

THERMOLYSIS OF 2-CHLOROPHENOXYALUMINUM COMPOUNDS FOLLOWED BY MASS SPECTROMETRY

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ABSTRACT

Within the study of the formation of chlorinated dibenzodioxins and dibenzofurans the thermolysis of 2-chlorophenoxy aluminum compounds was followed by mass spectrometry. Compounds were introduced into the ion source directly at sample temperature 550° K. The fragmentation pattern is examined by collision induced dissociation of the selected ion using Mass analysed ion kinetic energy (MIKE) technique.

INTRODUCTION

It has been established that formation of polychlorinated dibenzo-p-dioxins(PCDD) and polychlorinated dibenzofurans(PCDF) in municipal solid waste (MSW) incinerators (MWI) occurs with the participation of fly ash. MWI fly ash promotes the formation of PCDDs/PCDFs from chlorinated aromatic precursors and it has been proved that fly ash can promote "de novo" synthesis from elemental carbon. The presence of

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elemental aluminum in the solid urban waste is relatively high^{1,2} and the HCl concentration in urban waste combustion gases is sufficiently high as well to enable the formation of aluminum chlorides in combustion chamber which could react with aromatic compounds (phenols or chlorophenols) and form volatile organoaluminum compounds, which may act as reactive intermediates at thermal waste processing.

This work is directed toward an understanding of the gas-phase reaction of the phenoxy-aluminum compounds like PCDD/F precursors. It is also a step for understanding of the thermolysis on the fly ash chemisorbed chlorophenols.

Mass fragmentation pattern of selected 2-chlorophenoxy aluminum derivate as model compounds give us a better understanding of formation of hydroxydiphenylethers acting as PCDD precursors from ortho chloro-derivate in comparing with meta-chlorophenoxy aluminum derivate where the formation of diphenylethers, precursors of PCDF is preferred^{3,4}.

EXPERIMENTAL

Samples

Phenoxyaluminum chlorides were prepared with the reaction in the melt between 2-chloro phenol and freshly sublimated $AlCl_3$ at stoichiometric ratio. The samples so prepared were used for direct introducing to ion source.

Analyses

For the MS- analyses AUTOSPEC mass spectrometer (Fisions, VG - Analytical) under EI conditions was used. Fragmentation processes of the selected parent ions were examined by MIKE scann.

RESULTS AND DISCUSSION

From the mass spectrum (see **Figure 1**) which is obtained at 550°K through the direct introduction of Al-2-chlorophenoxyde, a mixture of compounds $(R_nAlCl_{3-n})_m$, ($m = 1,2,$), ($R = ClC_6H_4O$) is evident. The simultaneous intra and intermolecular exchange of ligands⁵ of monomer/dimer are in equilibrium.

The generalized collision - induced dissociation(CID) scheme for the 2-chlorophenoxyaluminum compounds is presented in reactions from **1** to **7**

(R= cyclohexadienon, OArCl = 2-chlorophenoxy, abundance % of ion intensity in parenthesis).

