



THERMOLYSIS OF PHENOXYALUMINUM COMPOUNDS AND FORMATION OF PCDD/F AND THEIR PRECURSORS *

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KEYWORDS

Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, mechanism, aluminum, fly ash, incineration

ABSTRACT

Within the study of the formation of chlorinated dioxins and dibenzofurans and their precursors the thermolysis of hexachloroethane over the aluminum melt was investigated. "De novo" synthesis of precursors of PCDD/F was studied in the model system $AlCl_3$ /elemental carbon. Totally chlorinated heterocyclic compounds have been detected parallel with the formation of organochlorine compounds. The possibility of inserting oxygen to aluminum organyls was presented. In order to gain more detailed knowledge of the catalytic behaviour of fly ash the chemistry of thermolysis of phenoxy- and chlorophenoxy aluminum compounds at 300°C with the presence and absence of Al_2O_3 was investigated. Reagent compounds and products of thermolysis were followed by mass spectrometry.

INTRODUCTION

It has been established that the 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 such as chlorinated benzenes and phenols, diphenylethers or PCBs¹⁻⁷.

It also has been proven that fly ash can promote "de novo" synthesis of PCDD/F from elemental carbon⁸⁻¹¹ and acts as a (de)chlorination catalyst. A number of researchers demonstrated that the formation of PCDD/F takes place through the copper or iron catalytic action on Mg-Al-silicate matrix as artificial fly ash¹²⁻¹⁶.

The presence of elemental aluminum in the solid urban waste is relatively high^{17,18}. The HCl concentration in urban waste combustion gases is in the order of magnitude of 10^2 - 10^3 mg/nm³ and therefore sufficiently high to enable the formation of aluminum chlorides in the combustion chamber which could react with aromatic compounds (phenols or chlorophenols) and form volatile organoaluminum compounds¹⁹.

The primary interest of our research was the formation mechanism of PCDD/F and their precursor compounds in the processing of secondary aluminum at the introduction of chlorine in form of hexachloroethane (HCE) into the aluminum melt. The experiments described below investigate the role of aluminum in the formation of PCDD/F and give us a better understanding of the nature of fly ash as catalyst. We believe that a similar catalytic mechanism may be acting on the fly ash surface.

EXPERIMENTAL

Samples

A:) 1300 g of secondary aluminum was inserted in an adapted laboratory oven. Direct introducing of 25.0 g of hexachloroethane over the aluminum melt, flow of the air through the oven and capture of emissions from the oven were controlled. Experiments were carried out at $780 \pm 20^\circ\text{C}$. The air flow was 0.3 to $0.4 \text{ m}^3/\text{h}$. The residence time of gasses in the oven was 9 to 12 s. Thermolysis products that volatilized during the reaction were collected in cooled (with solid CO_2) impingers located downstream outside of the oven. After the hydrolysis, the products were extracted into benzene.

B:) 100.0 mg of elemental carbon (Carbopak C) and 25.0 mg of AlCl_3 were heated in a closed glass vessel at 300°C for 24 hours. After the addition of 0.1 ml of water products were extracted into benzene.

C:) 1 ml of benzene or 1,2-dichlorobenzene was added to 50.0 mg AlCl_3 . Oxygen was purged slowly through the sample at the room temperature for 30 minutes.

D:) The reaction of the fourth experiment was conducted in a tubular quartz reactor (length 500 mm, internal diameter 20 mm), packed with reactants in a ceramic vessel, which was placed in the center of the reactor. Reactants were prepared from 10.0 g of adsorbent Al_2O_3 (activity 1) and 0.564 g of phenol. The mixture was gently heated to the temperature of phenol melting point. Powdered AlCl_3 was added to the cooled mixture. After homogenization the sample was inserted in the ceramic vessel. The experiment was carried out for 30 minutes at $300 \pm 5^\circ\text{C}$ in a stream of 10 ml air/ min. Volatile reaction products were retained on adsorbent SiO_2 and analyzed separately. Reaction products retaining on adsorbent Al_2O_3 after 30 minutes of heating at 300°C were removed from the oven. After hydrolysis at $\text{pH}=2-3$, products were extracted into benzene and analyzed separately.

E:)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 according to the reaction /1/.



