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THERMOLYSIS ON ALUMINUM OXIDES CHEMISORBED 2,4,6-TRICHLOROPHENOL AS EXAMPLE FOR THE FLY ASH MEDIATED SURFACE CATALYSIS REACTION IN PCDD/PCDF FORMATION

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Introduction: The objective of this work is to acquire a better understanding of the gas-phase thermolysis of volatile chlorophenoxyaluminum compounds and to clarify the thermolysis on the fly ash chemisorbed chlorophenols. In our efforts to study the reaction mechanisms of polychlorinated phenols as precursor compounds in the formation of PCDD/PCDF the influence of aluminum cation as a strong electrophilic centre to the course of thermolysis on the $\text{Al}(\text{OH})_3$ surface chemisorbed chlorophenol^{1,2,3,4)} is investigated. In the experimental model study the thermolysis of the system 2,4,6-trichlorophenol/ AlCl_3 and 2,4,6-trichlorophenol/ $\text{Al}(\text{OH})_3$ is presented. In the first system we have a directly formed tris-2,4,6-trichlorophenoxyaluminum compound, while in the second one we have adsorbed and chemisorbed 2,4,6-trichlorophenol on the surface of $\text{Al}(\text{OH})_3$. It has been confirmed by thermolysis experiments and mass spectrometric investigations that the thermic transformation of tris-2,4,6-trichlorophenoxyaluminum compound or on the surface of $\text{Al}(\text{OH})_3$ chemisorbed derivative yields the same reaction compounds with practically the same concentration ratio.

Materials and Methods: Mass spectrometry: 2,4,6-trichlorophenoxyaluminum compounds were prepared with the reaction in the melt between 2,4,6-trichlorophenol and freshly sublimated AlCl_3 at stoichiometric ratio. The samples so prepared were used for the thermolysis experiment with direct introducing of chlorophenoxyaluminum compounds into the ion source. The fragmentation pattern of selected parent ions was examined on AUTOSPEC mass spectrometer (Fisons, VG-Analytica) by mass analysed ion kinetic energy (MIKE) technique. The thermolysis of 2,4,6-trichlorophenol/ $\text{Al}(\text{OH})_3$ was performed in a closed vessel for 30 min. at 300°C. The products were extracted with hexane/toluene/triethylamine (1:1:1) to avoid acid catalysis and analysed with Ion trap mass spectrometer Finnigan GCQ, where positive and negative EI spectra were examined. Derivatization of hexachlorinated cyclohexadienons isomers with trimethylsilyl cation as supplement for the proton catalysis (MSTFA with 3% J_2 w/v as catalyst for enolization of carbonyl group) has been performed. Ab Initio Computations: Molecular orbital methodology with 3-21+G basis set (Gaussian 96, Pittsburgh, USA) has been used to explore the energetics of ortho-ortho products.

Results and discussion: Thermolysis is carried out at 300°C. The spontaneous rupture of the bond between aluminum and oxygen of phenol takes place in the temperature range from 260 - 280°C. The thermolysis of chlorophenoxy aluminum compounds is occurred through homolytic and heterolytic bond cleavage^{3,4)}. It is important where the reactions are performed: in the homogenic gas phase or under conditions of heterogenic catalysis on the surface of fly ash or under conditions of acid-base catalysis. At homolytic cleavage of the Al-O bond the chlorophenoxy radical is formed. The isolation of reaction products of the thermolysis of the system $\text{Al}(\text{OH})_3/2,4,6$ -trichlorophenol gave five isomers of dimeric

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compounds of resonance stabilised 2,4,6-trichlorophenoxy radical (Fig.1). All five possible dimeric isomers, namely three isomers of C-C bonded, (ortho-ortho, ortho-para, para-para) and two isomers of C-O bonded (O-ortho, O-para) compounds were successfully determined by gas chromatographic separation and subsequent mass spectrometric detection. These products were shown to be nonaromatic hexachloro-cyclohexadienone dimers. The presence of dimeric compounds indicates that processes of radical reactions occur parallel to ionic reactions of heterolytic cleavage of the Al-O bond.

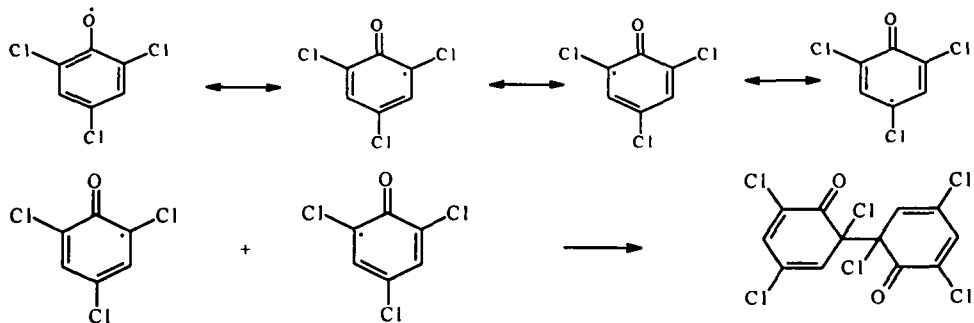


Figure 1: The resonance structures of 2,4,6-trichlorophenoxy radical. The different products may arise from the reaction of decollated unpaired electron with resonance stabilised 2,4,6-trichlorophenoxy radical. The proposed structure of the compound M = 390, di-1,1'-(1,3,5-trichloro-2-oxocyclohexa-3,5-diene) which is the main product of dimerisation.

