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Gas-Phase Formation of Dioxin and Other Aromatic Products from 2,6-Dichlorophenol Pyrolysis

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Abstract

Gas-phase pyrolysis of 2,6-dichlorophenol was carried out in a 10-second flow reactor at temperatures ranging from 600 to 900°C. Aromatic products included three chlorinated dibenzo-p-dioxins (CDD) and several furans, as well as mono-aromatic products resulting from H-atom substitution reactions and unoxygenated polyaromatic products. At 600°C, with only one percent conversion of reactant, major products were 2-chlorophenol, 1,3-dichlorobenzene, and 1,6- and 1,9-diCDD. These results support the hypothesis that CDD formation is favored from phenols with *ortho*-chlorine substituents, and that ring closure occurs via a five-member ring intermediate to produce isomer pairs. Higher yields of the 1,6-diCDD isomer were observed, consistent with consideration of steric hindrance in CDD structure. At 700°C and higher, aromatic products include 1-monoCDD, several mono- and dichlorodibenzofurans, monochlorobenzene, naphthalene and several mono-, di- and trichloronaphthalenes, and various isomers of molecular formula $C_{16}H_{10-x}Cl_xO$ hypothesized to be benzonaphthofurans and/or benzoxanthenes. Pathways to observed products are postulated. With increasing temperature, the relative yields of CDD decrease, the relative total furan yield remains constant with the distribution shifting to less chlorinated congeners, and the relative yield of unoxygenated aromatic species increases with the distribution shifting to less chlorinated congeners.

Introduction

Formation of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from municipal solid waste and hazardous waste incineration is well known. Chlorinated phenols have been identified as potential precursors of PCDDs and PCDFs in combustion systems. There have been several experimental studies[1-3] and theoretical analyses[4,5] on the homogeneous formation of PCDDs and PCDFs from chlorinated phenols in combustion processes. Nonetheless, much is still unknown about the detailed reaction pathways involving both direct routes and routes from intermediate products. The goal of this work is to gain a better understanding of these pyrolysis pathways through analysis of aromatic product distributions from gas-phase 2,6-dichlorophenol pyrolysis over the temperature range 600-900°C.

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Experimental Methods

Pyrolysis experiments with 2,6-dichlorophenol were conducted using an electrically-heated, quartz tube reactor. The quartz tube is 40 cm in length and 2 cm in diameter. A known quantity (50 mg) of reactant is vaporized and swept into the reactor through heated transfer lines by helium carrier gas. The residence time in the reactor is approximately 10 seconds.

Reaction products are collected at the outlet of reactor by a filter and solvent trap assembly. A 0.2 µm PTFE filter is used to collect high molecular weight products, with aromatic products extracted in hexane. Lighter aromatic products that pass through the filter are collected directly in hexane. Sample analysis is performed by GC/MS (Varian 3600/ Saturn 2000) with a DB-5ms column (30m, 0.25 mm ID, 0.25 µm film thickness). Commercially available chemical standards used in this study to identify and quantify individual products were 2,6-dichlorophenol, 2-chlorophenol, 1,3-dichlorobenzene, monochlorobenzene, naphthalene, dibenzofuran, dibenzo-*p*-dioxin, and 1-monoCDD. In addition, standards containing 1,6- and 1,9-diCDD, compounds identified in this study, were obtained from researchers at the Centers for Disease Control (CDC).