The samples so prepared were used for the thermolysis experiment and for direct introducing into the ion source. The thermolysis was performed in the closed vessel for 30 min. at 300°C . For GC/MSD analysis we prepared after hydrolysis at $\text{pH}=2-3$ the benzene extract of products. The same preparation method as described above was used for the second set of experiment. After the preparation, the products (phenoxyaluminum compounds) were diluted with hexane and refluxed at the boiling point of hexane for one hour or let stand in a closed vessel in hexane for more than three weeks, and then the sample was analyzed by GC/MSD without hydrolysis.

Analyses

VC AUTOSPEC Q-FISONS and HP -5971 GC/MSD instruments equipped with 30 m SPB-5 column. were used for the MS- analyses.

RESULTS AND DISCUSSION

A:) From the first experiment it is evident that the thermolysis of HCE as a " precursor" compound over aluminum melt was carried out primarily with the process of dechlorination and further cyclisation of radicals to the stable structures . Due to the practical absence of the hydrogen in the system, the formation of totally chlorinated compounds is favored (see **figure1**). So relatively 94% of hexachlorobenzene , 4% of octachlorostirene and 1% of decachlorobiphenyl , and less then 1% other compounds were determined . Beside organochloric compounds, AlCl₃ is the main product. It can be formed with reactions²⁰:

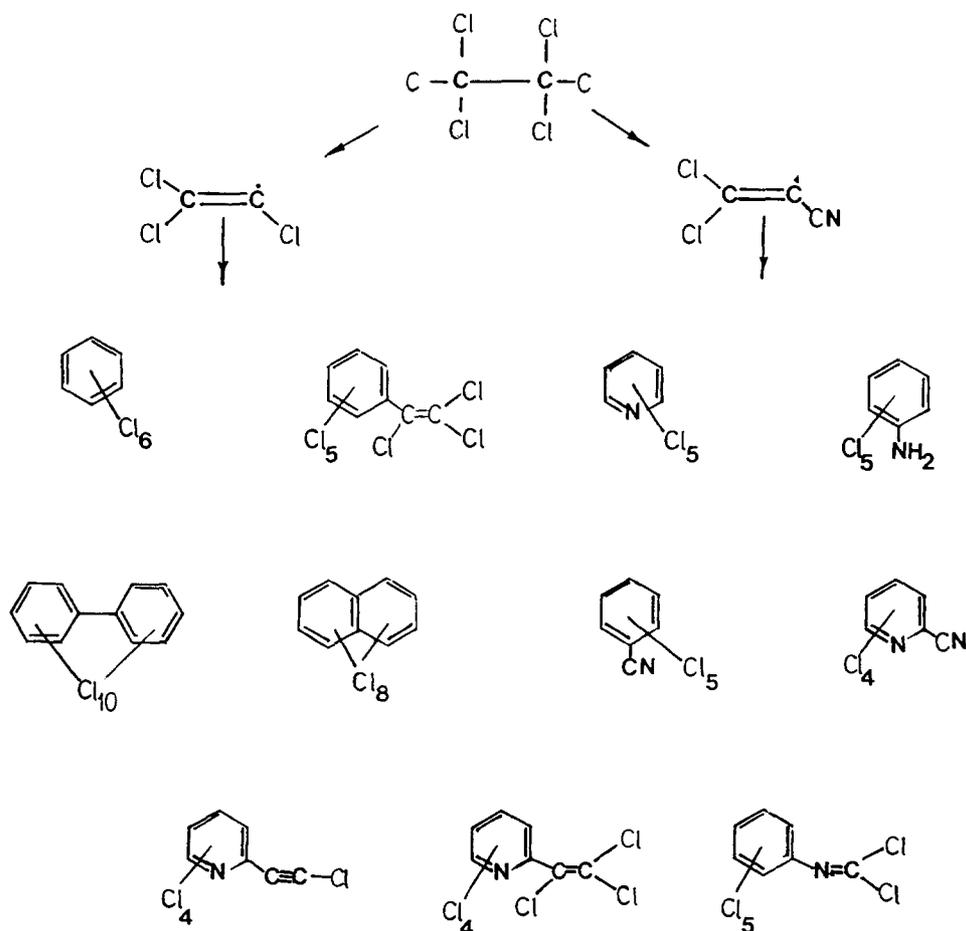
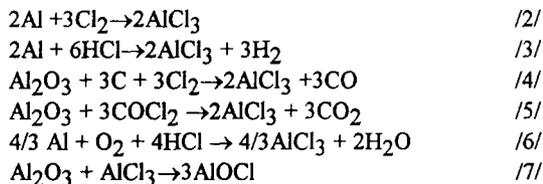


Figure 1: Formation of chlorinated cyclic and heterocyclic compounds

Totally chlorinated heterocyclic compounds have been detected parallelly with the formation of organochloric compounds. A source of nitrogen is probably air or nitrogen compounds from secondary aluminum. 1,1,2-trichloro-acrylonitrile as a starting compound for heterocyclic compounds has been detected.

