

THE STABILITY OF THE ETHER BOND OF PCDD/PCDF STRUCTURE BY METHYLATION REACTION IN THE INJECTOR OF GC/MS AT 300°C USING REAGENT TRIMETHYLANILINIUMHYDROXYDE IN METHANOL

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Introduction

Chlorinated dibenzo-p-dioxins and dibenzofurans are thermally and chemically stable compounds. Most frequently they are degraded by thermic destruction by incineration. The second possibility of degradation is catalytic oxidation or reduction. During the analytical procedures of isolation and cleaning of extracts with concentrated sulphuric acid or with strong bases they stay practically unchanged. The most applicable method for laboratory degradation of dioxins is photolysis in an adequate solvent with UV light.

The stability of the aromatic ether bond of dibenzo-p-dioxin structure was studied by the reaction of methylation with trimethylaniliniumhydroxyde (TMAOH) in a methanol solution in the injector of the gas chromatograph at 300°C. This reagent is often used for derivatisation in the analytical determination of traces of organic compounds. The stability and the reactivity of related compounds should be known in advance.

Materials and Methods

The Ion trap mass spectrometer Finnigan GCQ was used for direct derivatisation in the injector of the gas chromatograph. The chromatographic column was fused silica DB-5, 30 m × 0.25 mm i.d. The temperature of the injector was 300°C. The splitless technique was applied. The conditions for the separation were: carrier gas helium 1 ml min⁻¹ the ion trap detector temperature was 250 °C. The temperature was programmed from 125 to 300°C at 10°C min⁻¹ with the final time of 10 min. The standard solution of 1,3,6,8-TCDD and 1,2,8,9-TCDD (concentration 5 ngµl⁻¹) in nonane with was used. The experiments were performed by the following procedure: the first injection of dioxin solution was performed without the reagent. In the second experiment the reagent (TMAOH) in methanol and the dioxin solution were injected together.

Results and discussion

The reagent in the injector was thermally decomposed probably by the heterolytic or homolytic way^{1,2}. Methanol as a solvent with a high dielectric constant and a reasonably low reactivity makes the coexistence of ion pairs and radical pairs possible. The cation of the quaternised nitrogen of anilin and methanol as a nucleophilic solvent exert influence on the cleavage of the aromatic ether bond. The cleavage of dioxin ether bond is performed at 300°C very easily. The GC/MS chromatogram and the chromatograms of two traces of the characteristic mass

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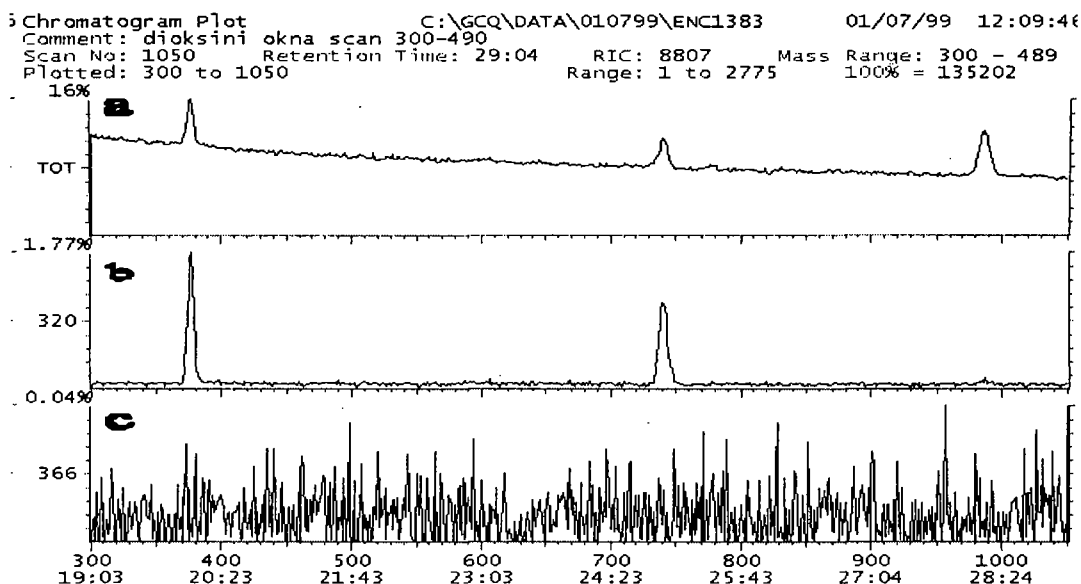


Figure 1: GC/MS chromatogram (a) and traces of mass fragments m/z 320 (b) for 1,3,6,8-TCDD and 1,2,8,9-TCDD and the fragment m/z 366 (c) which represents 2,2'-dimethoxy-tetrachloro-diphenylethers at injection without TMAOH/MeOH.