Results and Discussion

Conversion of 2,6-dichlorophenol to products was 1% at 600°C, 27% at 700°C, and 100% at 800 and 900°C. The overall aromatic product distribution consisted of three classes of compounds: mono-aromatic species (2-chlorophenol and two chlorinated benzenes), oxygenated polyaromatic species (PCDDs and various furans), and chlorinated and unchlorinated polycyclic aromatic hydrocarbons (PAHs). Product yields are shown in Figs. 1A through 1F, computed as a percentage of the total aromatic product yield on a mass carbon basis. Unreacted 2,6-dichlorophenol is not included in these data. At 600°C, major products were 2-chlorophenol, comprising over 50% of the total aromatic product yield, 1,6- and 1,9-diCDD (about 30%), and 1,3-dichlorobenzene (about 12%). Minor products included 1-monoCDD and mono- and dichlorodibenzofurans. As pyrolysis temperature was increased, 2-chlorophenol and PCDD product yields decreased and naphthalene and furan product yields increased. The degree of chlorination of the aromatic products decreases with increasing temperature. At 900°C, major products were unchlorinated PAHs of even carbon number, ranging from 10 (naphthalene) to 20.

Based on our measured aromatic product distributions at low and intermediate pyrolysis temperatures and the results mechanistic studies reported by others, we postulate pyrolysis pathways to major aromatic products. Pyrolysis of 2,6-dichlorophenol is initiated by loss of H-atom to form the resonance-stabilized 2,6-dichlorophenoxy radical. Substitution of Cl or OH in 2,6-dichlorophenol by H-atom produces 2-chlorophenol or 1,3-dichlorobenzene, respectively. These reactions, particularly the former, are exothermic. Substitution of H or OH by Cl-atom, on the other hand, is endothermic. Heat of reaction estimates using the semiempirical molecular orbital method AM1 are shown in Table 1.

Table 1. AM1 Heat of Reaction for 2,6-Dichlorophenol Substitution Reactions.

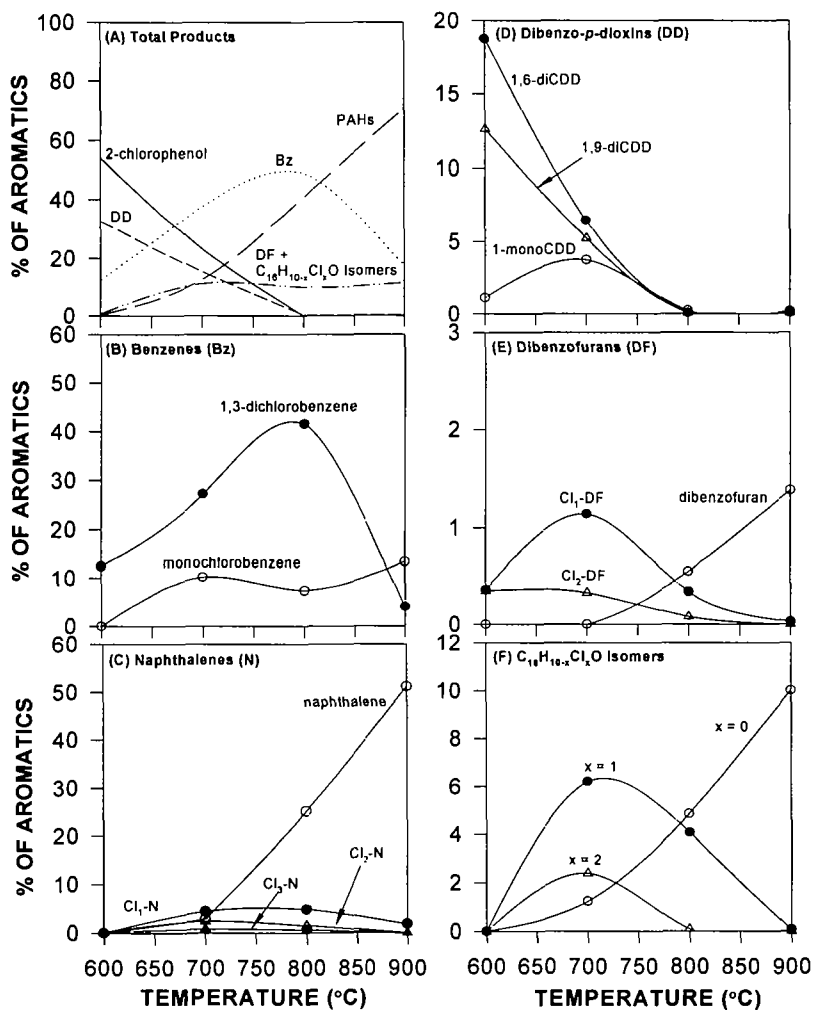|	kcal/mol
Cl + 2,6-dichlorophenol ----> H + 2,4,6-trichlorophenol	17.2
H + 2,6-dichlorophenol ----> Cl + 2-chlorophenol	- 19.4
Cl + 2,6-dichlorophenol ----> OH + 1,2,3-trichlorobenzene	12.2
H + 2,6-dichlorophenol ----> OH + 1,3-dichlorobenzene	- 10.9

