

MASS SPECTROMETRY OF PHENOXYALUMINUM CHLORIDES TYPE $(R_nAlCl_{3-n})_m$ ($m = 1,2,3$)

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ABSTRACT

Within the study of the formation of chlorinated dioxins and dibenzofurans and their precursors the thermolysis of phenoxy- and chlorophenoxy aluminum chlorides at 350°C was investigated. Reagent compounds and products of thermolysis were followed by mass spectrometry.

INTRODUCTION

The presence of elemental aluminum in the solid urban waste is relatively high¹. The HCl concentration in urban waste combustion gases is in the order of 10^2 - 10^3 mg/Nm³ and therefore sufficiently high to enable the formation of aluminum chlorides in combustion chamber which could react with aromatic compounds (phenols or chlorophenols) and form volatile organoaluminum compounds².

In the model study of the system phenol/ $AlCl_3$ or chlorophenol/ $AlCl_3$ we present the thermolysis of such compounds at 350 °C and a part of interesting fragmentation patterns of phenoxyaluminum chlorides is included.

EXPERIMENTAL

Samples

Phenoxyaluminum chlorides were prepared with the reaction in the melt between phenol or ortho-, meta-, para- chlorophenol and freshly sublimated $AlCl_3$ at stoichiometric ratio. The samples so prepared were used for

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thermolysis experiment and direct introducing to ion source. Thermolysis was performed in the closed vessel for 30 min. at 350 °C. For GC/MSD analysis we prepared the benzene extract of products.

Analyses

For the MS- analyses we used VG AUTOSPEC Q-FISONS and HP -5971 GC/MSD instruments equipped with 30 m SPB-5 column.

RESULTS AND DISCUSSION

It is evident from the mass spectrum (see Figure 1) that we obtained through the direct introduction of Al (III) phenoxide a mixture of compounds $(R_nAlCl_{3-n})_m$, ($m = 1,2,3$), ($R = C_6H_5O$). Due to simultaneous intra and intermolecular exchange of ligands³ we found an equilibrium of monomer/dimer/trimer.

