

## Chlorinated Aromatic Hydrocarbons in Heterogeneous Combustion Reactions of C<sub>2</sub> Aliphatics.

### Part I. Acetylene

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#### Introduction

Disparate *de novo* and precursor formation theories for the production of polychlorinated dibenzodioxins (PCDD) and -furans (PCDF) in combustion processes have dominated the literature in recent years<sup>(1-4)</sup>. These theories do not adequately consider the source of the aromatic precursor in the combustion system (precursor theory) or the relevance of fast, heterogeneous formation mechanisms (*de novo* theory). New light may be shed on the formation process by examining the importance of fast, heterogeneous combustion reactions of short chain aliphatics in the formation of simple aromatic compounds, such as chlorinated benzenes (Cl<sub>x</sub>Bz) and phenols (Cl<sub>x</sub>Ph), at temperatures in the 300-600°C range.

Recent investigations of high temperature gas-phase pyrolysis of chlorinated and non-chlorinated C<sub>1</sub> and C<sub>2</sub>-aliphatics with and without external chlorine sources<sup>(5-10)</sup> indicate that aromatic and chlorinated aromatic compounds can form from aliphatic precursors. In preliminary studies of heterogeneous reactions with C<sub>2</sub>HCl<sub>3</sub><sup>(11)</sup>, Cl<sub>x</sub>Bz and Cl<sub>x</sub>Ph were formed between 300-600°C. In this investigation, heterogeneous reactions of C<sub>2</sub> aliphatics were continued with reactions of acetylene.

#### Experimental

A glass and quartz reaction apparatus, constructed on-site, was used for all reactions. Acetylene was reacted with HCl/air under heterogeneous combustion conditions between 300-600°C and gas-phase residence times of < 2 s. Model catalyst mixtures of SiO<sub>2</sub>/metal oxides (Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and CuO) were compared with extracted and annealed municipal waste incinerator (MWI) flyash. Approximately 30-40mg C<sub>2</sub>H<sub>2</sub> were reacted in 30 min experiments. Reaction products were eluted from the catalytic material in the reaction tube and from the Carbotrap adsorbent tube. The sample extracts were concentrated, the chlorinated phenols derivatised, and the final sample extracts were analysed quantitatively by GC-MSD for

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chlorinated benzenes and phenols and qualitatively for additional volatile and semi-volatile products.

## Results

Chlorinated benzenes ( $\text{Cl}_x\text{Bz}$ ), chlorinated phenols ( $\text{Cl}_x\text{Ph}$ ) and PCDD/F were detected in both gas-phase products as well as catalyst-adsorbed products (Figure 1).  $\text{Cl}_x\text{Bz}$  production increased exponentially to  $600^\circ\text{C}$  (HCB:  $4 \times 10^4 \text{ ng/g C}_2\text{H}_2$ ), while  $\text{Cl}_x\text{Ph}$  (PCP) production peaked at  $400^\circ\text{C}$  ( $2.5 \times 10^4 \text{ ng/g C}_2\text{H}_2$ ). PCDF displayed a dramatic peak at  $500^\circ\text{C}$  (TCDF:  $2 \times 10^6 \text{ pg/g C}_2\text{H}_2$ ), in contrast to the accepted optimal formation temperature of  $300^\circ\text{C}$ . Comparison of gas-phase  $\text{Cl}_x\text{Bz}$  congener distribution patterns (Figure 2) revealed that the CuO catalysed reaction closely matched the pattern produced in the reactions with MWI flyash, providing further evidence of the importance of Cu in the flyash matrix. For PCDD/F formation, however, less similarity was observed between the homologue pattern produced using CuO as catalyst and that produced over flyash. While Cu has been reported to be instrumental in the formation of PCDD/F in the  $300^\circ\text{C}$  range<sup>(12)</sup>, competing formation and destruction mechanisms at  $600^\circ\text{C}$  may have resulted in greater catalytic contributions of other components of the flyash. Comparison of flyash catalysed gas-phase  $\text{Cl}_x\text{Bz}$  with MWI flue gas<sup>(13)</sup> and  $300^\circ\text{C}$  *de novo* synthesized<sup>(14)</sup>  $\text{Cl}_x\text{Bz}$  (Figure 3) demonstrated the relevance of fast ( $< 2 \text{ s}$ ), mid temperature ( $600^\circ\text{C}$ ) heterogeneous combustion reactions of  $\text{C}_2$ -aliphatics in real combustion systems.

