

THERMOLYSIS ON ALUMINUM OXIDES CHEMISORBED 3-CHLOROPHENOL AS EXAMPLE FOR THE FLY ASH MEDIATED SURFACE CATALYSIS REACTION IN PCDD/F FORMATION

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ABSTRACT

The purpose of this work was to elucidate the mechanism of the thermolysis of 3-chlorophenol chemisorbed on the surface of aluminum oxide as an example of the surface mediated catalysis reaction where 3,3'-dichlorodiphenylether and three derivatives of dichloro-hydroxy-diphenyls are formed as the main thermolytic products. The proposed formation mechanism of 3,3'-dichlorodiphenylether and dichloro-hydroxy-diphenyls isomers is based on the dimerisation of the 3-chlorophenoxy radical with the 3-chlorophenyl radical, which is formed by the expulsion of CO₂ in the reaction of CO with the 3-chlorophenoxy radical.

INTRODUCTION

In our previous experiments we followed the thermic transformation of chlorophenoxyaluminum compounds with mass spectrometry^{1,2,3}. Phenoxyaluminum compounds were prepared with the reaction in the melt between phenol or ortho-, meta-, para- chlorophenol and freshly sublimated AlCl₃ at stoichiometric ratio according to the reaction (1)⁴.



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The samples so prepared were used for the thermolysis experiment with direct introducing of chlorophenoxyaluminum compounds into the ion source and for experiments in which the thermolysis was performed in a closed vessel for 30 min. at 300°C. From the examination of mass spectra the fragmentation patterns differ substantially and depend quite strongly upon the position of the chloro substituent on the aromatic ring. In the case of ortho- position of the chlorine atom the migration of the halogen atom to the aluminum atom is obviously noticed, and in the case of meta- positioned chlorine atom the abstraction of ortho hydrogen and subsequent loss of original phenol occurs. These facts are the main reasons that explain why the thermolysis of tris-2-chlorophenoxyaluminum in comparison with tris-3-chlorophenoxyaluminum compounds at 300°C shows us a different mechanism of thermal decomposition with different products. In the model study of the system 3-chlorophenol/ AlCl_3 and 3-chlorophenol/ $\text{Al}(\text{OH})_3$, we present the thermolysis of such meta-chlorophenol compounds. In the first system we have a directly formed tris-3-chlorophenoxyaluminum compound, but in the second one, we have adsorbed and chemisorbed 3-chlorophenol on the surface of $\text{Al}(\text{OH})_3$. With $\text{Al}(\text{OH})_3$ we simulated naturally occurring aluminum oxides, oxyhydroxides and oxychlorides on fly ash. Specific adsorption involves physical and chemical interaction of phenol with individual sites on the oxide surface, where the influence of the aluminum atom is important. The objectives of this research are to elucidate the mechanism of decomposition of chemisorbed 3-chlorophenol onto $\text{Al}(\text{OH})_3$, as a surrogate for real fly ash.

EXPERIMENTAL

Analyses: HP-5970 GC/MSD, ^{13}C -NMR and ^1H -NMR Variant VXR 300 instruments.

Samples: Tris-3-chlorophenoxyaluminum compounds were prepared with the reaction in the melt between 3-chlorophenol and freshly sublimated AlCl_3 at stoichiometric ratio. $\text{Al}(\text{OH})_3$ was prepared⁵ from high purity aluminum by cutting the metal into strips,. The metal pieces were covered with a layer of amalgam by a short immersion in the 0.1M HgCl_2 solution. The metal pieces were left under distilled water in a covered flask for several days, when white crystals were slowly formed. The crystals were air dried and pulverised. For the chemisorption^{6,7)} experiment we first physisorbed the 3-chlorophenol on fine pulverised aluminum hydroxide by heating the sample to the melting temperature of phenol. Thermolysis was then performed in a closed vessel for 30 min. at 300°C. For the GC/MSD analysis we prepared the hexane extract of products after hydrolysis at pH=2. The resulting dichlorodiphenylether was isolated from the reaction mixture by column chromatography with silicagel and n-hexane as eluent. The structure of the obtained dichlorodiphenylether was confirmed by MS, ^1H -NMR and ^{13}C -NMR (Figure 1).

RESULTS AND DISCUSSION

It has been confirmed by our experiment that the thermic transformation of 3-chlorophenoxy derivate as tris-3-chlorophenoxyaluminum or on the surface of $\text{Al}(\text{OH})_3$ chemisorbed derivate yields the same reaction compounds with practically the same concentration ratio. Consequently, 3,3'-dichlorodiphenylether and three derivatives of dichloro-hydroxy-diphenyls were detected. The coupling of two chlorophenoxy radicals is practically not noticed.