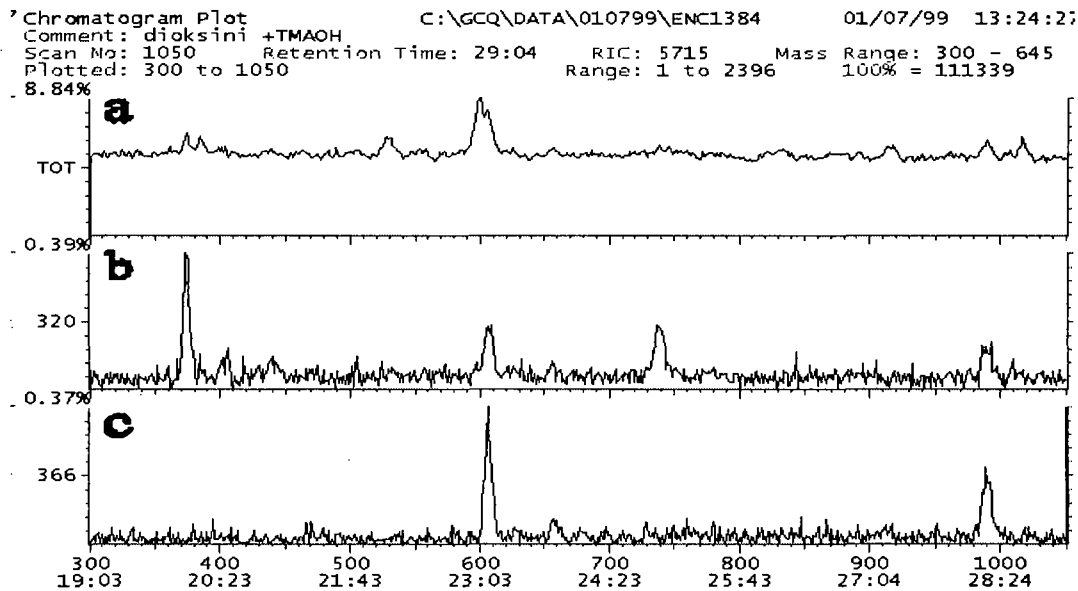


Figure 2: GC/MS chromatogram (a) and traces of mass fragments m/z 320 (b) for 1,3,6,8-TCDD and 1,2,8,9-TCDD and the fragment m/z 366 (c) which represents 2,2'-dimethoxy-tetrachloro-diphenylethers formed in injector of gas chromatograph at the reaction with TMAOH/MeOH.

ORGANOHALOGEN COMPOUNDS

fragments are presented in Figure 1 and 2. The fragment m/z 320 represent 1,3,6,8-TCDD and 1,2,8,9-TCDD, and the fragment m/z 366 represents the reaction products with TMAOH / MeOH. One of the spectra of 2,2'-dimethoxy-tetrachloro-diphenylethers formed is presented in Figure 3. The opening of the ether bond of both PCDD and PCDF is performed very easily. 2,2'-dimethoxy-diphenylethers are formed from dioxins.