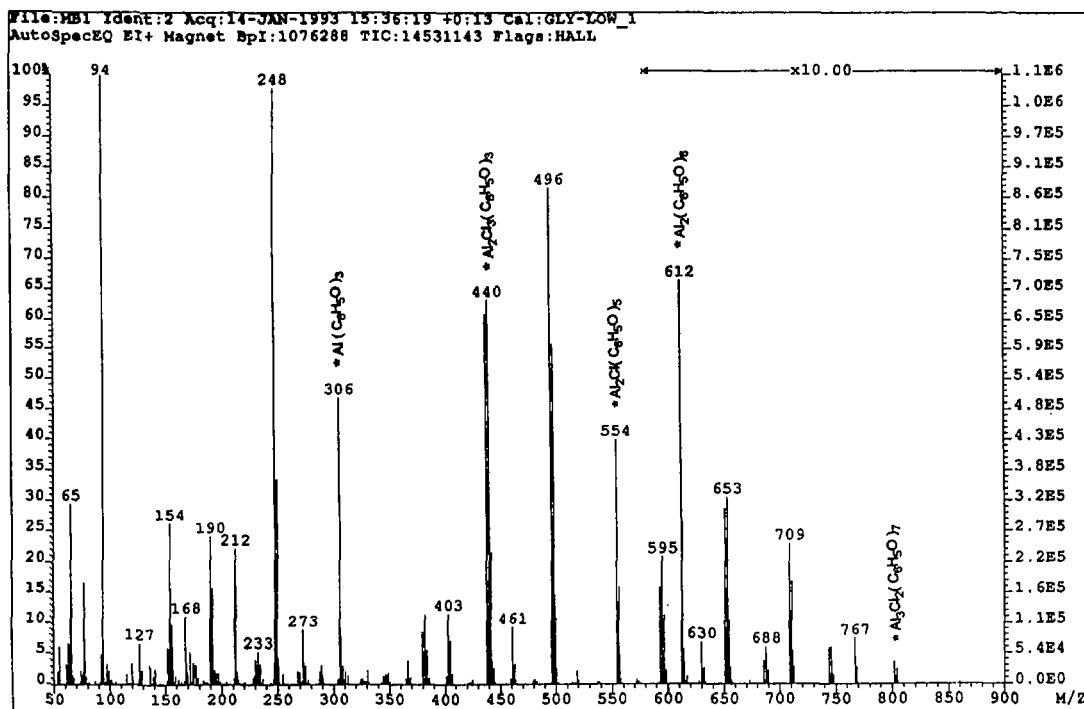


Figure 1: Mass spectra of directly introduced phenoxyaluminum chlorides at sample temperature 400 °C. Compounds in equilibrium are presented.

So we have detected in the experiment with phenol mass fragments which confirm an occurrence for instance: of trimers $\text{Al}_3\text{Cl}_2(\text{C}_6\text{H}_5\text{O})_7\dots$, dimers $\text{Al}_2(\text{C}_6\text{H}_5\text{O})_6$, $\text{Al}_2\text{Cl}_3(\text{C}_6\text{H}_5\text{O})_3\dots$, and monomers $\text{Al}(\text{C}_6\text{H}_5\text{O})_3$, $\text{AlCl}(\text{C}_6\text{H}_5\text{O})_2$ and $\text{AlCl}_2(\text{C}_6\text{H}_5\text{O})$. In the process of thermolysis a further fragmentation of compounds $\text{AlCl}(\text{C}_6\text{H}_5\text{O})_2$, $\text{AlCl}_2(\text{C}_6\text{H}_5\text{O})$, $\text{Al}(\text{C}_6\text{H}_5\text{O})_3$ or transformation of corresponding ortho-, meta- and para- chlorophenoxy aluminum chlorides respectively is decisive.

