

THERMOLYSIS ON ALUMINUM OXIDES CHEMISORBED 2-CHLOROPHENOL AS EXAMPLE FOR THE FLY ASH MEDIATED SURFACE CATALYSIS REACTION

Ernest Vončina¹, Tomaz Šolmajer²

¹Public Health Institute, Prvomajska 1, SLO-2000 Maribor, Slovenia

²National Institute of Chemistry and Lek, d.d., SLO-1000 Ljubljana, Slovenia

INTRODUCTION

The purpose of this work was to elucidate the mechanism of the thermolysis of 2-chlorophenol chemisorbed on the surface of amorphous aluminum oxide. This is an example of the fly ash mediated surface catalysis reaction where mono and dichloro-hydroxy-diphenylether and derivatives of dichloro-dihydroxy-diphenyls are formed as the main thermolytic products. In this work some electronic and structural properties of aluminum-2-chlorophenolate intermediates are discussed. The influence of Al atom as catalyst is explicitly provided for in the computational model.

Although aluminum ions are frequently present in fly ash relatively little attention has been paid to its role as catalyst. Thus, we have introduced in our model specific physical and chemical interactions of chlorophenols with aluminum ion. Phenoxyaluminum compounds were prepared with the reaction in the melt between ortho-chlorophenol and freshly sublimated AlCl_3 . We have simulated naturally occurring aluminum oxides, hydroxides, oxihydroxides and oxichlorides on fly ash with $\text{Al}(\text{OH})_3$. Their highly active sites, covered with reacting precursors including the influence of aluminum ion were introduced in a model for PCDD/F formation. The objectives of this work were: in the experimental model study of the system 2-chlorophenol/ AlCl_3 and 2-chlorophenol/ $\text{Al}(\text{OH})_3$ we present the thermolysis of ortho-chlorophenol compounds. In the first system we have a directly formed tris-2-chlorophenoxyaluminum compound, while in the second one, we have adsorbed and chemisorbed 2-chlorophenol 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 2-chlorophenoxy derivate as tris-2-chlorophenoxyaluminum or on the surface of $\text{Al}(\text{OH})_3$ chemisorbed derivate yields the same reaction compounds with practically the same concentration ratio. To confirm the proposed mechanism of decomposition of chemisorbed 2-chlorophenol onto aluminum based on experimentally observed mass spectrometric fragmentation we have performed Ab Initio computational experiments.

MATERIAL AND METHODS

Analyses: HP-5970 GC/MSD instruments were used for the MS- analyses. The fragmentation pattern of selected parent ions were examined on AUTOSPEC (Fisions, VG-Analytica) by MIKE technique. Samples: Tris-2-chlorophenoxyaluminum compounds were prepared with the reaction in the melt between 2-chlorophenol and freshly sublimated AlCl_3 at stoichiometric ratio. $\text{Al}(\text{OH})_3$ was prepared as described previously [1-4] For the chemisorption[5-7] experiment we first

activated the $\text{Al}(\text{OH})_3$ by preheating to 105°C for 20 min. for removing physisorbed water and setting free active sites. After cooling the sample to room temperature 2-chlorophenol was added and the mixture was heated 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 $\text{pH}=2$. Ab Initio Computational Calculations: We have used Ab Initio molecular orbital methodology with 3-21+G basis set (Gaussian 96, Pittsburgh, USA). Electron densities were plotted by using program package Spartan.

RESULTS AND DISCUSSION

Thermolytic degradation and mass spectrometric fragmentation: Two sets of thermolytic degradation experiments were performed: firstly, tris-2-chlorophenoxyaluminum was thermolysed into mono- and dichloro-hydroxy-diphenylethers and derivatives of dichloro-dihydroxy-diphenyls. Secondly, identical reaction products were observed by thermolysis on the surface of $\text{Al}(\text{OH})_3$ chemisorbed 2-chlorophenoxy derivate with practically the same concentration ratio as in the former reaction. Typical compositions of reaction compounds are presented in Fig. 1.

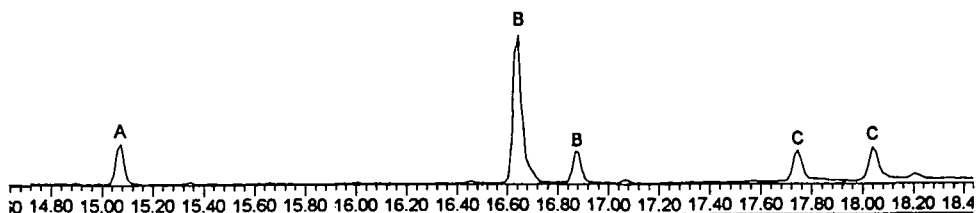


Fig.1: Thermolytic products of 2-chlorophenol chemisorbed on $\text{Al}(\text{OH})_3$ at 300°C . The decomposition of 2-chlorophenoxy derivate to monochloro-hydroxydiphenylether (A), dichloro-hydroxydiphenylether (B) and dichloro-dihydroxy-diphenyls (C) is preferential.

