PIC FORMATION MECHANISMS IN THE THERMAL DECOMPOSITION OF 1,2-DICHLOROBENZENE

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ABSTRACT

The PICs in this study were formed by three types of mechanisms. Chlorination by chlorine free radicals was the major reaction forming PICs. The second source of PICs was from fragmentation of the aromatic ring. The third source of PICs was from disproportionation reactions.

INTRODUCTION

The production of hazardous wastes in the world increases each year. In the United States, waste minimization is now part of every waste stream evaluation aimed towards selection of the ultimate disposal process for a waste stream. Incineration is a key process for the disposal of these wastes. One of the uncertainties associated with the incineration of these wastes is the formation of products of incomplete combustion (PICs). This work was undertaken to address those conditions that lead to the formation of these PICs.

Studies of the variables which affect the formation of PICs have been conducted by several different researchers. Choudhry, Olie and Hutzinger[1] reviewed the literature on the mechanisms for the formation of PICs by selected thermal processes. They proposed mechanisms involving radicals such as dichlorocarbene, benzyne, and ketocarbene leading to the formation of PICs.

Gas-phase free radicals were proposed as controlling PIC formation in high temperature gas-phase reactions by Dellinger and co-workers[2,3,4]. At incineration temperatures, the formation of PICs resulted from recombination of radical fragments and abstraction reactions. When compounds were decomposed in mixtures, additional pathways become available for the decomposition of compounds.

Ballschmiter and co-workers[5,6,7] have reported the importance of intermediates in the formation of PICs. Compounds such as chloroethenes and chloroethynes can lead to the formation of aromatic compounds. The formation of PCBs was proposed as an intermediate in the formation of dibenzofurans. They proposed the reaction pathway for the formation of PCDDs from chloro-phenols involved the formation of a chlorinated diphenyl ether.

This work looked at the types and concentrations of PICs formed during the thermal decomposition of 1,2-dichlorobenzene (DCB). The PICs identified were an indication of the fragments present in the combustion environment of the test system. These fragments were used to examine the reaction pathways that lead to the PICs formed during combustion operations.

EXPERIMENTAL

The test combustion system allowed for the introduction of test compounds into a heated reaction chamber as a vapor. Test conditions (temperature, oxygen concentration, residence time, and compounds in the feed) were varied to determine their effect on PIC formation. Compounds exiting the reaction chamber were collected in a series of impingers containing solvents to condense and absorb organic compounds. The PICs were identified using GC/MS.

RESULTS AND DISCUSSION

Conditions tested in this study included variations in temperature, residence time, oxygen concentrations, and compounds present in the feed to the system. There was little variation in the chemical classes of PICs formed under these various conditions.

Formation of PICs resulted from a combination of several processes adding to the complexity of the combustion reaction. These formation processes include free radical generation and recombination, chlorination, and disproportionation reactions. Classes of compounds identified from the thermal decomposition of the various feed samples included chlorinated benzenes, chlorinated phenols, chlorinated aromatic compounds, chlorinated fused ring heterocyclic compounds, and straight-chain chlorinated compounds.

Those PICs trapped in the impinger solutions indicate the identity of the fragments produced in the decomposition atmosphere. Examination of these compounds indicates a chlorinating agent is one of the major species present in the decomposition atmosphere. Chlorinated compounds were found in series of the mono-chloro to the perchlorinated species. Chlorinated benzenes were the PICs found in the highest concentration. Chlorination of the compounds takes place by the chlorine free radicals initially produced from the decomposition of dichlorobenzene.

Cleavage of the aromatic ring by oxygen generates short-chain radical fragments. These fragments then go on to add to other compounds present or become involved in disproportionation reactions. Chlorinated naphthalenes, alkyl benzenes, and chlorinated straight chain hydrocarbons were all formed from the cleavage fragments. A proposed mechanism for the cleavage of the aromatic ring involves formation of a four membered ring between an oxygen molecule and two carbon atoms of the aromatic ring. The four membered ring was then postulated to cleave between the two carbons and also between the two oxygens forming a di-acid compound. The molecule decarboxylates leaving the chlorinated butadiene molecule.

Disproportionation reactions play an important part in the reactions taking place in the combustion environment. These types of reactions produce less saturated compounds such as vinylacetylenes, ethynyl benzenes, and dichlorobutadiyne (C_4Cl_2).

These compounds would be disproportionation products of chlorinated butadiene or result from bond rupture to form radicals such as ethenyl and ethynyl radicals. Theses radicals subsequently react with DCB to form alkyl benzenes and naphthalenes. These processes result in a complex mixture of reactive species capable of recombinations producing a wide variety of PICs which were identified in the impinger samples.

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