Formation Of Intermediates During Thermal Decomposition Of 1,2-Dichlorobenzene

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Abstract

The formation of products of incomplete combustion (PICs) during flameless thermal decomposition of chlorinated compounds like 1,2-dichlorobenzene has been investigated as a function of temperature, oxygene content and residence time. For various conditions a survey of the occurring intermediates is given. The results obtained are showing the crucial influence of the combustion parameter investigated.

Introduction

During the last years most of the investigations performed on incineration of chlorinated hydrocarbons have been focused on special compounds of main interest, such as PCDD/Fs (1),(2). As reaction pathways of chlorinated hydrocarbons are not yet completely understood, it seems to be necessary to study the formation of intermediates under well defined, reproducible conditions like: temperature, oxygen content and residence time.
In this work a wide range of intermediates has been identified during flameless decomposition of 1,2-dichlorobenzene and their occurrance has been investigated under various experimental conditions for gaining a better understanding of reaction pathways.

Experimental

1,2-Dichlorobenzene vapor is mixed with the main flow of air/nitrogene in a mixing chamber to provide a homogeneous distribution. The concentration of 1,2-dichlorobenzene is measured continuously by FID. The gas mixture then passes the decomposition chamber which is heated from outside.
The sampling system consists of three impingers filled with water to absorb the reaction products HCl and H_2O, followed by $CaCl_2$ drying tube. Organic compounds were finally absorbed in n-hexane at a temperature of -70°C.
The absorbing solution could directly be applied to measuring the concentration of several chlorinated compounds by GC/ECD and GC/FID. After evaporating hexane to a small volume reaction products were identified by GC/MS.

Results and Discussion

During flameless thermal decomposition of 1,2-dichlorobenzene, a wide range of chlorinated compounds as well as some non-chlorinated substances can be identified as decomposition products of incomplete combustion (PIC) which are listed in table 1. Three sets of data are obtained by systematic variation of: residence time (range: t_v=1.9-5s, standard t_v=2.7s), oxygen excess (range: corresponding λ=1-10, standard λ=2.6) and temperature (range: T=850-1020°C, standard T=900°C).

The results achieved, which are confirmed by Young et al. (3), are clearly showing the influence of combustion parameter on the formation of PICs: at large oxygene excess, long residence time and high temperature only a few reaction products can be identified. Furthermore some PICs like chlorinated cyclopentadiens and benzenes are only found at certain conditions (λ=5, t_v=2.7s and T=900°C).

The degree of PIC formation can be described as the results of reactions which are determined by interacting combustion parameter. Figure 1 shows the effect of temperature and oxygene content on the formation of monochlorobenzene which was measured quantitatively by GC/FID. When the degree of formation is plotted against temperature, typical curves are obtained for intermediates which are characterized by substance- and temperature-specific maxima. Decreasing oxygene content from large excess to stochiometric conditions makes the formation degree maximum of an intermediate move to higher temperatures. Under stochiometric conditions a temperature of 1000°C is not sufficient to decompose monochlorobenzene completely, whereas with increasing oxygene content (corresponding to λ=2.5 and higher values) the intermediate could not be measured any more at 1000°C.

Almost the same effect shows the variation of residence time: the formation degree maximum will move towards higher temperatures with decreasing residence time.

For different chlorinated benzene intermediates (mono- to hexachlorobenzene) the formation degree is displayed as a function of temperature in figure 2. At 850°C, residence time 2.7s and λ=2.5, formation of monochlorobenzene reaches its maximum whereas formation of tetra-, penta- and hexachlorobenzene has not yet started.

Additionally at 1020°C monochlorobenzene is not detectable any more in the exhaust gas and the higher chlorinated benzenes are already degrading but still detectable.

It is interesting to see, that the formation degree maxima of different intermediates are shifted towards higher temperatures with increasing degree of chlorination (from mono- to hexachlorobenzene). This makes clear that not all of the PICs listed in table 1 can be measured in the exhaust gas under any conditions investigated, as formation of some PICs may not have started yet whereas other intermediates are already completely degraded. Furthermore some of the intermediates reported only can be observed at flameless conditions when the concentration of free OH-radicals (which act as scavengers) is relatively low.

The characteristic sequence of formation degree maxima at increasing temperature, observed for mono- to hexachlorobenzene intermediates, reflects a part of the reaction pathway. After dechlorination of 1,2-dichlorobenzene, the chlorine-radicals formed are partially consumed by recombination, causing the inhibition of CO/CO_2-oxidation (4). The rest of the free Cl-radicals finally react with decomposition fragments (like benzene) resulting in the formation of PICs with

increasing degree of chlorination.

As a result of this work it can be shown that for intermediates the degree of formation depends on combustion conditions. On the other hand, the fundamentals of decomposition mechanism look like to be always the same.

References

(1) Ballschmiter, K.; Braunmiller, F.; Niemczyk, R.; Swerev, M.
Chemosphere 17 (1988) 6, pp 995-1005.

(2) Olie, K.; v.d. Berg, M.; Hutzinger, O.
Chemosphere 12 (1983) 4/5, pp 627-36.

