

Acetylene Addition and Cyclization Reactions as a Possible Route for Dioxin Formation

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Introduction

The formation of polynuclear aromatic hydrocarbons (PAH) in flames can be described by the hydrogen-abstraction-acetylene-addition (HACA) mechanism (1-3): In aliphatic fuel combustion the first aromatic ring is formed by radical addition (C_2+C_4 , C_3+C_3 , etc.), then the addition and cyclization of acetylene on the first aromatic ring lead to two- and three-ring compounds and other PAHs. In aromatic fuel combustion the direct condensation of aromatics to PAH is important only at the initial stage of combustion; when the aromatic concentration is decreased and the concentration of acetylene as a major decomposition product of aromatics is increased, the HACA mechanism becomes predominant for PAH growth. Dioxins are PAHs containing hetero ring oxygen and having chlorine substitution for hydrogen; they may be formed in a way similar to the HACA mechanism when oxygen species are also involved. This hypothesis will be tested through a chemical kinetic modeling.

Reaction Mechanism

In Table 1 the reactions R1-13 are the same as in ref. (4), describing mainly the coupling of phenol molecule and phenoxy radical to PCDD. R14 describes the coupling of two phenoxy radicals to PCDF (5). R15-23 represent PCDD and PCDF formation through acetylene addition on a single aromatic ring and cyclization, postulated in analogy to the HACA mechanism. The rate constant of elementary steps R15,17,18,20,22,23 is from ref. (6), and that of R16,21 is from ref. (7), while that of R19 is taken to be a factor 0.1 of the rate constant of reaction $\phi + O_2 \rightarrow \phi O + O$ given in ref. (8). The decomposition and oxidation of various intermediates and products (R24-30) are written following similar reactions in ref. (4).

Computation Methods

The reaction set in Table 1 is integrated to simulate a plug flow reactor; the integration has been done using the Euler method with an integration interval 10^{-6} sec. The model inputs are the concentrations of (chloro)phenol, O_2 and other fuels R, and reaction temperature and time. When starting with aromatic fuels, C_2H_2 is the decomposition product of the aromatics, so it is assumed that the concentration of

C₂H₂ increases linearly from zero at reactor inflow to an assumed or experimentally measured level at reactor outflow. The concentration of hydroxyl radicals is calculated by: $[OH] = 10^{-1.7} \exp[-35000/(RT)]$ M as in ref. (4). The model outputs are the concentrations of all the species in the reaction mechanism. The formation and destruction of PCDD and PCDF from the routes R4,5,14,18,23 are calculated and the results are listed separately.

Results and Discussion

In Table 2 the experimental data in a laboratory gas-phase flow reactor reported by Kanters (9) are compared to our calculation results. The outflow phenol concentration calculated is in good agreement with experimental data, suggesting that the oxidation behaviour of phenol is well predicted by the reaction mechanism. The calculated formation levels of benzofuran and dibenzofuran are lower than the experimental measurements by one and two orders of magnitude, respectively, which may be considered to be within the uncertainties of the experimental data and the elementary steps and their rate constants in the mechanism. The dibenzodioxin formation level from coupling of a phenol molecule and a phenoxy radical is about the same as the dibenzofuran formation level from coupling of two phenoxy radicals, which is some four orders of magnitude lower than the experimental measurements. The dependence of the various postulated routes for PCDD and PCDF formation on the phenol concentration is demonstrated in Table 3; when the phenol inflow concentration is lowered by three orders of magnitude from case A to B, the PCDD and PCDF formation levels from the aromatic dimerization routes R4,14 decrease by six orders of magnitude, showing second-order kinetics, while those from the acetylene addition routes R18,23 decrease by three orders of magnitude, showing first-order kinetics. Case B is typical for combustion conditions; it appears from this modeling calculation that acetylene addition and cyclization reactions are a possible route for dioxin formation.

References

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Table 1. Gas-phase mechanism of PCDD and PCDF formation from chlorophenol.