B:) Compounds detected in experiment B as "de novo" synthesis are the same and of the same relative ratios as at experiment A. Hexachlorethane, hexachlorobenzene, octachlorostirene, and pentachloropyridine from heterocyclic compounds have been detected as the main product. We believe that the formation mechanism of organochloric and heterocyclic organochloric compounds is the same for both experiments.

C:) Aluminum organyls are strong Lewis acids. The multiple insertion of the ethylene unit into the Al-C bond of tris(alkyl)aluminum compounds and the insertion of oxygen are possible according to the scheme / 8,9/19.



In the experiment C the following products were detected: phenol and biphenyl from benzene as reactant and 3,4-dichlorophenol and tetrachlorobiphenyls from 1,2-dichlorobenzene respectively.

D:) Besides phenol, chlorophenols were the main products of reactions in the experiment D (mostly monochlorophenols, the ratio of others was decreased down to pentachlorophenol). Also other compounds were detected whose basic structures without isomeric compounds are presented in **figure 2** Only hexachlorobenzene without lower chlorinated homologues was detected. The presence of hexachlorobenzene without lower chlorinated benzenes suggests that a radical chlorination reaction may occur. Another possibility is the formation of hexachlorobenzene at a multiple insertion of the ethylene unit into the Al-C bond and subsequent chlorinating. The catalytic function of aluminum is incorporated. Furthermore, gas phase free radical chlorination is also likely to occur, but the electrophilic aromatic chloro-substitution reaction is predominant.

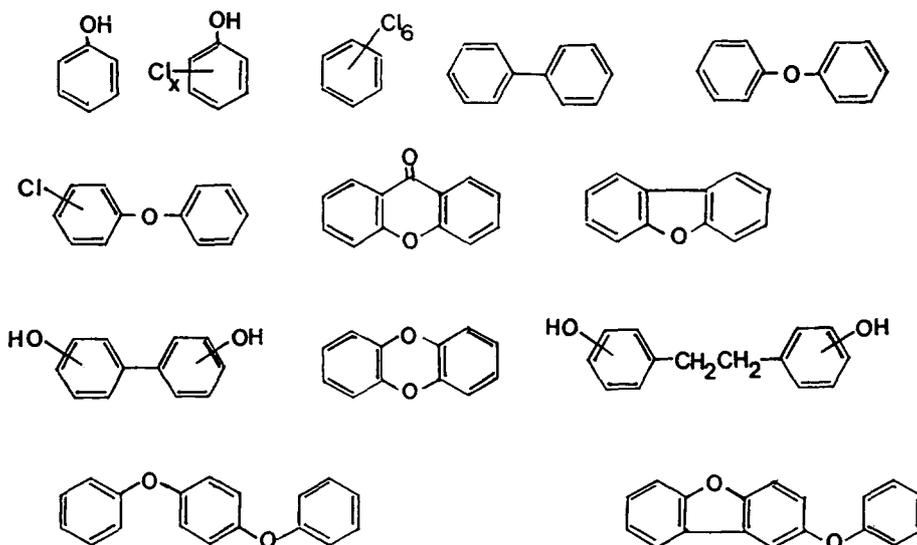


Figure 2: Volatile reaction products of experiment D.

Structures of undesorbed compounds retained on Al_2O_3 without isomeric compounds are presented in the **figure 3**. It is evident that most of the compounds are those with a hydroxyl or carboxyl functional group. Both functional groups participated in the link Al-O before hydrolysis. We believe that in real incineration conditions the reaction // or similar is responsible for the formation of reactive organoaluminum compounds. For aluminum(III)phenoxyde the melting point with decomposition is 264°C ²¹. There exist no literature data for other similar compounds, for instance aluminum adducts with hydroxydiphenylethers, dihydroxybenzene or hydroxybenzoic acid and their chlorinated analogs. Their thermolysis is in the temperature range from $250\text{-}350^\circ\text{C}$, which is also the optimum temperature range for the formation of PCDD/F.