(3) Young, C.M.; Voorhees, K.J.
Preprints of Papers - American Chemical Society, Division of Fuel Chemistry 34 (1989) 1, pp 280-87.

(4) Chang, W.-D.; Senkan, S.M.
Environ. Sci. Technol. 23 (1989) 4, pp 442-50.

Table 1: decomposition products of 1,2-dichlorobenzene

	COMBUSTION CONDITIONS										
	standard conditions: t=2.7s;T=900°C				standard conditions: λ=2.5;T=900°C			standard conditions: λ=2.5;t=2.7s			
IDENTIFIED INTERMEDIATES	OXYGEN EXCESS (λ)				RESIDENCE TIME(s)			TEMPERATURE(°C)			
	10	5	2.5	1	1.9	2.7	5	850	910	970	1020
Hexachlorbutadiene		X								X	X
Tetrachlorcyclopentadiene		X								X	
Pentachlorcyclopentadiene		X								X	
Hexachlorcyclopentadiene		X								X	
Chlorobenzene	X	X	X	X	X	X	X	X	X	X	X
Dichlorobenzene	X	X	X	X	X	X	X	X	X	X	X
Trichlorobenzene		X	X	X	X	X		X	X	X	
Tetrachlorobenzene		X	X	X	X	X		X	X	X	X
Pentachlorobenzene		X	X			X		X	X	X	X
Hexachlorobenzene		X	X			X		X	X	X	X
Dichlorophenol	X	X	X	X	X	X		X	X		
Trichlorophenol		X		X							
Tetrachlorophenol		X									
Naphthalene	X	X	X	X	X	X	X	X	X	X	X
Chloronaphthalene	X	X	X	X	X	X	X	X	X	X	
Dichloronaphthalene	X	X	X	X	X	X	X	X	X	X	
Trichloronaphthalene	X	X	X	X	X	X	X	X	X	X	
Tetrachloronaphthalene		X	X	X	X	X		X	X	X	
Biphenyl			X	X	X	X		X	X		
Chlorobiphenyl				X							
Dichlorobiphenyl			X	X		X		X	X		
Trichlorobiphenyl			X	X	X	X		X	X		
Tetrachlorobiphenyl			X	X		X		X	X	X	
Acenaphthene			X	X	X	X		X	X		
Anthracene	X	X	X	X	X	X		X	X	X	X
Fluoranthene	X	X	X	X	X	X	X	X	X	X	
Pyrene	X	X	X	X	X	X	X	X	X	X	X

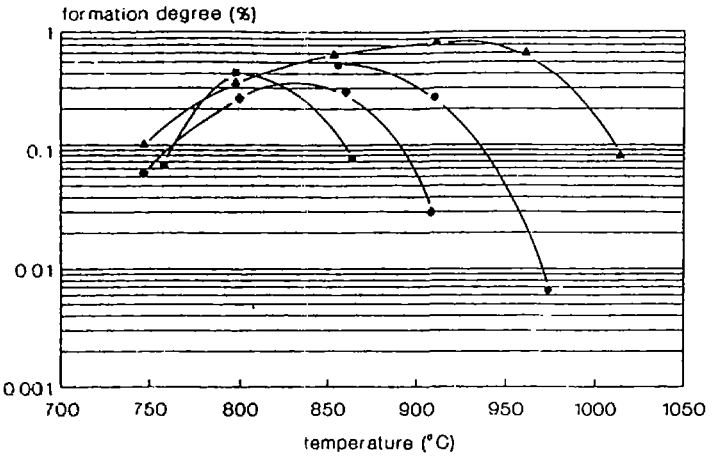

Figure 1: formation degrees of monochlorobenzene under varied oxygen content (▲ = λ 1; ● = λ 2.5; ◆ = λ 5; ■ = λ 10) vs temperature conditions: t_v=2.7s

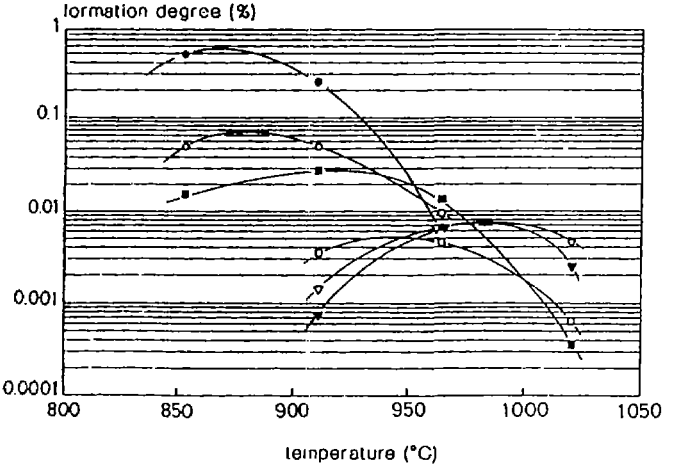

Figure 2: formation degrees of monochlorobenzene (●),1,3-dichlorobenzene (○),1,2,4-trichlorobenzene (■),1,2,3,4-tetrachlorobenzene (□),pentachlorobenzene (▼) and hexachlorobenzene (▽) vs temperature conditions: λ=2.5, t_v=2.7s