

The Formation of Chlorinated Benzenes in Flyash Catalysed Reactions of Trichloroethylene

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Introduction

Research investigations on the mechanism of formation of PCDD/F in combustion processes have concentrated primarily in 2 areas: catalytic reactions of aromatic precursors¹⁻⁵ and de novo synthesis⁵⁻⁸ from inorganic carbon. While pathways from aromatics and chlorinated aromatics to PCDDs and PCDFs have been heavily investigated, relatively little, in comparison, is known about the potential formation of these aromatic precursors from aliphatic starting compounds.

Many studies indicate that the 300°C post-combustion region provides the optimum conditions for PCDD/F formation. The key aromatic precursors may, however, be formed prior to this, in the 400-600°C region of the post-combustion zone. Incomplete combustion of fuel materials and the subsequent release of aliphatic fragments and radicals, combined with flyash catalytic particles, provide a potentially rich reaction environment for the formation of aromatics and halogenated aromatics. The investigations on the de novo pathway for the formation of PCDD/F indicated that chlorobenzenes and chlorophenols are key intermediates. However, the actual formation of the first aromatics in the de novo system has not been investigated.

A number of recent studies indicate the potential importance of the role of the aliphatic compounds in the formation of aromatics and chlorinated aromatics in combustion systems. Strömberg⁹ observed that chlorinated aromatics, including PCDDs and PCDFs, can be formed by surface catalysed reactions of HCl with CO₂, CH₄, C₃H₈, or synthetic flue gas. The reported optimum temperature was 280-300°C for chlorinated aromatic formation. Born et al.¹⁰ investigated the fly ash or Cu catalysed oxychlorination and oxidation of ethylene between 250 and 500°C. Only the gaseous products were analysed, showing primarily the production for 1,2-dichloroethane and vinyl chloride. Small quantities of chlorinated benzenes were identified in some reactions. Mulholland¹¹ and Yasuhara and Morita¹² have recently shown that the pyrolysis of C₂HCl₃ results in the production of a wide range of chlorinated hydrocarbons, including chlorinated benzenes and perchloroaromatics. Yasuhara reports the formation of CCl₄, C₂Cl₄, C₂Cl₆, C₄Cl₆, and C₆Cl₆, from the pyrolysis of trichloroethylene.

C₂HCl₃ (TCE) was chosen as a promising compound for investigating flyash catalysed formation of chlorinated aromatics from simple C₂ starting compounds. TCE is one of the top ten compounds found at toxic waste disposal sites, and incineration is a primary method of TCE disposal. Chlorinated

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benzenes ($\text{Cl}_x\text{-Bz}$) were chosen as model target compounds for reaction product analysis due to their ease of analysis, they are among the simplest aromatics and they have been linked to PCDD/F formation.

Experimental

The experimental apparatus constructed on-site consists of a reagent gas/carrier gas control panel (flow control, flow measurement), vapourisation of liquid reagents, a gaseous reagent/carrier gas mixing chamber, thermostated reaction chamber and a reaction product collection system.

Fly ash (**Fa**) was Soxhlet extracted two times with toluene, rinsed with acetone, dried at 120°C overnight to remove solvents, and then heated in a synthetic air stream (ca. 50 mL/min) at 600°C for 24 h. The Fa was stored in a desiccator. 0.5 g was used for each reaction.

Synthetic air was set to a flow rate of 45 mL/min and bubbled through ice-cooled TCE to carry a constant flow of TCE to the reaction oven. Reactions were performed at 400, 500 and 600°C, with $t = 15$ min., allowing 0.1 g TCE to react. The temperature corrected reaction chamber residence time was from 1.5 - 1.2 s.

Gas phase reaction products were trapped on Carbotrap (Supelco) adsorbent tubes. The adsorbent tubes were eluted with 4 mL dichloromethane followed by 4 mL toluene at room temperature. The reaction tubes were suspended in the reaction oven, heated to 90°C, and eluted with 50 mL toluene.⁵ A second 90°C elution using 25 mL toluene in a control run showed no $\text{Cl}_x\text{-Bz}$.

A mixture of $^{13}\text{C}_6$ -labelled internal standards containing $\text{Cl}_2\text{-}$, to $\text{Cl}_6\text{-Bz}$ was added to the eluates and the samples were concentrated to 100 μL . A GC-MSD system (HP5890/5970) was used for the $\text{Cl}_x\text{-Bz}$ analyses.