## References

1. Vogg, H., Stieglitz, L. *Chemosphere*, **1986**, *15*, 1373.
2. Stieglitz, L., Zwick, G., Beck, J., Roth, W., Vogg, H. *Chemosphere*, **1989**, *18*, 1216.
3. Hutzinger, O., Blumlich, M.J., Berg, M.V.D., Olie, K. *Chemosphere*, **1985**, *14*, 581.
4. Karasek, F.W., Dickson, L.C. *Science*, **1987**, *237*, 754.
5. Tirey, D.A., Taylor, P.H., Dellinger, B. in Emissions from Combustion Processes: Origin, Measurement, Control. R.Clement, R.Kagel, eds., Lewis Publishers, Inc., Chelsea, MI, 1990.
6. Tirey, D.A., Taylor, P.H., Kasner, J., Dellinger, B. *Combust. Sci. and Technol.*, **1990**, *74*, 137.
7. Eklund, G., Pedersen, J., Stromberg, B. *Chemosphere*, **1988**, *17*, 575.
8. Pederson, J., Källman, B., Simonson, M., Olsson, J.O. *Chemosphere*, **1991**, *22*, 67.
9. Stromberg, B. *Chemosphere*, **1991**, *23*, 5151.
10. Miller, J.A., Melius, C.F. *Combust. Flame*, **1992**, *91*, 21.
11. Froese, K.L., Hutzinger, O. *Chemosphere*, **1994**, *28*, 1977.
12. Bruce, K.R., Gullet, B.K., Beach, L.O. in Proceedings of the 1991 Incineration Conference, 13-17 May 1991, EPA/RREL, Knoxville, TN, .
13. Ballschmiter, K., Braunmiller, I., Niemczyk, R., Swerev, M. *Chemosphere*, **1988**, *17*, 995.
14. Milligan, M.S., Altwicker, E. *Environ. Sci. Technol.*, **1993**, *27*, 1595.