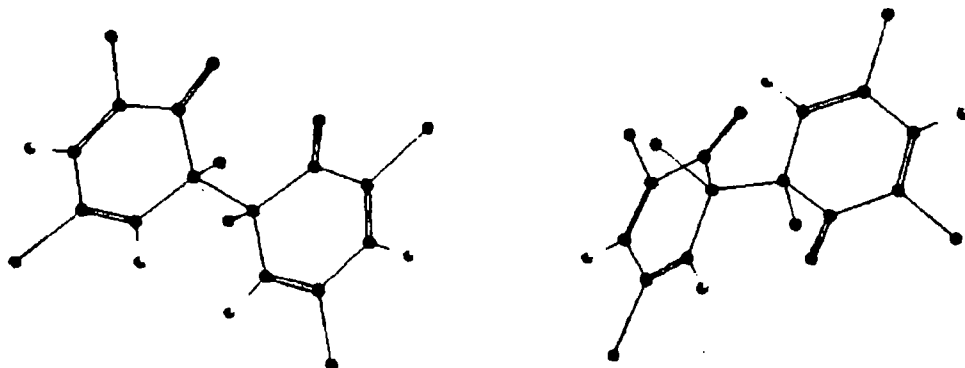


Figure 2: Conformational equilibria in ortho-ortho cyclohexadienonic dimers. Ab Initio fully optimised (3-21+G basis set) structures of cis and trans rotational isomers are shown. The trans isomer is by 5.8 Kcal/mol more stable than the cis isomer. This is explained by favourable interactions of the monomers LUMO (Lowest Unoccupied Molecular Orbital) and HOMO (Highest Occupied Molecular Orbital) and steric considerations.

The compounds are stable in nonaqueous, aprotic conditions, but they are very sensitive to acid catalysis and the consequence is that they are quickly transformed into aromatic hydroxydiphenylethers precursors of PCDD. The special attention is focused to the process of aromatisation, rearrangement of cyclohexadienonic dimers with C-C linked ring into the aromatic hydroxydiphenylethers.

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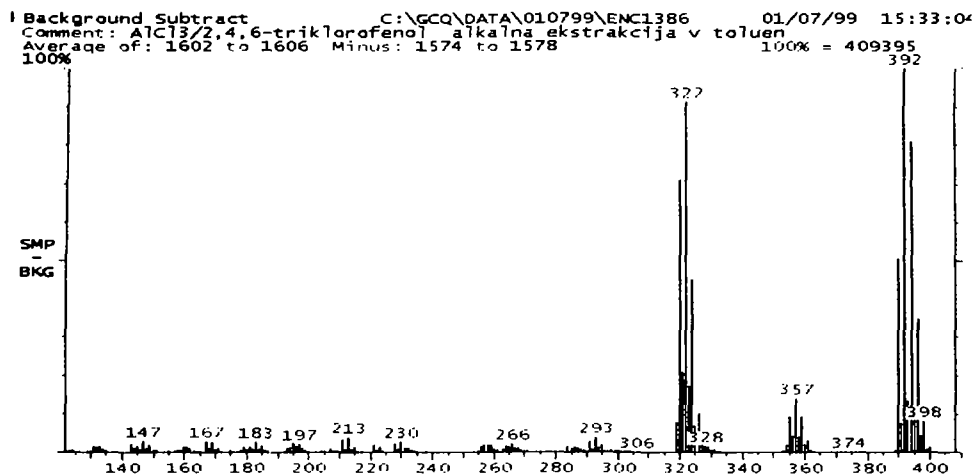


Figure 3: EI(+) mass spectra of positive ions of di-1,1'-(1,3,5-trichloro-2-oxocyclohexa-3,5-diene). The abstraction of two chlorine atom from 1,1'-position is favoured.

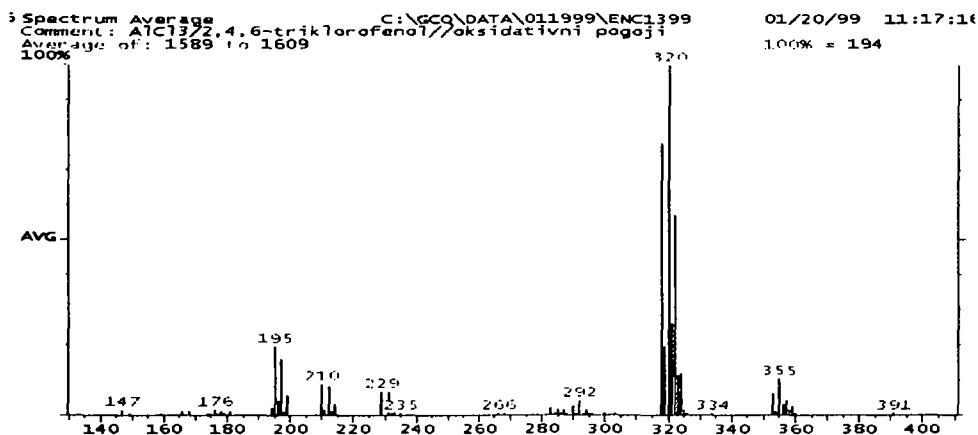


Figure 4: EI(-) mass spectra of negative ions of di-1,1'-(1,3,5-trichloro-2-oxocyclohexa-3,5-diene). The abstraction of two molecules of hydrogen chloride from 1,1'-position is favoured.