no.	reaction step	rate constant
R1	$P \rightarrow P \cdot + H$	$10^{15.5} \exp[-86500/(RT)]$
R2	$P + OH \rightarrow P \cdot + H_2O$	10^9
R3	$P \cdot \rightarrow Pr$	$10^{13.6} \exp[-57654/(RT)]$
R4	$P + P \cdot \rightarrow PD + Cl$	$10^9 \exp[-26000/(RT)]$
R5	$PD \rightarrow D + HCl$	$10^{14} \exp[-45000/(RT)]$
R6	$PD + OH \rightarrow D + H_2O$	10^9
R7	$P \cdot + R \rightarrow P + R \cdot$	$10^8 \exp[-26000/(RT)]$
R8	$P \cdot + OH \rightarrow Pr$	10^9
R9	$D \rightarrow Pr$	$10^{15.5} \exp[-80000/(RT)]$
R10	$D + OH \rightarrow Pr$	10^8
R11	$P \cdot + O_2 \rightarrow Pr$	10^8
R12	$R + OH \rightarrow R \cdot + H_2O$	10^9
R13	$R \rightarrow Pr$	$10^{16} \exp[-90000/(RT)]$
R14	$P \cdot + P \cdot \rightarrow F$	$1.6 \times 10^{11} \exp[-11080/(RT)]$
R15	$P \cdot + C_2H_2 \rightarrow BF$	$2 \times 10^9 \exp[-3989/(RT)]$
R16	$BF + OH \rightarrow BF \cdot + H_2O$	$2.1 \times 10^{10} \exp[-4563/(RT)]$
R17	$BF \cdot + C_2H_2 \rightarrow BFC_2H_2 \cdot$	$2 \times 10^9 \exp[-3989/(RT)]$
R18	$BFC_2H_2 \cdot + C_2H_2 \rightarrow F$	$2 \times 10^9 \exp[-3989/(RT)]$
R19	$P \cdot + O_2 \rightarrow BQ$	$10^{8.32} \exp[-7471/(RT)]$
R20	$BQ + C_2H_2 \rightarrow BD$	$2 \times 10^9 \exp[-3989/(RT)]$
R21	$BD + OH \rightarrow BD \cdot + H_2O$	$2.1 \times 10^{10} \exp[-4563/(RT)]$
R22	$BD \cdot + C_2H_2 \rightarrow BDC_2H_2 \cdot$	$2 \times 10^9 \exp[-3989/(RT)]$
R23	$BDC_2H_2 \cdot + C_2H_2 \rightarrow D$	$2 \times 10^9 \exp[-3989/(RT)]$
R24	$BF + OH \rightarrow Pr$	10^8
R25	$BF \cdot + O_2 \rightarrow Pr$	10^8
R26	$BQ \rightarrow Pr$	$10^{13.6} \exp[-57654/(RT)]$
R27	$BD + OH \rightarrow Pr$	10^8
R28	$BD \cdot + O_2 \rightarrow Pr$	10^8
R29	$F \rightarrow Pr$	$10^{15.5} \exp[-80000/(RT)]$
R30	$F + OH \rightarrow Pr$	10^8

The units of the rate constants are s^{-1} for unimolecular reactions and $M^{-1} \cdot s^{-1}$ for bimolecular reactions. $R=1.987 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. P=polychlorinated phenols, $P \cdot$ =polychlorinated phenoxy radicals, Pr=unspecified products, PD=polychlorinated 2-phenoxyphenols, D=PCDD, R=fuel molecules, F=PCDF, BF=polychlorinated benzofurans, BQ=polychlorinated benzoquinones, BD=polychlorinated benzodioxins.

Table 2. Comparison of experimental data with calculation results.

	experimental data	calculation results
Input:		
phenol/M	1.7×10^{-4}	1.7×10^{-4}
O ₂ /M	1.8×10^{-3}	1.8×10^{-3}
temperature/K	973	973
reaction time/sec	11	11
Output (all in M):		
phenol	8×10^{-6}	8.3×10^{-6}
C ₂ H ₂	1.1×10^{-5}	a
benzofuran	7.7×10^{-7}	8.8×10^{-8}
dibenzofuran	6.9×10^{-7}	5.2×10^{-9} (from R18)
		4.7×10^{-11} (from R14)
dibenzodioxin	n.a.	3.6×10^{-8} (from R23)
		8.6×10^{-11} (via R4)
O ₂	n.a.	1.6×10^{-3}
P ϕ	n.a.	1.3×10^{-11}
PD	n.a.	2×10^{-17}
BF ϕ	n.a.	2.9×10^{-13}
BFC ₂ H ₂	n.a.	2.9×10^{-13}
BQ	n.a.	3.3×10^{-11}
BD	n.a.	3.1×10^{-7}
BD ϕ	n.a.	1×10^{-12}
BDC ₂ H ₂	n.a.	1×10^{-12}

^aThe C₂H₂ concentration is assumed to vary linearly from zero at reactor inflow to 1.1×10^{-5} M at reactor outflow. n.a.=not available.

Table 3. Calculated PCDD and PCDF formation levels at varied input conditions.

	case A	case B
Input:		
phenol/M	1×10^{-3}	1×10^{-6}
O ₂ /M	4.09×10^{-3}	4.09×10^{-3}
C ₂ H ₂ /M ^a	1×10^{-3}	1×10^{-3}
temperature/K	1100	1100
reaction time/sec	1	1
Calculated PCDD and PCDF formation levels (all in M):		
D (via R4)	4.4×10^{-9}	4.1×10^{-15}
F (from R14)	3.1×10^{-9}	2.7×10^{-15}
F (from R18)	4.1×10^{-5}	3.2×10^{-8}
D (from R23)	8.1×10^{-6}	7.5×10^{-9}

^aAs in Table 2.