamellar silicate layer of the Cu(II)-montmorillonite could be too small for dibenzop-dioxins which are on both benzene rings chloro substituted (see table I). No formation of dimeric, substituted or dechlorinated products could be observed with OCDD and OCDF.

As discussed in the literature the dimerisation or oligomerisation is induced by a strong interaction of the Cu(II) ion with the aromatic molecule through *pi*-electrons at vacant ligand positions, leading to formation of radical cations (reduction of Cu(II) to Cu(I)), followed by recombination (3,4).

#### Literature

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