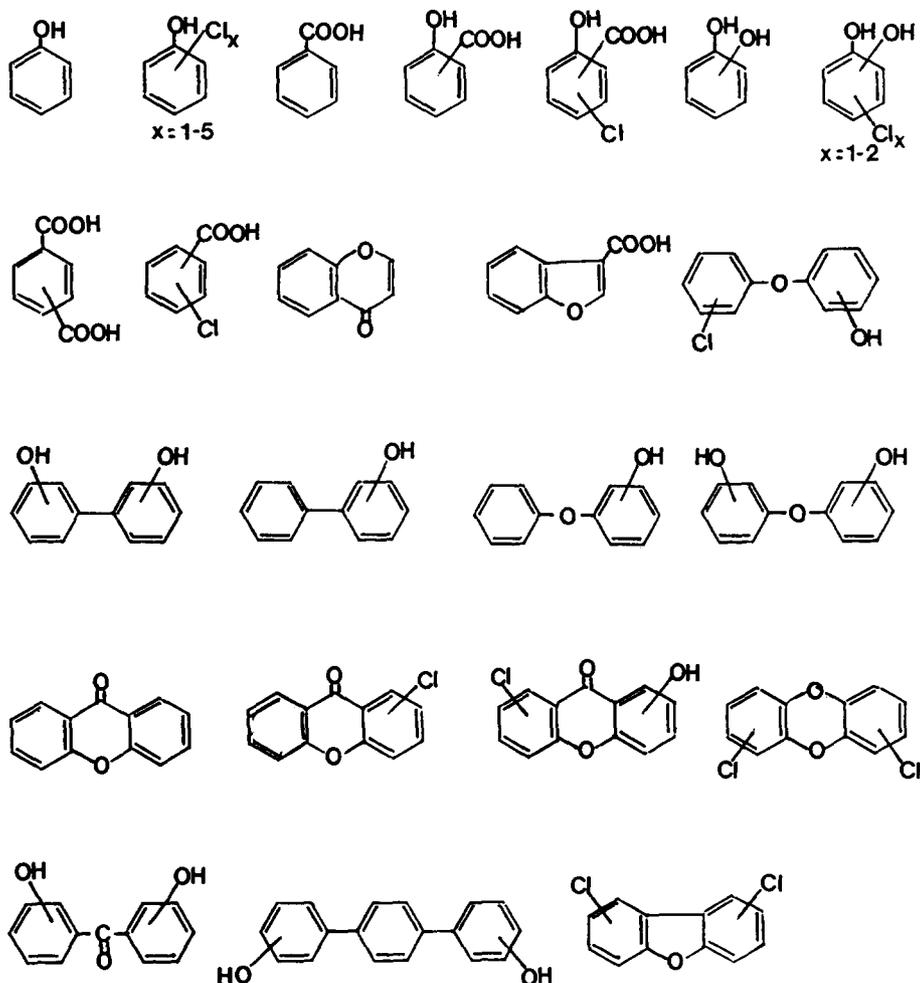


Figure 3: Reaction products of experiment D retaining on Al_2O_3 .

E:) It is evident from the mass spectrum (see **Figure 4**) that through the direct introduction of Al (III) phenoxide into the ion source we obtained a mixture of compounds $(\text{R}_n\text{AlCl}_{3-n})_m$, ($m = 1, 2, 3$), ($\text{R} = \text{C}_6\text{H}_5\text{O}$). Due to simultaneous intra and intermolecular exchange of ligands we found an equilibrium of monomer/dimer/trimer ²².