Results and Discussion

The TCE reactions were performed in duplicate. The adsorbent tube (gas phase products) and reaction tube (adsorbed products) extracts were worked up and analysed separately. The lower chlorinated homologues were found almost exclusively in the gas phase products, while the majority of the $\text{Cl}_5\text{-Bz}$ (~65-80%) and HCB (~95-99%) were found in the adsorbed products.

The $\text{Cl}_x\text{-Bz}$ produced in the reactions are listed in Table 1. Total production at 400 and 500°C was nearly equal, however, the homologue distribution was shifted from the lower toward the higher chlorinated homologues. Total production is >100x greater at 600°C. The dichloro and trichloro homologues were dominated by the 1,2 and 1,2,3 isomers.

The reaction oven is capable of a maximum of 600°C, therefore, we cannot conclude that this is the maximum for $\text{Cl}_x\text{-Bz}$ production. However, these results contrast markedly from those obtained by Strömberg⁹, who observed 280-300°C as the optimum temperature range for chlorinated aromatic formation from non-aromatic starting materials, and Schwarz et al.¹³, who reported maximum total $\text{Cl}_x\text{-Bz}$ production at 470°C and maximum HCB production from 350-400°C.

Table 1. Total Cl_x-Bz produced.

	(ng/sample)x10*			(ng/g TCE)*		
	Fa 4	Fa 5	Fa 6	TFa 4 (n=2)**	TFa 5 (n=2)	TFa 6 (n=2)
1,3-Cl ₂ -Bz	3,8E+01	3,7E+01	0,0E+00	1,5E+03	7,5E+02	2,9E+03
1,4-Cl ₂ -Bz	0,0E+00	0,0E+00	0,0E+00	8,9E+01	1,4E+02	8,4E+02
1,2-Cl ₂ -Bz	1,7E+02	2,0E+02	1,3E+03	9,0E+03	5,3E+03	8,7E+03
1,3,5-Cl ₃ -Bz	0,0E+00	0,0E+00	0,0E+00	0,0E+00	6,0E+01	1,3E+03
1,2,4-Cl ₃ -Bz	0,0E+00	0,0E+00	0,0E+00	2,0E+02	4,9E+02	2,9E+03
1,2,3-Cl ₃ -Bz	1,6E+02	1,7E+02	3,9E+02	3,1E+03	1,5E+03	7,7E+03
1,2,4,5-Cl ₄ -Bz	2,7E+01	4,9E+01	0,0E+00	8,9E+01	6,3E+02	1,4E+04
1,2,3,4-Cl ₄ -Bz	3,8E+01	5,2E+01	0,0E+00	2,1E+02	3,0E+02	4,8E+03
Cl ₅ -Bz	4,0E+01	5,7E+01	5,0E+01	9,5E+01	7,8E+02	3,9E+05
HCB	0,0E+00	0,0E+00	0,0E+00	0,0E+00	1,1E+03	3,0E+06
Total Cl_x-Bz	4,8E+02	5,7E+02	1,7E+03	1,4E+04	1,1E+04	3,4E+06

* The Fa blanks have been multiplied by 10 in order to compare directly with the TCE reactions.

** Total amounts from the adsorbent tube + the reaction tube, averaged over the 2 samples.

Conclusions

Even at higher temperatures, Cl₅-Bz and HCB adsorb very strongly to the flyash. Analysis of the gas-phase products alone is not sufficient to monitor the reactions of TCE over Fa. This must be considered in the catalytic reactions of any aliphatics.

A maximum in the production of Cl_x-Bz, particularly Cl₅-Bz and HCB, was observed at 600°C, clearly contrasting earlier published studies. Chlorinated aromatics may be formed from non-aromatic compounds in the higher temperature post-combustion zone, allowing further reactions in the 300°C zone to produce PCDD/Fs. While further results are required, the temperature dependency and isomeric distributions of Cl_x-Bz formed in the flyash catalysed reactions of TCE should provide valuable mechanistic information regarding the formation of aromatics from aliphatics. The massive production of HCB at 600°C encourages further investigations and more intensive mechanistic studies. Further evidence should ultimately show that the de novo and precursor theories are inseparable in an overall mechanism of PCDD/F formation.

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