

Oxychlorination and Combustion of Propene on Fly-Ash. Formation of Chlorinated Benzenes, Dibenzodioxins and Dibenzofurans

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Abstract

Heterogenous reactions of propene on fly-ash in the presence of air and hydrochloric acid between 300-580 °C have been investigated. At mild conditions the formation of polychlorinated C₁, C₂, and C₃ species was noticed. At the high temperature end of this study substantial amounts of polychlorinated benzenes, dibenzodioxins and mono- and dibenzofurans are observed. This is in contrast with similar experiments using ethene instead of propene. Clearly fly ash behaves not only as a potent catalyst for deep oxidation and chlorination, but accelerates condensation reactions of simple short chain olefins.

Introduction

In general the formation of PCBz, PCDD and PCDF in combustion processes is a well established phenomenon. Any combination of carbon, chlorine under flame conditions can lead to minute but detectable amounts of these organochlorine compounds. The mechanisms of formation involve presumably a cascade of primarily homogenous free-radical gas-phase reactions in the direct post-flame zone. Of particular (public) concern is the production during the thermal destruction of waste in Municipal Waste Incinerators. The inorganic fraction of the waste stream is partially converted into fly-ash which ends in the flue gas. Especially the conditions present in an electrostatic precipitator, designed to remove the fly-ash, appear to be chemically ideal¹. In this environment remaining organic material together with hydrochloric acid is catalytically (partially) converted into a large variety of new halogenated compounds. Several laboratory studies have dealt with the question of the nature of the precursors involved. Obvious structures like toluene² or phenol³ in the presence of HCl and fly-ash can act as a building blocks in PCDD/DF

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formation.

In the past we have studied the behavior of ethene⁴ under various relevant fly-ash conditions. It was shown that fly-ash was a potent catalyst to convert ethene into chlorinated C₁, and C₂ species. Already at 250 °C the reaction sets in with the formation of 1,2-dichloroethane comparable to a Cu catalyzed oxychlorination process. At more elevated temperatures also complete oxidation to CO and CO₂ was observed. A kinetic analysis revealed that both chlorination and oxidation routes stem from the same surface-bound intermediate.

In order to gain more detailed knowledge of the catalytic behavior of fly-ash, the chemistry of the mixture propene/HCl/H₂O/O₂ in the presence of fly-ash was investigated.

Experimental

A conventional flow system operating at atmospheric pressure equipped with a tubular quartz flow reactor of 10 ml was used. A fixed bed of fly-ash (2-3 g) was situated in the middle part of the reactor section by means of quartz wool. The fly-ash used in this study stems from a regular MWI. Once installed, the fly-ash was pretreated in a gentle stream of air at 550 °C to remove the remaining organics and carbon particulates until no CO and CO₂ in the exit gas could be detected. Gaseous flows (N₂, O₂, and propene) were regulated by electronic mass flow controllers. Concentrated HCl was introduced into the gas stream by a motor driven syringe pump, the liquid stream was allowed to evaporize in the preheated inlet tube before entering the reaction zone. The outlet tube of the reactor was wrapped with heating tape to prevent condensation before the sampling point. The hydrochloric acid in the effluent gas was removed by an alkaline trap and the organic contents subsequently analyzed by GC. In some cases the effluent gas was trapped in a cold alkali/pentane mixture to allow GC and GCMS analyses of the higher boiling compounds. These samples were also quantitatively analyzed for PCDDs and PCDFs using a HP-5890 equipped with a CP-Sil-5CB column and a HP 5970 MSD in the SIM mode .

Results and Discussion

In table 1 representative examples are given for the product distribution between 350 and 548 °C. With the fly ash bed used a propene conversion of 34 % was achieved at the highest reaction temperatures. It appears that the product pattern is quite similar when using ethene instead of propene. The main product at low reaction temperature is the addition of Cl₂ to the double bond forming 1,2 dichloropropane. Free chlorine gas may be generated through a Deacon type reaction ($2\text{HCl} + 0.5 \text{O}_2 \rightleftharpoons \text{H}_2\text{O} + \text{Cl}_2$). With increasing temperature this compound is thermally instable; consecutive loss of HCl and rechlorination results in the apparently more stable Z and E isomers of 1,3 dichloropropene. Moreover, deep oxidation as measured by the amounts of CO and CO₂ gains relatively