Fragmentation Processes of di-2-chlorophenoxyaluminumchloride: The parent ion m/z 316 MIKE spectra of experiments in which we directly introduced the tris-2-chlorophenoxyaluminum compound in mass spectrometer ion source and thermolysed at the sample temperature 300°C are represented in Fig. 2. The scheme of the tentative fragmentation pattern is shown in the Fig. 3.

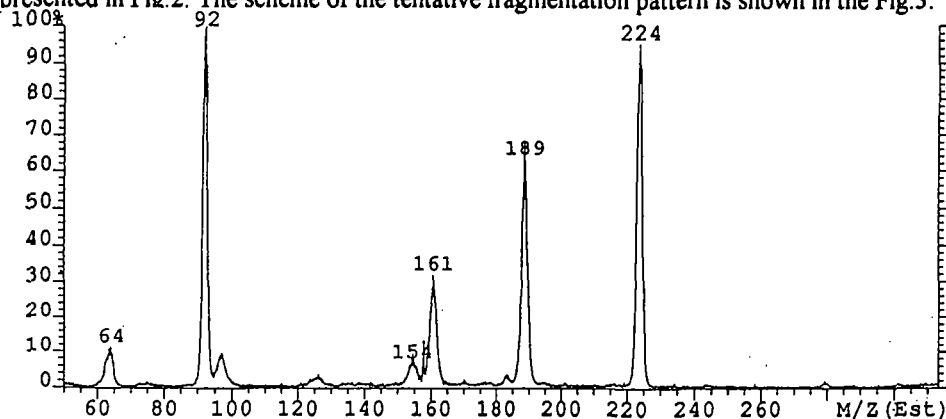


Fig.2: The breakdown pattern of ion m/z 316. It is evident from MIKES spectra of molecular ion $\text{Al}(\text{III})\text{di}(2\text{-chlorophenoxy})\text{chloride}$ that the main fragments are m/z 224, m/z 189 and m/z 161.