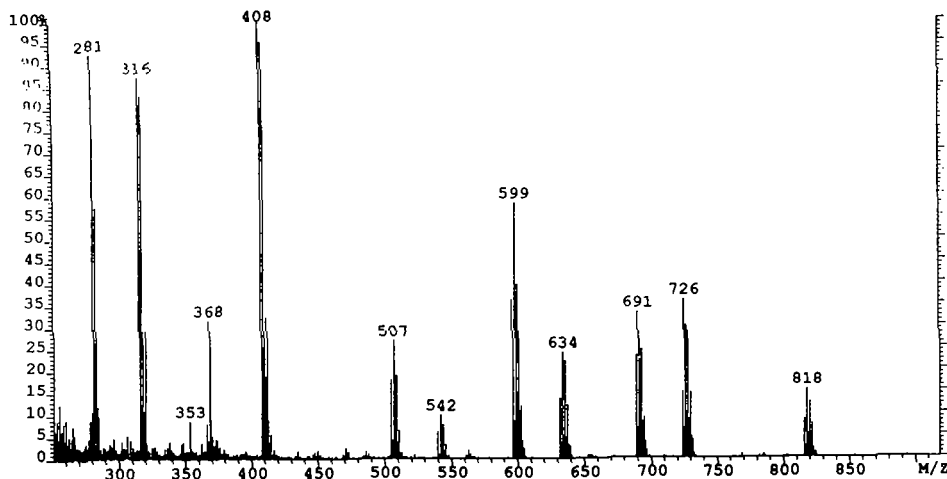
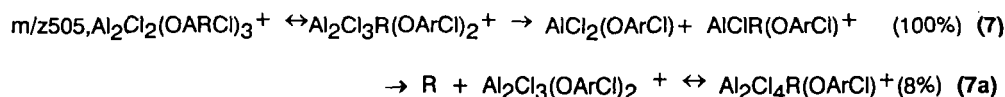
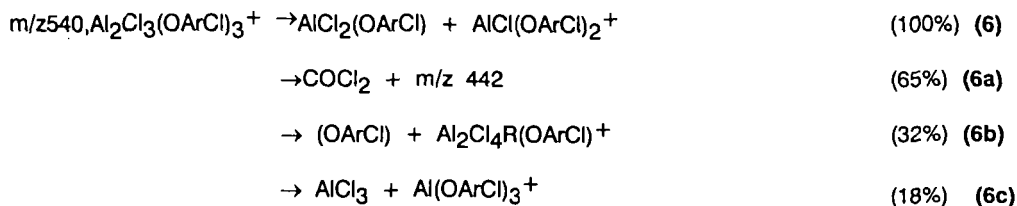
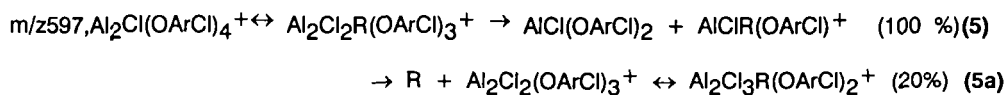
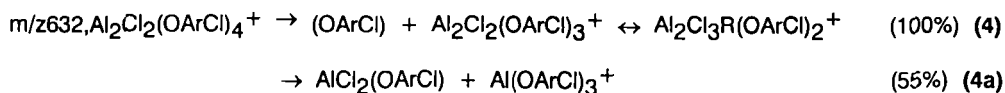
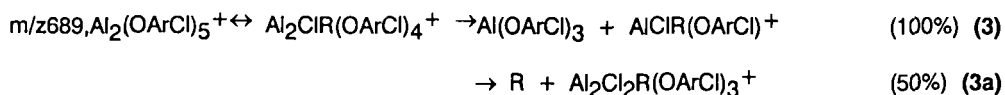
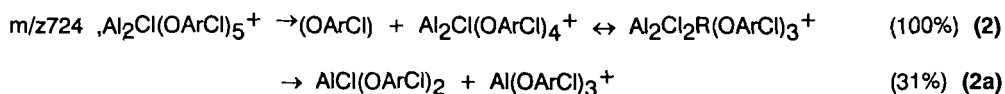
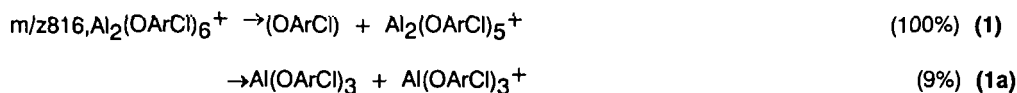


Figure 1: Mass spectra of directly introduced 2-chlorophenoxy aluminum compounds at sample temperature 550°K.



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Fragmentation can include the transfer of the *ortho*-chlorine from the phenol to the aluminum with the simultaneous formation of the cyclohexadienon. With this transformation in the dimer aluminum atom is retained in his tetrahedral environment, whereas in the monomer it finds itself in a trigonal coordination⁵.

From the general revision of fragmentation pattern is the basic and almost frequent loss of 2-chlorophenoxy and cyclohexadienon fragment.