Derivatization of hexachlorinated cyclohexadienons isomers with trimethylsilyl cation as supplement for the proton catalysis has been performed. The purpose of this reaction which yields derivatives of silylated hexachloro hydroxydiphenylethers is to establish the reaction path where the reactive dimers are transformed into stable hydroxydiphenylethers, precursors of PCDD. The example of one tentative path of rearrangement is presented in Fig.5. At conditions of thermolysis in the homogenic gas phase or at heterogenic catalysis the formation of stable aromatic compounds is possible with the process of dechlorination. It is evident from MS(EI) spectra of positive ions (Fig. 3) that the loss of two chlorine atoms from position 1,1' of di-1,1'-(1,3,5-trichloro-2-oxocyclohexa-3,5-diene) is occurred. At the same time the MS(EI) spectra of negative ions (Fig. 4) show the loss of two hydrogen chloride molecules. The hydrogen atom from position 6,6' of di-1,1'-(1,3,5-trichloro-2-oxocyclohexa-3,5-diene) also participates in the process of enolization of the

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first ring at a simultaneous rearrangement of one of the two chlorine atoms from position 1,1' to the position 6,6' in dimeric compound.

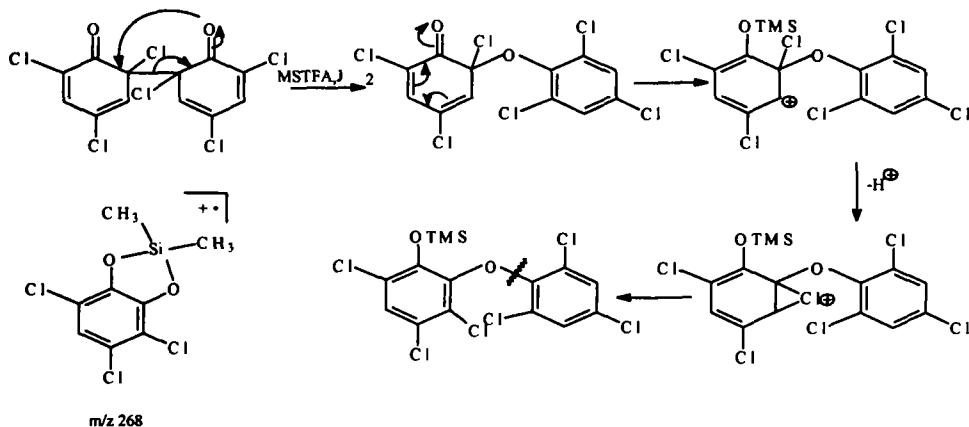
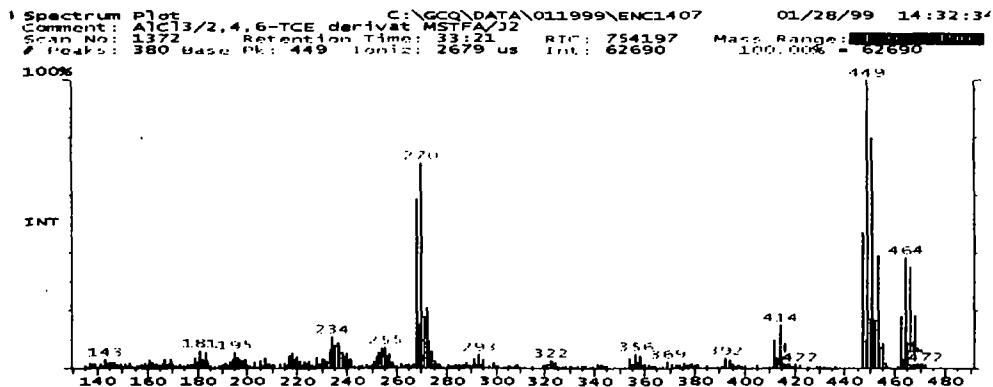


Figure 5: The tentative path of rearrangement of di-1,1'-(1,3,5-trichloro-2-oxocyclohexa-3,5-diene) into the silylated hexachlorodiphenylether and the proposed structure of fragment m/z 268.

If the hydrogen atom on position 1,1' in the dimeric compound is available, the aromatic system is formed owing to keto-phenol tautomerism. Theoretical studies by using Ab Initio approach has shown that trans orientation of ortho-ortho products has lower energy than its cis isomer (Fig.2). This was interpreted by frontier orbital theoretical reasoning.

References

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