In order to confirm identity of 3,3'-dichlorodiphenylether we reported the chemical shifts in ppm with reference to internal TMS (J coupling constants in Hz)

$^1\text{H-NMR}$: δ : 7.3, (t, 8Hz), δ : 7.1, (ddd, 8Hz, 2Hz, 1Hz)
 δ : 7.0, (t, 2Hz), δ : 6.9, (ddd, 8Hz, 2Hz, 1Hz)

$^{13}\text{C-NMR}$: δ : 157.4, 135.2 (quaternised carbons)
 δ : 130.6, 124.0, 119.4, 117.2 (CH carbons)

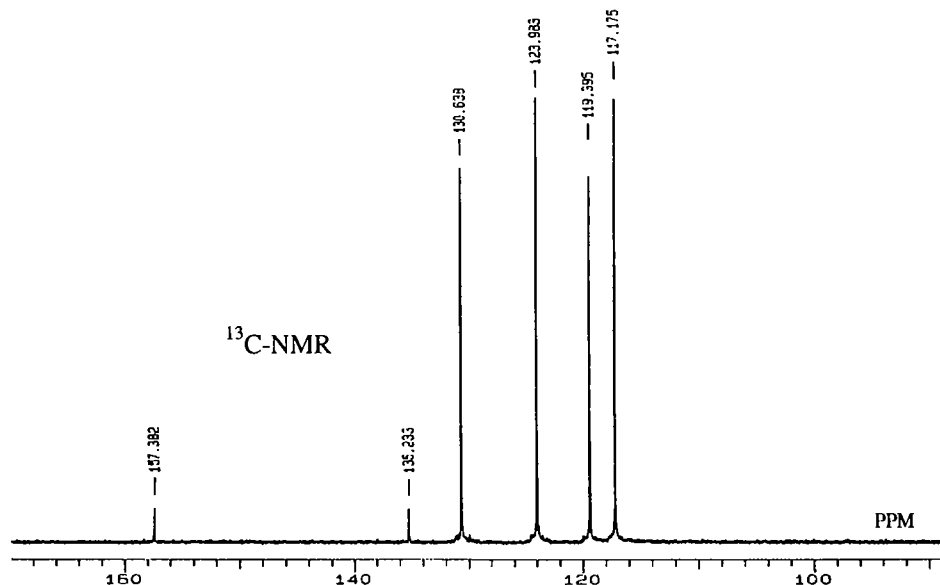


Figure 1: $^{13}\text{C-NMR}$ spectra of isolated 3,3'-dichlorodiphenylether

From the experiments in which we directly introduced the tris-3-chlorophenoxyaluminum compound in a mass spectrometer ion source and thermolysed it at the sample temperature 300°C and from the examination of MIKE scan spectra (Figure 2) it is evident that the basic and almost frequent loss of carbon monoxide and the chlorophenoxy unit occur at the same time. It is quite clear that the explanation for the formation of 3,3'-dichlorodiphenylether must include the mechanism by which the phenoxy radical lose the oxygen atom. The proposed mechanism includes the reaction between carbon monoxide and phenoxy radical with subsequent expulsion of carbon dioxide and the formation

