

AN ELEMENTARY REACTION KINETIC MODEL OF THE GAS-PHASE FORMATION OF POLYCHLORINATED DIBENZOFURANS FROM CHLORINATED PHENOLS.

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INTRODUCTION

Combustion and thermal processes are generally recognized as the major source of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F or simply “dioxins”) in the environment¹⁻³. A previously developed, simple mechanism of gas-phase formation of PCDD from chlorinated phenols suggested that the gas-phase formation pathway was too slow to account for concentrations of PCDD observed in full-scale combustors⁴. As a result, most research on formation of PCDD/F in combustion sources focused on surface-mediated formation.

The existing dioxin formation models⁴⁻⁶ have been recently reexamined. Based on new literature data and the importance of stability of phenoxyl radical, a modified approach was suggested to explain gas phase formation rates of dioxins by purely gas phase reactions of phenoxyl radicals⁷⁻⁹. It has now been demonstrated that the potential yields of dioxins from gas-phase, chlorinated phenol precursors were grossly underestimated by the dioxin research community. As a result, it seems plausible to argue that gas-phase pathways for formation of dioxins and furans deserve renewed consideration.

Recently we reported our revisions to the original Shaub and Tsang (ST) model^{7,8}. We added radical-radical reactions for formation of PCDD and removed the erroneously fast reaction of chlorinated phenoxyl radicals with oxygen from the scheme. This modified (expanded) Shaub and Tsang model was developed based on the experimentally observed formation of PCDD from the oxidation of TCP in the presence of dry air⁵ and the oxidation of 2,4,6 - trichlorophenol in the presence of 4% O₂ and hexane¹⁰. Formation of PCDFs was also observed in the latter study; however, a full mechanistic or reaction kinetic model that accounted for its origin has not been previously reported.

In this manuscript, we report the development of a modified model for the purely gas-phase formation of polychlorinated dibenzofurans (PCDFs) that is based on the experimentally observed formation of PCDF from the oxidation of 2,4,6-trichlorophenol (TCP) in the presence of hexane¹⁰.

Methods and Materials

Table 1 presents our proposed reaction kinetic model for the gas-phase formation of PCDDs and PCDFs. It combines the PCDD formation sub-model (rxns 1-13) discussed elsewhere ⁷ and a new additional PCDF formation sub-model (rxns 14-30). The rate parameters for the reactions in the PCDD sub-model were the same as in our previous model ⁷ with the exception of the activation energy of rxn1 (as well as for the similar reactions 15, 28) which was reduced by ~ 5 kcal/mol to 81.5 kcal/mol. This reduction is based on the new suggestions reported in the literature ¹¹ as well as on our own *ab initio* calculations for o- and p-chlorophenols.

We focus our attention on the reactions of PCDF sub-model, rxns 14-30. Some of the reaction rate parameters were assigned based on the analogous reactions in the ST model (rxns 15, 17, 22, 25-27) ⁴⁻⁶ and our revised-ST model (rxns 16, 24) ⁷. High level *ab initio* calculations were utilized to calculate the activation energies most of the key reactions involved in the gas-phase formation of PCDF.