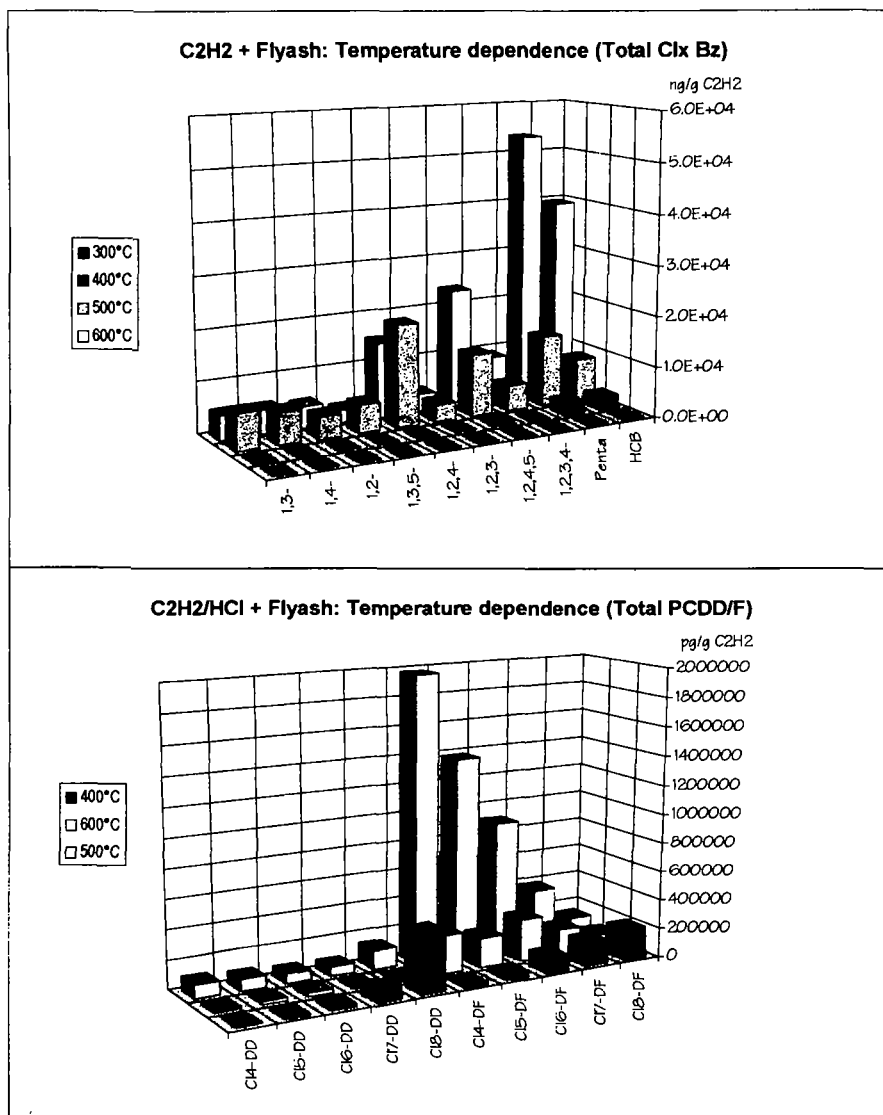
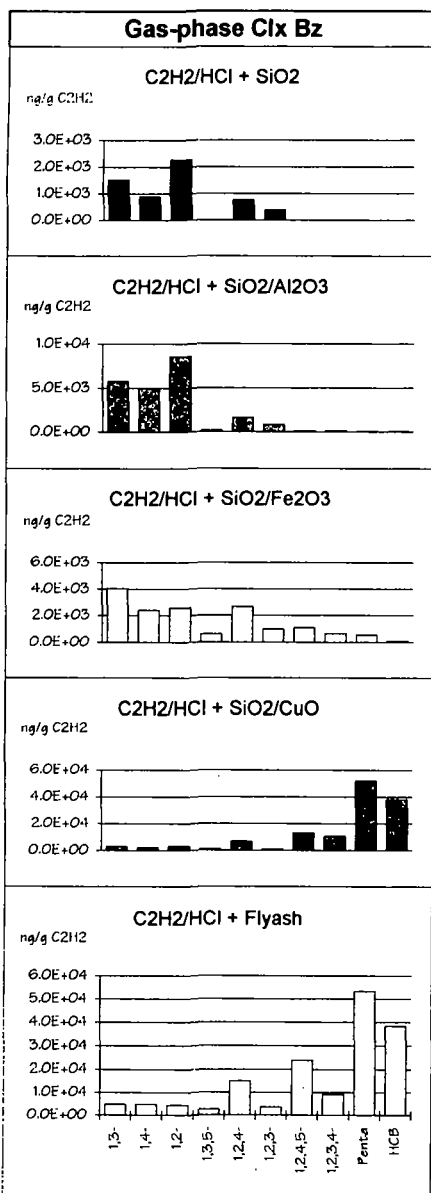
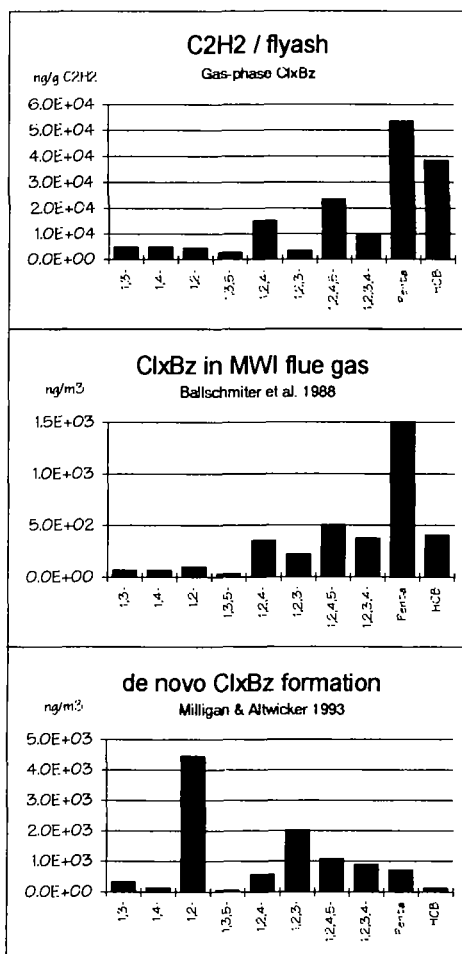


Figure 1. Temperature dependence of total Cl<sub>x</sub>Bz and PCDD/F production in the reaction of acetylene/HCl over flyash.



**Figure 2.** Congener patterns of gas-phase Cl<sub>x</sub>Bz production in the 600°C reactions of acetylene/HCl with various catalysts.



**Figure 3.** Comparison of Cl<sub>x</sub>Bz congener patterns from flyash catalysed acetylene reaction products, MWI flue gas<sup>(13)</sup>, and de novo synthesis<sup>(14)</sup>