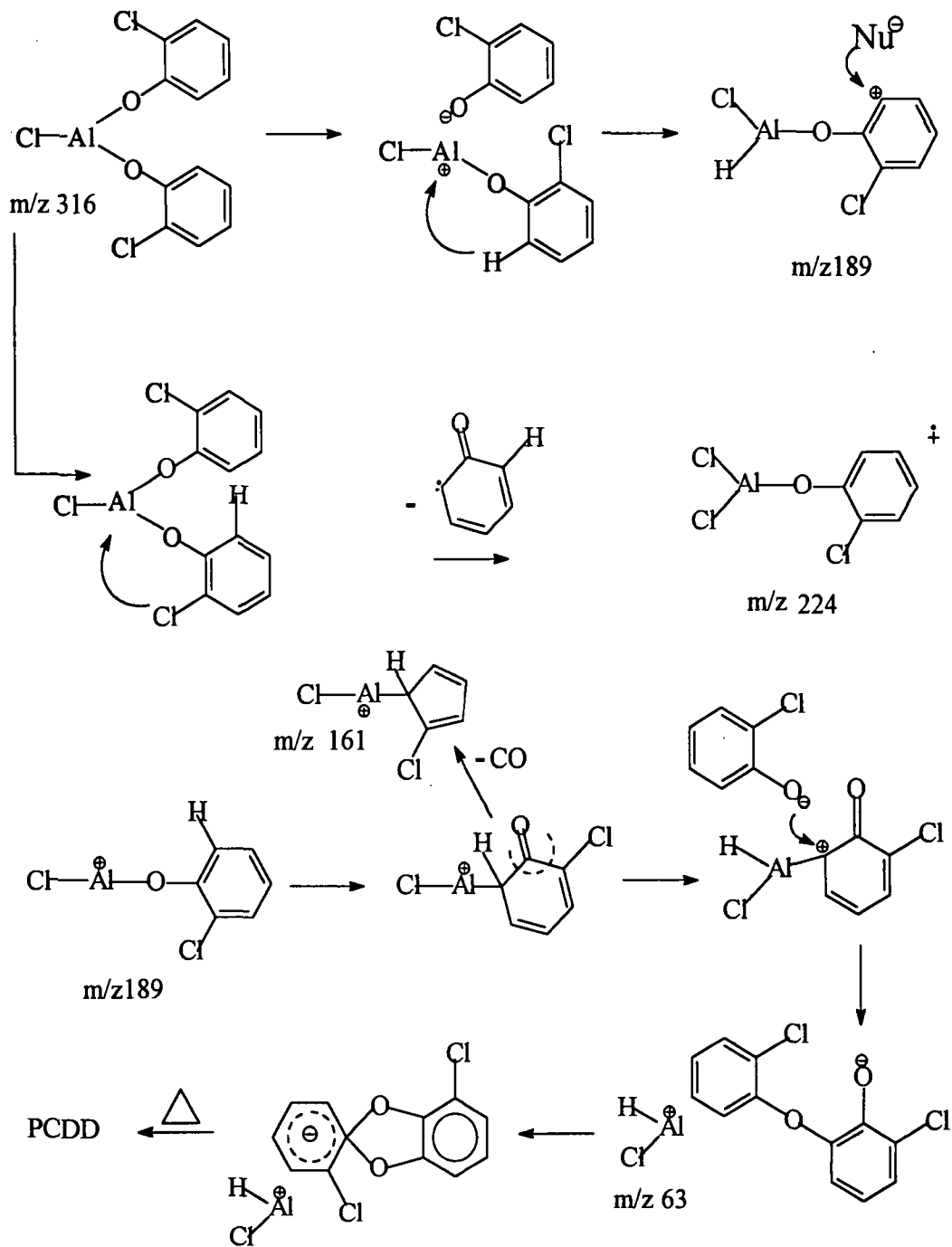
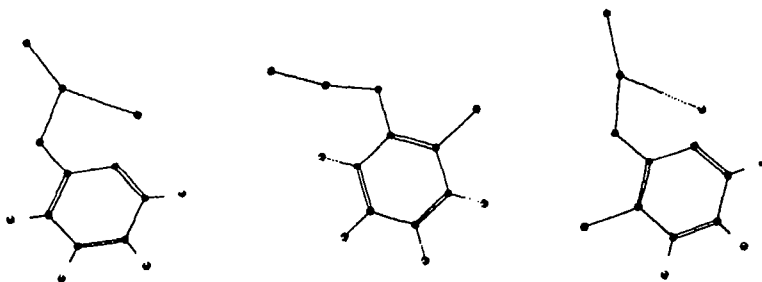


Fig. 3: The scheme of the tentative fragmentation of 2-chlorophenoxyaluminum chlorides.

From MIKE spectra the following breakdown pattern can be observed: molecular ion Al(III)di(2-chlorophenoxy)chloride (m/z 316) fragmentates into ions m/z 224, m/z 189 and m/z 161 with greatest intensity. In the first step of the fragmentation of peak m/z 316 Al-O bond cleavage is included with the loss of 2-chlorophenoxy group which gives ion m/z 189. This leaving 2-chlorophenoxy anion generates Al-ion which is driving force for the reorganisation of unstable intermediates. Migration of the halogen atom to the aluminum atom by subsequent elimination of the oxocyclohexadienylidene derivative is noticed and the ion m/z 224 is observed.

Results of Ab Initio computations of position 2-chloro vs 6-hydrogen transfer in 2-chlorophenoxyaluminum intermediates show that aluminum cation acting as catalyst promotes the 6-hydrogen transfer over the 2-chloro position. We have used isodesmic reaction on the Ab Initio level to evaluate the energetic differences in this process because they enable a simple and accurate means to study such reactions in vacuo. It has been previously suggested that metal cations could act as electrophiles[8,9]. Our results with inclusion of aluminum ion in the model support this conjecture since the energetic barrier to ortho-chlorine in a favourable spatial position to aluminum ion is higher by approximately 12 Kcal/mol than its hydrogen substituted counterpart at position 6.



Scheme 1: The scheme shows fully optimised structures (3-21G+basis set) of key intermediates for the competing alternative rearrangement path ways

These results are further illustrated with plots of electron densities. The transfer of chlorine or hydrogen generates a carbocation structure which is further rearranged into 2-oxocyclohexa-3,5-dienylidene derivative or takes part in the nucleophilic attack by the leaving chloro-phenoxy anion. The latter intermediate, aluminum bonded ortho-hydroxy-diphenylether is further thermochemically rearranged into Smiles like dibenzo dioxin structure. Also consistent with the proposed formation mechanism are the resulting heats of formation of the fragmentation intermediates. Detailed account of the case will be given in our subsequent work.

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