Table 1. Reaction kinetic core model for formation of PCDF from TCP

	Reaction Step	Rate Constant*
1	$\text{TCP} \rightarrow \text{TCP} + \text{H} \cdot$	$3.16 \times 10^{15} \exp(-81500/\text{RT})$
2	$\text{TCP} + \text{O}_2 \rightarrow \text{TCP} \cdot + \text{HO}_2 \cdot$	$2.0 \times 10^{12} \exp(-41400/\text{RT})$
3	$\text{TCP} \cdot + \text{TCP} \rightarrow \text{PD} + \text{Cl} \cdot$	$1.0 \times 10^{12} \exp(-26000/\text{RT})$
4	$\text{TCP} + \cdot\text{OH} \rightarrow \text{TCP} \cdot + \text{H}_2\text{O}$	10^{12}
5	$\text{PD} \rightarrow \text{D} + \text{HCl}$	$1.0 \times 10^{14} \exp(-45000/\text{RT})$
6	$\text{PD} + \cdot\text{OH} \rightarrow \text{PD} \cdot + \text{H}_2\text{O}$	10^{12}
7	$\text{TCP} \cdot \rightarrow \text{PR1}$	$2.5 \times 10^{12} \exp(-45000/\text{RT})$
8	$\text{TCP} \cdot + \cdot\text{OH} \rightarrow \text{PR2}$	10^{12}
9	$\text{TCP} \cdot + \text{TCP} \cdot \leftrightarrow \text{P-P}$	$k_8 = 8.64 \times 10^{11} \exp(1254/\text{RT})$ $k_{-8} = 3.16 \times 10^{15} \exp(-51000/\text{RT})$
10	$\text{P-P} \rightarrow \text{PD} \cdot + \text{Cl} \cdot$	$1.0 \times 10^{15} \exp(-44500/\text{RT})$
11	$\text{PD} \cdot \rightarrow \text{D} + \text{Cl} \cdot$	$1.0 \times 10^{12} \exp(-36500/\text{RT})$
12	$\text{D} + \cdot\text{OH} \rightarrow \text{PR3}$	10^{12}
13	$\text{D} \rightarrow \text{PR4}$	$3.16 \times 10^{15} \exp(-80000/\text{RT})$
14	$\text{TCP} + \cdot\text{H} \rightarrow \text{DCP} + \text{Cl} \cdot$	$1.5 \times 10^{13} \exp(-7500/\text{RT})$
15	$\text{DCP} \rightarrow \text{DCP} \cdot + \text{H} \cdot$	$3.16 \times 10^{15} \exp(-81500/\text{RT})$
16	$\text{DCP} + \text{O}_2 \rightarrow \text{DCP} \cdot + \text{HO}_2 \cdot$	$2.0 \times 10^{12} \exp(-41400/\text{RT})$
17	$\text{DCP} + \cdot\text{OH} \rightarrow \text{DCP} \cdot + \text{H}_2\text{O}$	10^{12}
18	$\text{DCP} \cdot \rightarrow \text{A} \cdot_{\text{keto}}$	1.0×10^{13}
19	$\text{A} \cdot_{\text{keto}} + \text{A} \cdot_{\text{keto}} \leftrightarrow \text{A}_{\text{keto}}-\text{A}_{\text{keto}}$	$k_{19} = 8.64 \times 10^{11} \exp(1254/\text{RT})$ $k_{-19} = 1.0 \times 10^{15} \exp(-43000/\text{RT})$
20	$\text{A}_{\text{keto}}-\text{A}_{\text{keto}} \rightarrow \text{Pr1}$	$1.0 \times 10^{13} \exp(-23000/\text{RT})$
21	$\text{A}_{\text{keto}}-\text{A}_{\text{keto}} (\text{interring}) \rightarrow \text{A}_{\text{keto}}-\text{A}_{\text{en}}$	$1.0 \times 10^{13} \exp(-37980/\text{RT})$
22	$\text{A}_{\text{keto}}-\text{A}_{\text{en}} + \cdot\text{OH} \rightarrow \text{A}_{\text{keto}}-\text{A}_{\text{en}} \cdot + \text{H}_2\text{O}$	10^{12}
23	$\text{A}_{\text{keto}}-\text{A}_{\text{en}} \cdot \rightarrow \text{DF} + \cdot\text{OH}$	$1.0 \times 10^{12} \exp(-39500/\text{RT})$
24	$\text{DCP} \cdot \rightarrow \text{Pr2}$	$2.5 \times 10^{12} \exp(-45000/\text{RT})$
25	$\text{DCP} \cdot + \cdot\text{OH} \rightarrow \text{Pr3}$	10^{12}
26	$\text{DF} + \cdot\text{OH} \rightarrow \text{Pr4}$	10^{12}
27	$\text{DF} \rightarrow \text{Pr5}$	$3.16 \times 10^{15} \exp(-80000/\text{RT})$
28	$\text{A}_{\text{keto}}-\text{A}_{\text{en}} \rightarrow \text{A}_{\text{keto}}-\text{A}_{\text{en}} \cdot + \text{H} \cdot$	$3.16 \times 10^{15} \exp(-81500/\text{RT})$
29	$\text{A}_{\text{keto}}-\text{A}_{\text{en}} + \text{O}_2 \rightarrow \text{A}_{\text{keto}}-\text{A}_{\text{en}} \cdot + \text{HO}_2 \cdot$	$2.0 \times 10^{12} \exp(-41400/\text{RT})$
30	$\text{A}_{\text{keto}}-\text{A}_{\text{en}} \rightarrow \text{DF} + \text{H}_2\text{O}$	$1.0 \times 10^{15} \exp(-59670/\text{RT})$