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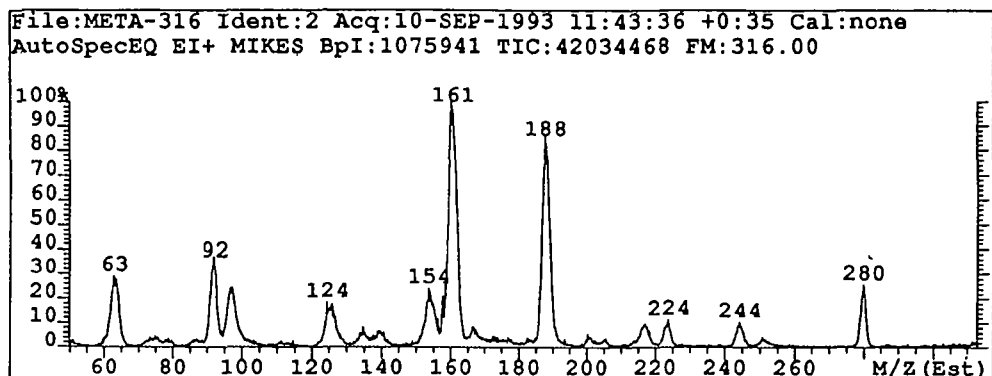
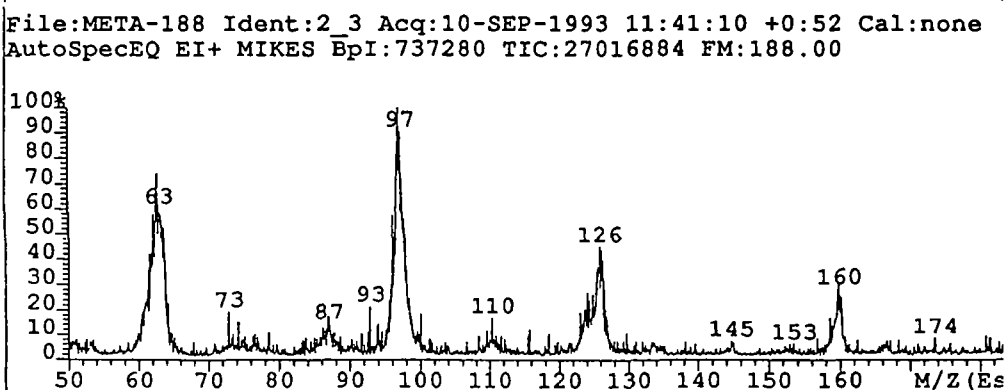
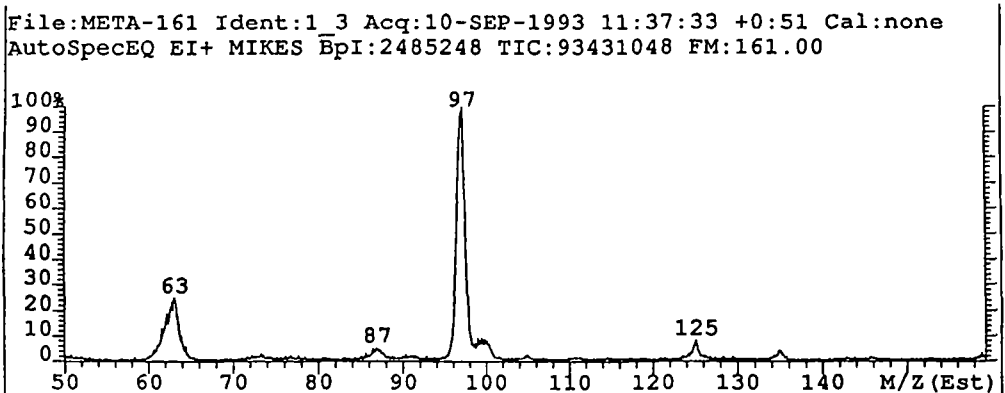
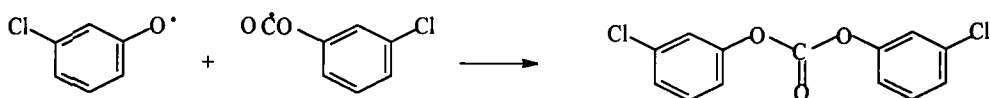


Figure 2: The breakdown pattern of some ions m/z 316, m/z 188 and m/z 161. The fragmentation pathways with their tentative ion structure are presented in the scheme in Figure 7. It is evident from MIKE spectra of molecular ion Al(III)di(3-chlorophenoxy)chloride (m/z 316) that the basic and almost most frequent loss of carbon monoxide and chlorophenoxy unit occurs at the same time (m/z 316 \rightarrow m/z 161). The second most frequent fragmentation occurs with the loss of neutral 3-chlorophenol (m/z 316 \rightarrow m/z 188).

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of phenyl radical. The scheme of the tentative mechanism is shown in the Figure 3. It is not so clear yet if the transformation is going on inside a tight chlorophenoxy/CO/aluminum complex cluster as a unimolecular transformation or it is in principle a bimolecular reaction. The condensation of two phenoxy radicals leading to hydroxy-diphenylethers or two non-ortho phenyl radicals leading to non ortho-PCBs are not dominant reactions in the case of 3-chlorophenol thermolysis so these products are not detected or their concentrations are much lower. The mechanism also indicates the possibility of the formation of di-3-chlorophenylcarbonate by catching another chlorophenoxy radical as shown below:



Chlorodiphenylcarbonates were detected by the thermic treatment of phenoxy aluminum compounds at low temperatures under reflux of hexane. Transformations were carried out in a cage of solvent hexane²⁾. These facts - the formation of di-3-chlorophenylcarbonate in a cage of solvent hexane and the loss of carbon monoxide and chlorophenoxy unit occurring at the same time, which is evident from MIKE spectra, support the proposed formation mechanism. The decomposition of the chlorophenoxy fragment included intermediary the conversion to 2-oxocyclohexa-3,5-dienylidene with subsequent carbon monoxide elimination and formation of cyclopentadienyl derivate.

CONCLUSIONS

The thermic transformation of the tris-3-chlorophenoxyaluminum compound or on the surface of Al(OH)₃ chemisorbed 3-chlorophenoxy derivate yielded the same reaction products: 3,3'-dichlorodiphenylether and isomeric dichloro-hydroxy-diphenyls. The formation of detected products is explained by the proposed mechanism.

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