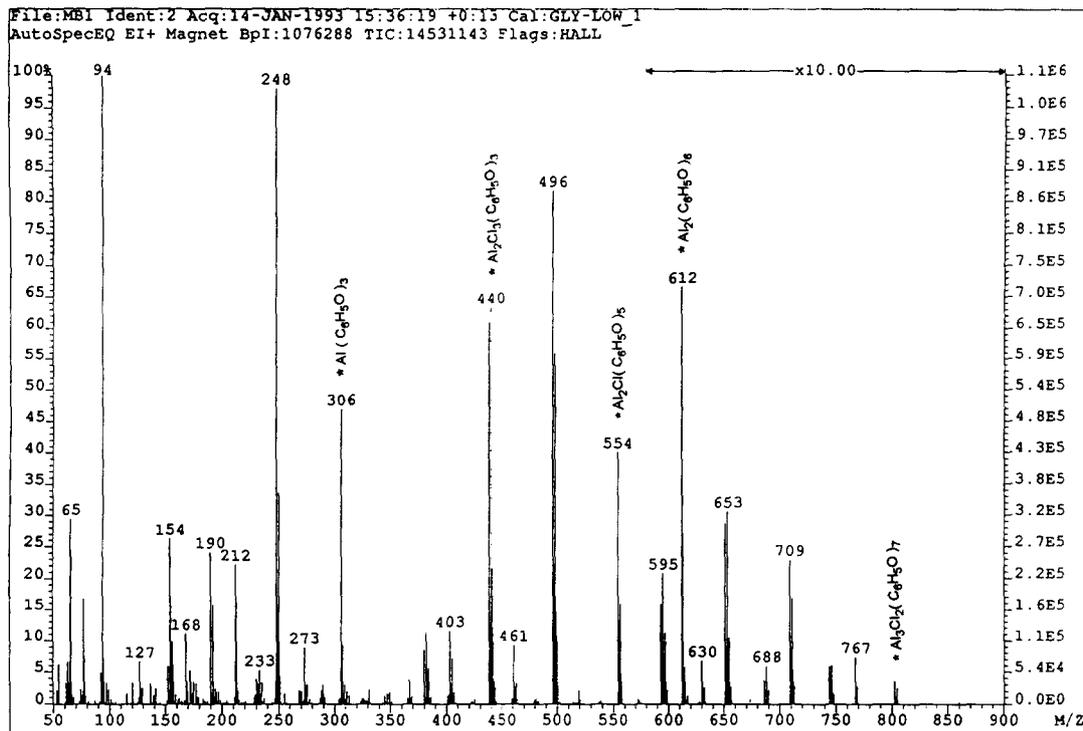


Figure 4: Mass spectra of directly introduced phenoxyaluminum chlorides at sample temperature 400 °C. Compounds in equilibrium are presented.

So in the experiment with phenol we have detected mass fragments which confirm an occurrence for instance: of trimers $\text{Al}_3\text{Cl}_2(\text{C}_6\text{H}_5\text{O})_7$., dimers $\text{Al}_2(\text{C}_6\text{H}_5\text{O})_6$, $\text{Al}_2\text{Cl}_3(\text{C}_6\text{H}_5\text{O})_3$., 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.

The role of mass spectrometry in establishing a fairly definitive mechanism for the thermal decomposition of compounds is quite adequate. The interesting fragmentation pattern is followed by unimolecular or collision induced dissociation of the ion m/e 316 using MIKES techniques (**Figure 5**).