Fig. 1. Aromatic product yields from 2,6-dichlorophenol pyrolysis.

The 2,6-dichlorophenoxy radical adds *ortho* to 2,6-dichlorophenol and eliminates one Cl-atom to form a phenoxyphenol intermediate. Subsequent ring closure of the phenoxyphenol via Smiles rearrangement produces the observed isomer pair 1,6- and 1,9-diCDD; this result is similar to that reported by Sidhu *et al.* for 2,4,6-trichlorophenol pyrolysis.[3] The yield of 1,6-diCDD was greater than the yield of 1,9-diCDD; the ratio of 1,6- to 1,9-diCDD yields is shown in Fig. 2. The chlorine substitution pattern in the 1,6 isomer is less crowded than in the 1,9 isomer, as reflected in an energy difference of 0.21 kcal/mol as predicted by the AM1. Our data with a ratio from lower temperature CDC synthesis experiments are consistent with an energy difference of less than 1 kcal/mol.
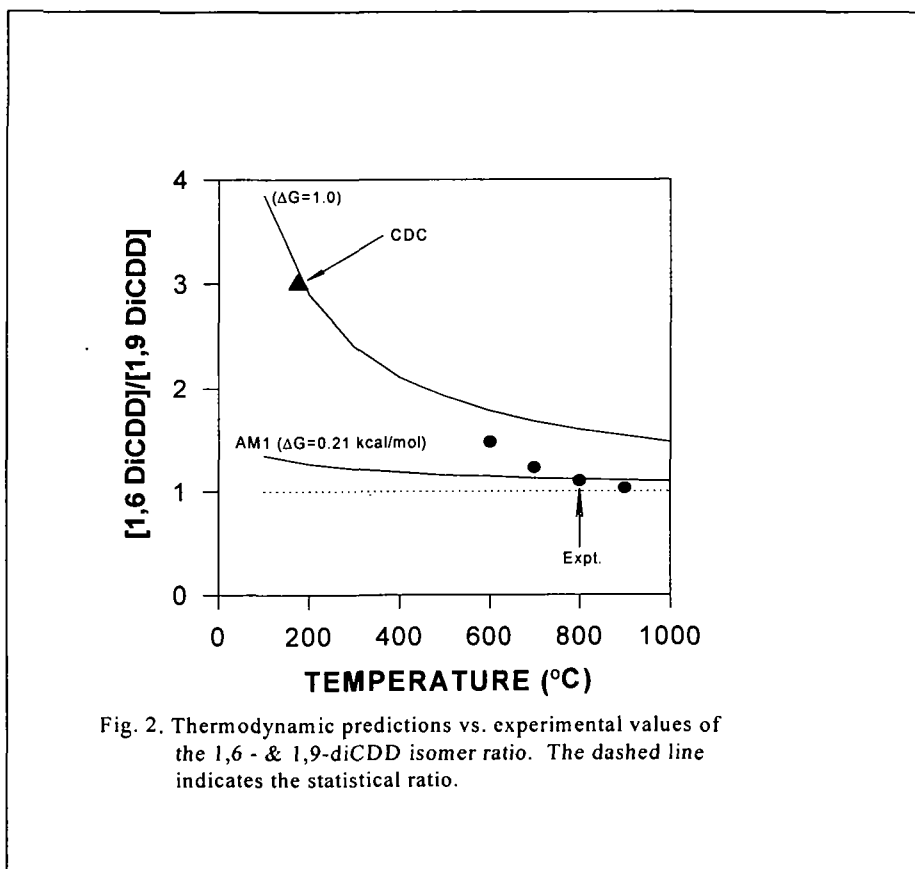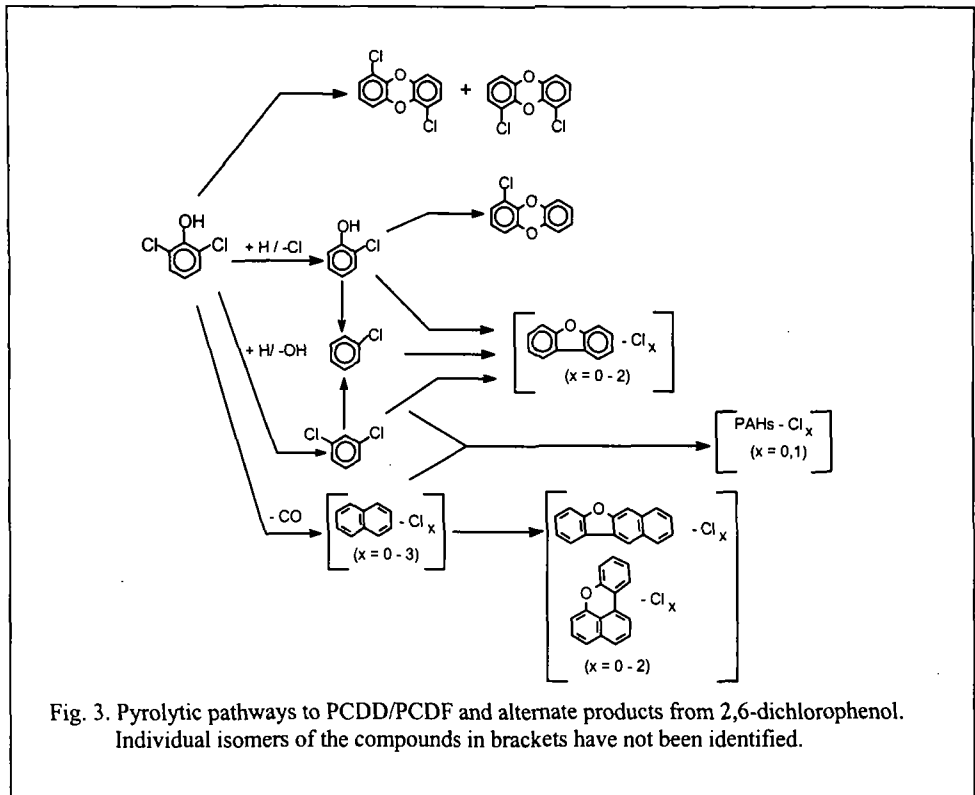

Fig. 2. Thermodynamic predictions vs. experimental values of the 1,6 - & 1,9-diCDD isomer ratio. The dashed line indicates the statistical ratio.

Formation of 1-monoCDD and the dibenzofurans is hypothesized to occur by reactions involving 2-chlorophenol. Formation of naphthalenes is believed to occur by CO loss from phenols to form biradicals which dimerize to form naphthalenes.[7] Formation of the benzonaphthofurans and benzoxanthenes is hypothesized to occur by phenoxy radical addition to naphthalenes. The results described are summarized in Fig. 3.

Fig. 3. Pyrolytic pathways to PCDD/PCDF and alternate products from 2,6-dichlorophenol. Individual isomers of the compounds in brackets have not been identified.

Acknowledgments

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