The loss of 2-chlorophenoxy unit before dissociation of dimer to monomer is favored in reaction (1). The CID MIKES of monomer $\text{Al}(\text{OArCl})_3$ is presented in the **figure 2**. Peak m/z 224 corresponding to the loss of 184 mass units from molecular ion is probably originated from the loss of two cyclohexadienon units. The resulting species is probably dibenzodioxin .

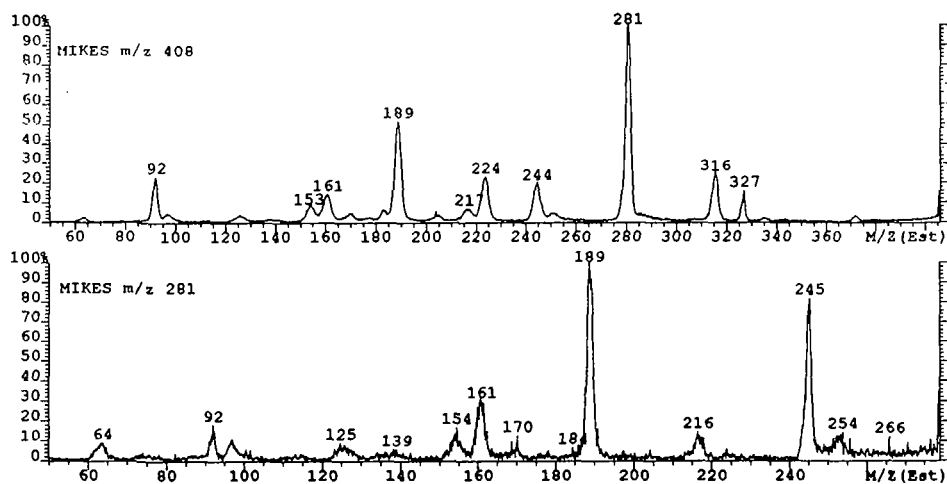


Figure 2: CID MIKE spectrum of the molecular ion of $\text{Al}(\text{III})$ 2-chlorophenoxyde (m/z 408)

Comparison of MIKE spectra of parent ion (m/z 540) under collision and unimolecular conditions evidently show elimination of COCl_2 (daughter ion m/z 442).

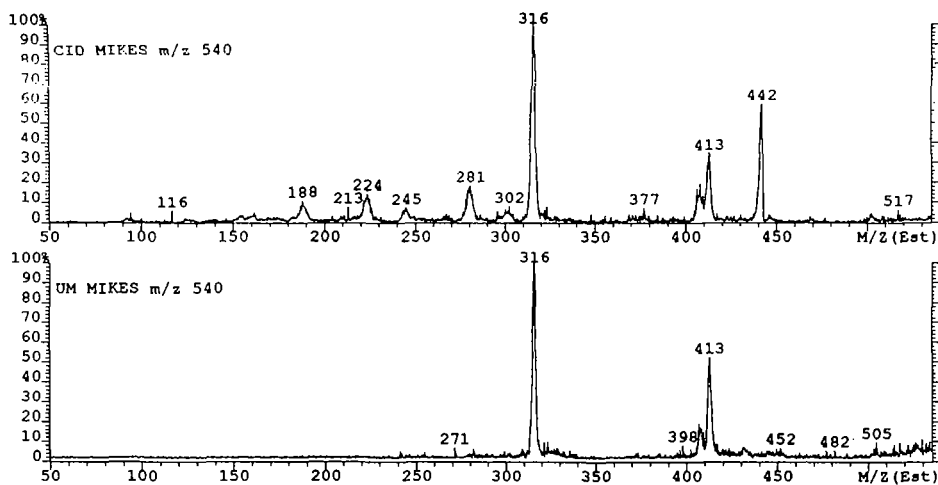


Figure 3: CID and UM MIKES spectra of parent ion (m/z 540)

CONCLUSIONS

It is evident from the mass fragmentations of 2-chlorophenoxyaluminum compounds , that phenoxy and cyclohexadienonic radical is frequently formed. The formation of hydroxydiphenyl ethers is so favored.

References

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