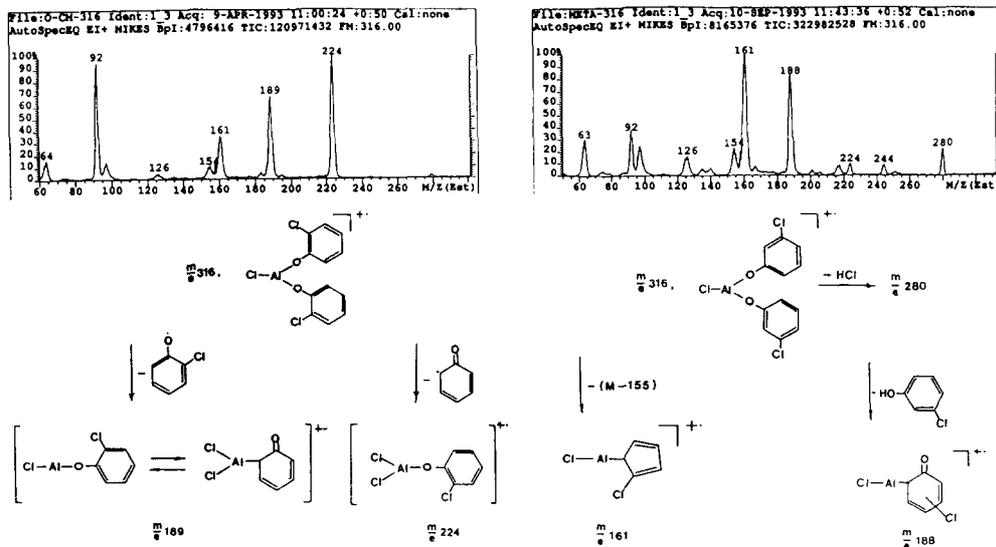


Figure 5: The fragmentation patterns differ substantially and depend quite strongly upon the position of chloro substituents on the aromatic ring. In the case of ortho- position of chlorine atom the rearrangement of chlorine atom to the aluminum atom is obviously noticed, and in the case of meta- positioned chlorine atom the rearrangement of hydrogen and subsequent loss of original phenol occurs.

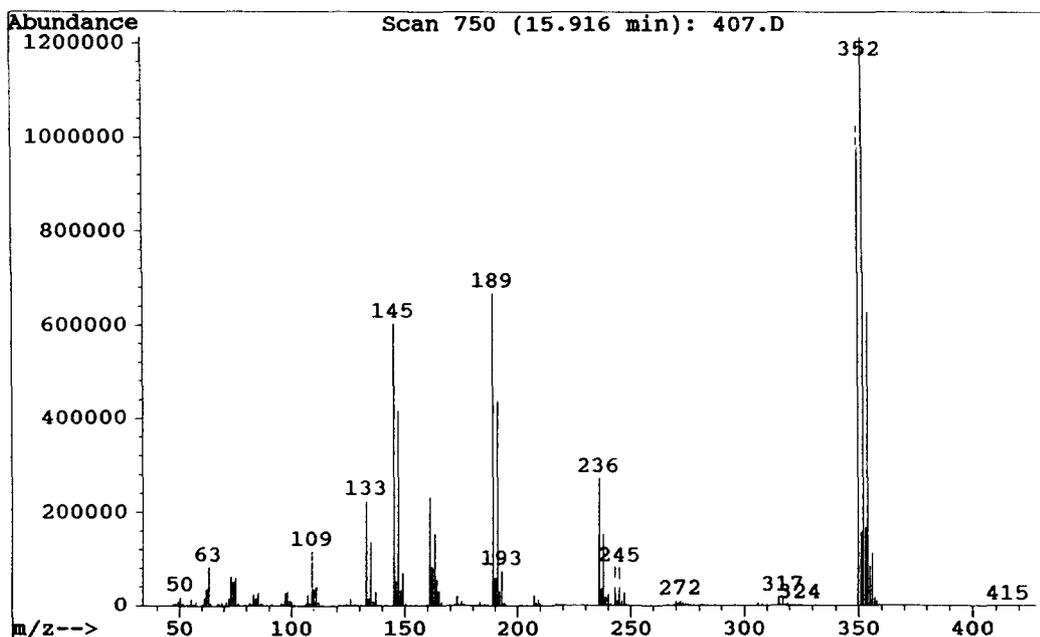


Figure 6: The mass spectrum of di-2,4-dichlorophenoxycarbonate. Mass fragment m/e 243 could originate from expulsion of CO_2 , CO and Cl . The identity of carbonate was not confirmed by spectrum of standard compound.

Interesting results were obtained by thermic treatment of phenoxyaluminum compounds at low temperatures. Unimolecular transformations were carried out in a cage of solvent hexane. Al-tris-(2,4-dichlorophenoxyde) in hexane is transformed spontaneously into the main product di-2,4-dichlorophenoxy carbonate (the mass spectrum is given in the figure 6).

Al-tris-(3-chlorophenoxyde) is also transformed into di-3-chlorophenoxy carbonate, which gives exclusively isomeric chlorinated diphenylethers, precursors of PCDFs at the temperature of thermolysis 300°C with the expulsion of CO₂. Audier and Morton²³ have shown that the expulsion of CO₂ from alkyl phenyl carbonate takes place by a C-O bond rupture and displacement of the CO₂ in the ion-neutral complex by the phenoxy radical. The reaction mechanism of transformation Al-tris-2-chlorophenoxyde may be different. The products we have detected are isomeric chlorinated hydroxydiphenylethers, precursors of PCDDs. Intermediary formed carbonate was not detected. Thermic transformation of Al-tris-(4-chlorophenoxyde) at higher temperature was carried out also over the carbonate.