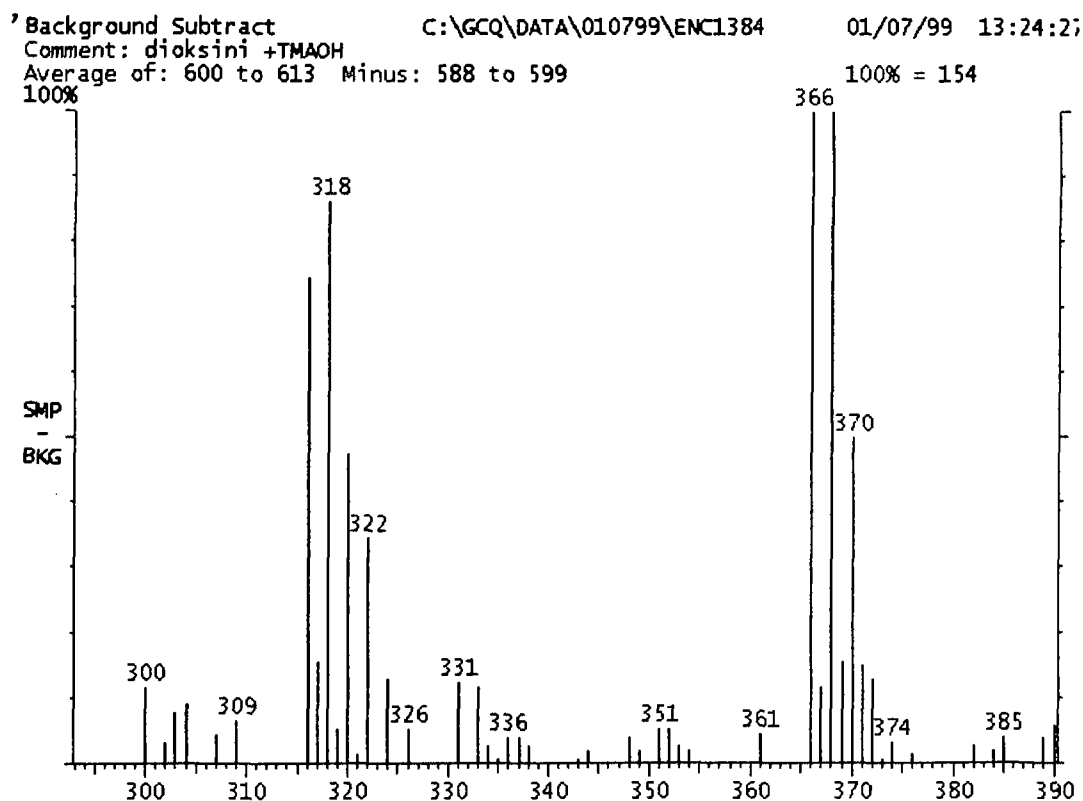


Figure 3: EI(+) mass spectra of the 2,2'-dimethoxy-tetrachloro diphenylether.

The mass spectrum in Figure 3 supports the structure of the chlorinated ortho-ortho dimethoxy-diphenylether. The opening of the ether bond is not restricted only to tetrachloro dioxin isomers but is performed also at highly chlorinated compounds from tetrachloro to octachloro derivatives of dibenzodioxins and dibenzofurans.

The reaction of ring opening with the TMAOH/MeOH reagent could be a step forward to the course of chemical degradation of these toxic compounds. The tentative path of formation of 2,2'-dimethoxy-tetrachloro-diphenylethers is presented in Figure 4.

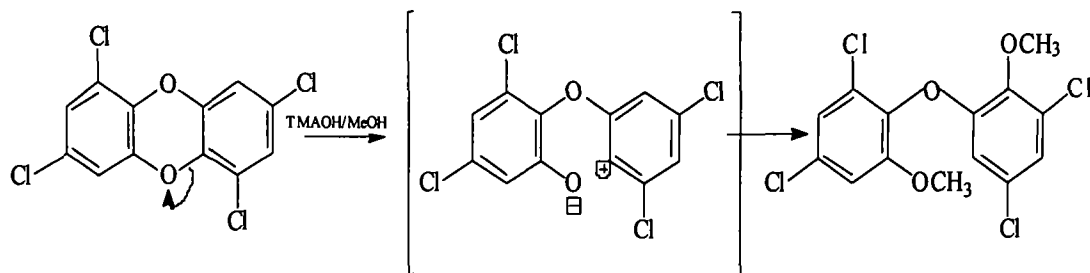


Figure 4: Methylation of the thermolytic products was performed with reagent trimethylaniliniumhydroxyde in methanol. At the opening of ether bond of 1,3,6,8-TCDD and 1,3,7,9-TCDD chlorinated derivatives of 2,2'-di-methoxy-diphenylether are formed.

References

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2. E.Voncina (2000) Formation Mechanism of Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans (Thesis), Ljubljana University, COBISS-ID 107195648