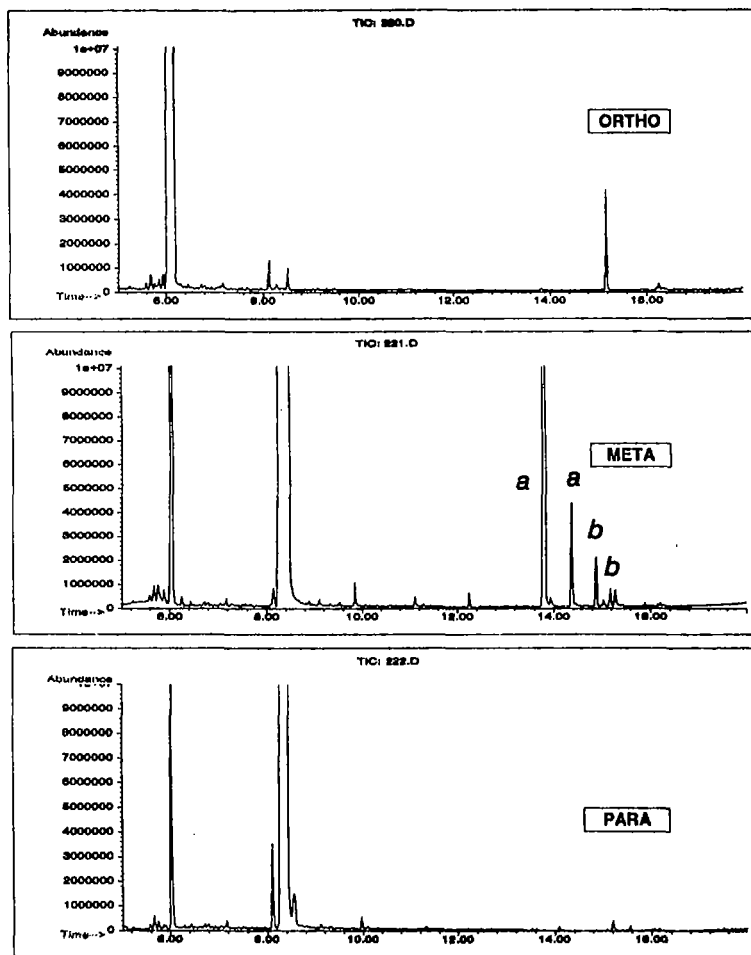


Figure 2: Comparison of the thermolytic products of ortho-, meta- and para-chlorophenoxy aluminum chlorides at 350 °C detected with GC/MSD. The decomposition of 3-chlorophenoxy derivate to dichlorodiphenylethers^a and to dichlorodibenzofurans^b is preferential. The isomerisation of basis phenols and the formation of dichlorophenols has occurred.

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Figure 2 shows the comparison of the thermolytic products of ortho-, meta- and para- chlorophenoxy aluminum compounds recorded with GC/MSD.

The role of mass spectrometry in establishing a fairly definitive mechanism for the thermal decomposition of compounds is quite well. The interesting fragmentation pattern is followed by unimolecular or collision induced dissociation of the ion m/e 316 using MIKES techniques (Figure 3).

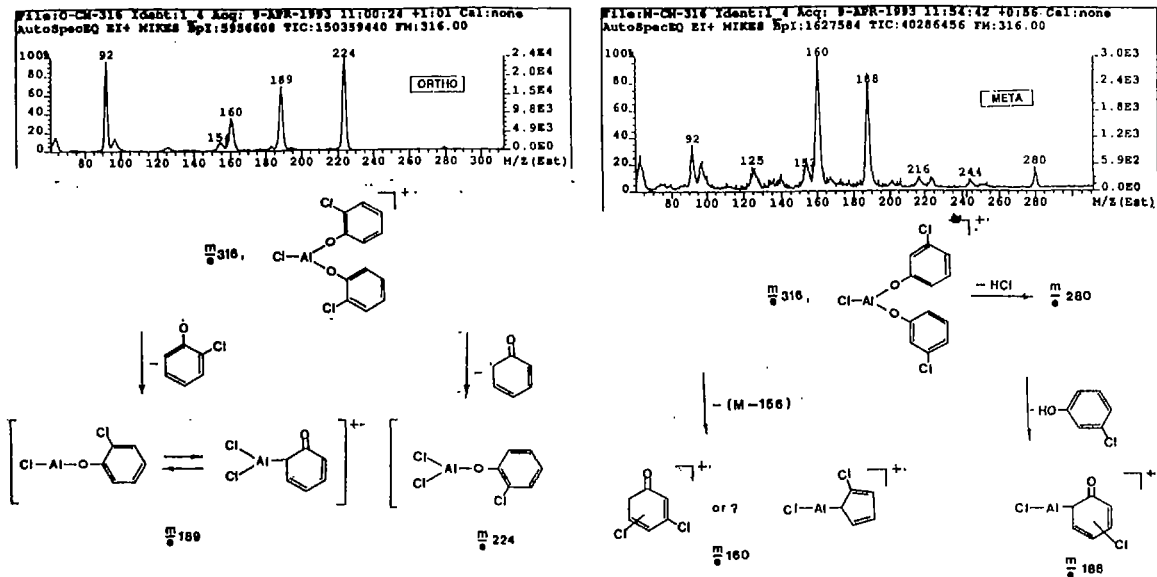


Figure 3: The fragmentation patterns differ substantially and depend quite strongly upon the position of chloro substituents on the aromatic ring. In the case of ortho- position of chlorine atom the rearrangement of chlorine atom to aluminum atom is obviously noticed, in the case of meta- positioned chlorine atom the rearrangement of hydrogen and subsequent loss of original phenol occurs.

Accurate knowing one of the numerous formation mechanisms of PCDD/F could offer a very important piece of data on requirements for waste composition before their thermal processing.

References

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