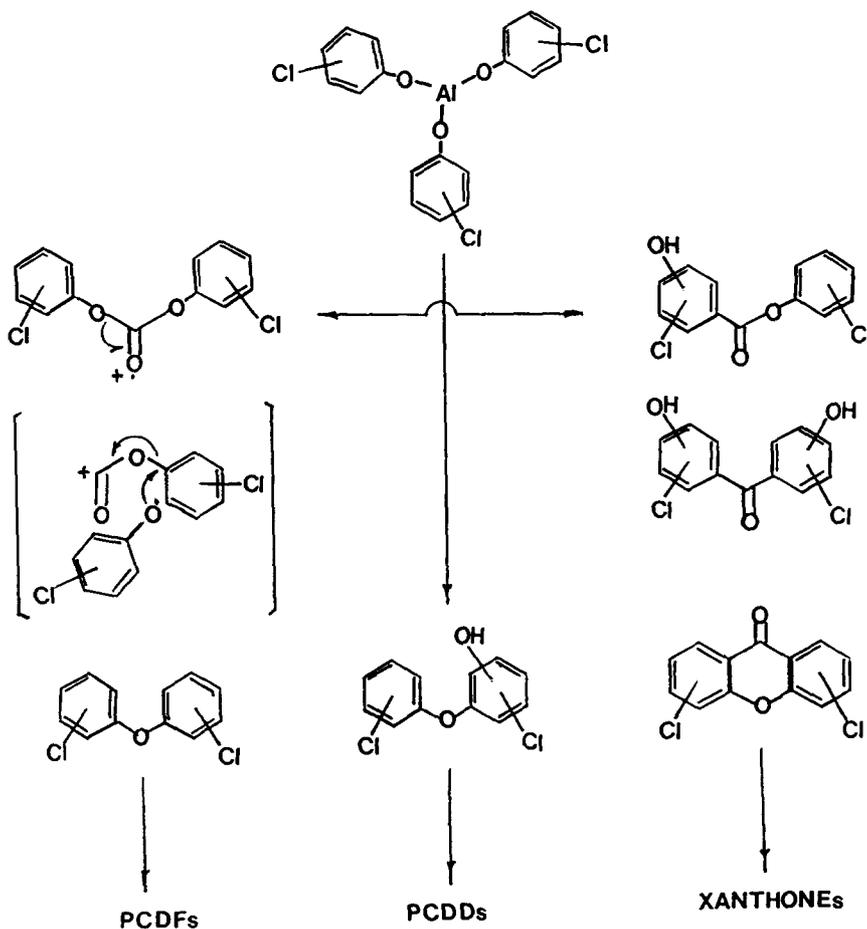


Figure 7: We believe that carbonates are further isomerised under catalytic action of Al₂O₃ (or fly ash in real conditions) as is shown from products formed in experiment D.

We can then assume that the geometry of the activated transition state is influenced by the position of the chlorine atom on the benzene ring. The ion neutral complex may decompose under given energetic conditions, the system tends to stabilize by forming different types of intermediates by unimolecular transformation.

CONCLUSIONS

Several conclusions can be drawn concerning the influence of aluminum on the formation mechanism of PCDD/F and their precursors. It is confirmed by our experiments that the formation mechanism from "precursors" HCE and from "de novo" synthesis organochlorine compounds and organochlorine heterocyclic compounds is the same in both cases as Froese and Hutzinger had expected²⁴.

The insertion of oxygen can take place into the Al-C bond of aluminum organyls. The thermic transformation of phenoxy aluminum compounds may include the formation of intermediary phenoxycarbonate. Further thermic conversion of carbonates yields precursor compounds of PCDD/Fs mainly diphenylethers, hydroxydiphenylethers and phenyl esters of hydroxybenzoic acid. These compounds are further converted to the more stable products like dibenzofurans, dibenzodioxins or xanthenes. Similar products could also be formed by direct dissociation of phenoxyaluminum compounds. Born et al.²⁵ reported on the fly ash catalyzed combustion of 2-chlorophenol. They showed that at relatively low temperatures of around 350 °C a large part of 2-chlorophenol is transformed into a typical combustion product like CO₂. In contrast, the principal product in homogeneous phenol oxidation is CO, which is stable under the present conditions. The catalytic destruction of 2-chlorophenol to CO₂ on the surface of fly ash is in accordance with our experiments.

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

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