

**PATHWAYS IN THE FORMATION OF AROMATICS AND CHLORINATED AROMATICS  
VIA GAS PHASE REACTIONS OF C<sub>1</sub> AND C<sub>2</sub> HYDROCARBONS.****PART I. ETHYLENE**

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PCDDs and PCDFs have been studied intensively in the past number of years; many hypotheses and much data have been gathered with respect to their formation via combustion processes. De novo synthesis has been postulated by Stieglitz et al.<sup>1</sup> as the principle pathway of formation of PCDD/F in MWI processes. Hutzinger et al.<sup>2</sup>, observed that PCDD/F is formed in the post-combustion zones of waste incinerators; Karasek and Dickson<sup>3</sup> later reported the catalytic reaction of precursors (eg. chlorobenzenes, chlorophenols) on the flyash surface in the post-combustion zone as being the major PCDD/F formation mechanism. Homogeneous (gas-phase) formation of PCDD/F from phenols was modelled by Shaub and Tsang<sup>4</sup>, and shown in the gas-phase pyrolysis and slow combustion of phenol and monochlorophenols by Born et al.<sup>5</sup>

Various investigations of the reactions and kinetics of methane or propane with O<sub>2</sub><sup>6</sup> or chlorine<sup>7</sup>, as well as studies of gas-phase atmospheric reactions<sup>8</sup> indicate that radicals (i.e., alkyl radicals, halogenated alkyl radicals and peroxy radicals) play extremely important roles in gas-phase reactions. For example, Pederson et al.<sup>9</sup>, report that chloromethyl radicals are known to react to form simple chlorocarbons, chloro-aromatics, chlorinated PAHs, and PCDD/F. Under certain conditions, unsaturated hydrocarbons such as acetylene or trichloroethylene can polymerize to form aromatic and chlorinated aromatic compounds.<sup>10,11</sup>

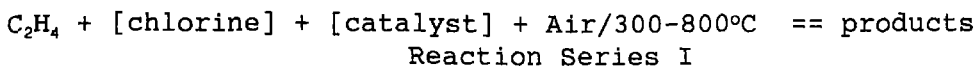
Choudhry et al.<sup>12</sup> prepared a comprehensive review of the potential mechanisms in the thermal formation of PCDD/F, as well as their potential precursors. In the past 10 years many studies on the formation of PCDD/F have been reported; many of the pathways postulated by Choudhry et al. are supported by published data. Investigators have a better understanding of the roles

played by flyash and other surfaces or particles in incineration processes.

In addition to flyash and soot particles in a post-combustion zone, metal cluster ions may also be present in the gas-phase. Such metal clusters could influence gas-phase reaction mechanisms of C<sub>2</sub> hydrocarbons.<sup>13 14</sup>

Altwickler<sup>15</sup>, however, indicates that gas phase reactions are likely not the major pathways to PCDD/F formation. He suggests, nevertheless, that it would be helpful to have a better understanding of the gas-phase formation of potential precursors, and investigating the potential role of surfaces in forming radical species which may initiate, promote or participate in the formation of potential precursors. The investigation of the gas-phase formation of potential precursors, with or without the help of catalytic reaction processes, may shed new light on all of these theories of PCDD/F formation in combustion processes.

From this perspective, the gas-phase reactions of ethylene with chlorine and potential catalysts (Reaction Series I) could provide some much needed "basic mechanistic" information regarding aromatic and chlorinated aromatic formation.



Preliminary experiments have been undertaken using a gas-phase reaction apparatus consisting of a gas mixing chamber and a heated quartz reaction chamber. Reacted gas is passed through quartz tubes containing graphitic carbon adsorbents. The adsorbent tubes are subsequently analysed by thermodesorption-gas chromatography (TD-GC) with FID or MSD. Results show that in at least one set of experiments, tetrachloroethylene has been tentatively identified as a major product in the 400°C reaction of C<sub>2</sub>H<sub>4</sub>, air, and HCl.

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