Table 1. Oxychlorination and combustion of propene on fly ash^a

Temp. °C	350	400	448	473	499	548
Time (s) ^b	1.3	1.2	1.1	1.1	1.0	1.0
Propene ^a	2.92	2.85	2.84	1.5	2.87	3.05
Products ^c						
CCl ₄	3.2	3.1	3.3	51.5	7.6	16.6
C ₂ HCl ₃	1.1	1.9	1.9	2.2	4.3	15.2
C ₂ Cl ₄	n.d.	1.0	3.0	2.9	7.5	39.0
C ₃ H ₆ Cl ₂ ^d	352.7	319.0	147.4	69.2	33.3	32.5
C ₃ H ₄ Cl ₂ ^e	0.9	2.5	3.2	4.6	8.3	24.4
C ₃ H ₄ Cl ₂ ^f	1.0	11.0	23.9	56.5	115.4	292.3
C ₃ H ₄ Cl ₂ ^g	0.7	7.2	16.1	40.7	81.7	227.5
C ₃ H ₃ Cl ₃	n.d.	n.d.	n.d.	0.5	3.4	29.2
C ₆ H ₆	1.6	1.7	1.9	1.9	4.0	59.0
C ₆ H ₅ Cl	9.0	5.5	5.8	2.5	4.8	15.2
CO	0.0	0.0	180.0	249.3	200.0	526.7
CO ₂	100.0	59.2	42.2	27.9	100.0	34.0

a: Intake in mmol/h O₂: 26.1, N₂: 110.7, HCl: 14.2, H₂O: 50.2 b: based on free volume c: in µmol/hr d: 1,2 dichloropropane e: 2,3 dichloropropane f: 1,3 dichloropropane (Z) g: 1,3 dichloropropane (E)

Table 2. Formation^a of chlorinated benzenes, benzofurans (BF), dibenzodioxines (DD) and dibenzfurans (DF) during the oxychlorination of propene at 576 °C on fly ash in µmol/h^b,

C ₆ H ₆	10.2	BF ^d	0.57	Cl ₂ DD ^{e,gh}	0.005	ClDF ^{e,hi}	0.012
C ₆ H ₅ Cl	6.9	ClBF	1.56	Cl ₃ DD ^{e,gh}	0.009	Cl ₂ DF ^{e,f}	0.05
C ₆ H ₄ Cl ₂ ^c	6.3	Cl ₂ BF ^e	4.55	Cl ₄ DD ⁱ	0.11	Cl ₃ DF ^{e,hi}	0.06
C ₆ H ₃ Cl ₃ ^c	15.9	Cl ₃ BF ^e	2.47	Cl ₅ DD ^{e,gh}	0.057	Cl ₄ DF ^{e,hi}	0.05
C ₆ H ₂ Cl ₄ ^c	7.5	Cl ₄ BF ^e	1.72			Cl ₅ DF ^{e,hi}	0.07
C ₆ HCl ₅	4.0	Cl ₅ BF ^e	0.91			Cl ₆ DF ^{e,hi}	0.07
C ₆ Cl ₆	1.7	Cl ₆ BF ^e	0.20				

a: See table 1, footnote a, propene 1.67 mmol/h b: quantification based on GC analysis c: sum of all possible and observed isomers e: sum of the observed congeners h: semi-quantification based on MS-response relative to Cl₄DD or Cl₂DF i: sum of 1378+ 1379 j: sum of 12468/12479+12368+12478

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in importance. It should be stressed that the observed chlorinated products are the result of the catalytic behavior of fly ash. Under comparable conditions but in the absence of a fly ash bed a low degree of homogenous propene oxidation was observed at 590 °C, which increases to 38 % at 700 °C. Since the catalytic features of fly ash are similar for short chain olefins and accepting Cu (or Fe) are the principal reactive elements on the surface, an attempt was made to inhibit this catalytic activity with NH₃ type compounds. A mixture of 2.3 fly ash and 0.4 NH₄Cl was applied with ethene as the reactant. Even in the absence of added hydrochloric acid, substantial amounts of chlorinated compounds could be observed at 400 °C. This can be explained by considering the equilibrium

$(\text{NH}_4\text{Cl})_g \rightleftharpoons (\text{NH}_3)_g + (\text{HCl})_g$ at that given temperature. It can be concluded based on the experimental results that HCl is retained on the fly ash while the NH₃ is likely to be purged by the carrier gas, making NH₄Cl not suitable to poison the fly ash bed. The poor retention was further substantiated by first saturating the bed with NH₃ gas at room temperature and then rapidly returning to the reaction temperature of 400 °C. Essentially no decrease in catalytic reactivity could be noticed.

Next a fresh fly ash bed was applied. After conditioning and maintaining a minimum temperature of 470 °C throughout, the effluent gas was now also analyzed for high boiling compounds. A representative product distribution is given in table 2. It should be noted that the propene conversion is essentially 100 % at this specific example while other volatile (chlorinated) C₂ and C₃ compounds are still present. Since the exit gas is trapped in an alkali/pentane mixture, the aqueous phase was analyzed for the presence of chlorinated phenols. These compounds were not found which is in accord with earlier observations that chlorinated phenols, if formed under the reaction conditions, are rapidly oxidized on the fly ash surface. After this experiment the fly ash bed was removed and extracted for a prolonged period (24 h) with toluene. In the liquid extract no additional relevant compounds could be identified. From table 2 it can be inferred that a wide range of chlorinated PCDD/BF are formed. Interestingly, PCDFs (>PCDDs) are also found. When using phenol (or toluene) as a reactant, this category of compounds was always absent in laboratory experiments⁵. It might well be that condensation reactions to yield PCDF are a result of consecutive additions of C₃ units on the fly ash surface at relatively high temperatures.

References

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