* - Rate Constants: $k = A \exp[-E_a (\text{cal/mol})/\text{RT}]$, cm^3 , mole, sec. Symbols: TCP and $\text{TCP} \cdot$ - 2,4,6-trichlorophenol and 2,4,6-trichlorophenoxy radical, respectively. PD and $\text{PD} \cdot$ - pre dioxin and radical, respectively. D- chlorinated dioxin, DCP and $\text{DCP} \cdot$ - 4,6 dichlorophenol and 4,6 dichlorophenoxy radical, respectively. $\text{A}_{\text{keto}}-\text{A}_{\text{keto}}$ - resonance structure of $\text{DCP} \cdot$ (keto form). $\text{A}_{\text{keto}}-\text{A}_{\text{keto}}$ and $\text{A}_{\text{keto}}-\text{A}_{\text{en}}$ - bis-keto and keto - enol dimer forms of $\text{DCP} \cdot$, respectively. DF - dibenzofuran. Pr or PR are not specified products.

Formation of 2,4-Dichlorophenol Molecule and Radical

Our previous model of the formation of PCDD from TCP resolves some of the impacts of hexane addition and demonstrates why the addition of hexane increases the yield of PCDD⁸. The hexane oxidation sub-model provides not only generation of main chain carriers such as hydroxyl radicals, but also hydrogen atoms. Hexane increases the probability of dichlorophenol formation by reaction $\text{H} \cdot + \text{TCP} \rightarrow \text{DCP} + \text{Cl} \cdot$. These facts suggest that the formation of

dichlorophenols (DCP) with at least one ortho- hydrogen is highly favorable during gas phase pyrolysis of a mixture TCP, O₂, and hexane in the middle- and high-temperature regimes where these reactions are energetically favorable.

Closed shell pathways to DF (rxn 21, 30)

The HF/3-21G *ab-initio* and AM1 calculations give activation energies of 37.98 and 38.71 kcal/mol, respectively, for conversion of the bis-keto to the keto-enol form through a transition state involving inter-ring H-transfer. From the keto-enol structure the barrier to DF formation according to HF/3-21G(d) is 59.67 kcal/mol

Open shell pathway to DF (reaction 23)

An activation energy of 39.65 kcal/mol is calculated (Fig.1) for the inter-ring displacement reaction 23. This activation energy is still relatively large and, in addition, requires abstraction of a hydrogen atom in reaction 22 for A_{keto}-A_{en}[•] to be formed.

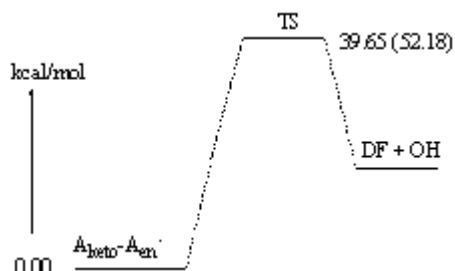
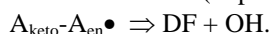


Fig.1 HF/3-21G and AM1 (in parenthesis) Energies for Rxn 23:



Thus the reaction 23 (and 22) as well as the unimolecular reaction 30 (and 21) appear to both contribute to DF formation.

Discussion

For the first time, a reaction kinetic mechanism for the formation of PCDF from chlorinated phenols has been developed with modest, but reasonable agreement with experimental results.

The core purely gas-phase scheme (rxns 1-30) provides agreement within a factor of 1.5-2 between experimental and calculated yields of PCDD/Fs using the REACT kinetic program¹³.

Reasonable agreement between calculated and experimental yields of PCDF are achieved above 950 K using this PCDF formation pathway in combination with excluding reactions of chlorinated phenoxy radicals with oxygen as was previously done in our previous model of PCDD formation^{7,8}. The model does not satisfactorily explain PCDF formation at low temperatures. A question is raised concerning the contribution of surfaces or reactive impurities in the mechanism of PCDD/F formation at low temperatures.

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