

DEVELOPMENT OF EXPANDED AND CORE KINETIC MODELS FOR THE GAS PHASE FORMATION OF DIOXINS FROM CHLORINATED PHENOLS.

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INTRODUCTION

The homogeneous, gas-phase mechanisms of PCDD/F formation have been generally considered to be unimportant since the publication of a simplified kinetic model of formation of PCDD from chlorinated phenols by Shaub and Tsang (ST)¹. The ST model predicted PCDD formation rates and yields that were several orders of magnitude less than those observed for full-scale systems. As a result, most research efforts have been directed towards surface catalyzed formation from various precursors discussed in the literature. It is now known that the potential contributions of the gas-phase pathways to dioxin formation were underestimated by the reaction kinetic ST model²⁻⁴. There are two principal reasons for this underestimation.

First, the self-reaction of chlorinated phenoxy radicals⁵ was not included in the ST model. As early as 1989⁵ and later⁶, it was proposed that radical-radical recombination reactions of the carbon-centered mesomers (resonance structures) of chlorinated phenoxy radicals dominated over radical-molecule displacement reactions in the gas-phase formation of PCDD/F.

Second, the rate of reaction of O₂ with 2,4,6 trichlorophenoxy radicals was overestimated in the original ST model. At the time of publication, there were no directly related experimental measurements reported in the literature, and the rate was estimated based on the typical rate of reaction of O₂ with alkyl radicals, viz. $\geq 1.0 \times 10^{11} \text{ cm}^3/\text{mol}\cdot\text{s}$. The lesser reactivity of phenoxy radicals due to their resonance stabilization was not recognized.

Recently, the reaction of phenoxy with O₂ has been shown to be $< 1.2 \times 10^6 \text{ cm}^3/\text{mol}\cdot\text{s}$ for temperatures up to 500 K^{7,8}. These results mean that chlorinated phenoxy radicals are likely to be consumed at the same or even slower rates than unchlorinated phenoxy radicals and are more available to react to form dioxins than originally believed.

Based on this newly available information, we have revised the original ST model^{9,10} and report here a new approach concerning the gas-phase formation mechanism of PCDD. This modified model has been developed based on the experimentally observed formation of PCDD from the oxidation of 2,4,6 - trichlorophenol at different experimental conditions^{2,11}

Methods and Materials

Because of large uncertainties in the kinetic parameters of chlorinated species and for simplicity we included a limited numbers of reactions in the proposed model. We have added radical-radical reactions for formation of PCDD and removed the fast reaction of chlorinated phenoxy radicals with oxygen from the ST scheme. Three sub-models were included in the model. An expanded, 24 step core model was developed for the homogeneous oxidation of 2,4,6-TCP and formation of the

two TCDD isomers. This sub-model included chain initiation reactions of chlorophenoxy radicals, propagation steps by atoms O, H, Cl and OH radicals as main chain carriers, radical-radical, and radical-molecule and decomposition reactions of chlorinated phenoxy radicals, and a few decay reactions of PCDD.

One additional initiation step, rxn 1', $C_6H_3Cl_3O \leftrightarrow C_6H_2Cl_3O + H$ was added to account for possible low energy initiation (such as surface or impurity initiation) of the otherwise homogeneous reaction sequence. The values of E_a and A were modified from the homogeneous values to reflect the lower activation energy and A-factors of surface-mediated reactions ($k_1=3.2 \cdot 10^{13} \exp(-66500/RT) \text{ s}^{-1}$). Next 25-45 reactions were characteristic reactions of H, O, OH from hydrogen oxidation classic scheme as well as reactions of Cl atoms, conversion of CO and HCl. In third sub-model the hexane oxidation well known reactions (46 - 70) were added for the oxidation of 2,4,6-TCP in the presence of hexane. Forward rate parameters were obtained from the literature when available. However, few elementary reactions of chlorinated aromatic hydrocarbons have been subjected to detailed study.

Reverse rate parameters were determined from the thermochemistry of the reactions in combination with detailed balancing. The thermochemistry of 30 chlorinated species (stable molecules, radicals and intermediates) were calculated¹². The fundamental vibrations of the species and their moments of inertia were calculated using the PM3 and AM1 semi-empirical methods. In a few cases DFT/B3LYP/6-31G* and HF/6-31G* *ab-initio* calculations were performed or extracted from the literature. Enthalpies of formation were obtained from the literature, calculated using Benson's group additivity method, or estimated using various other techniques. The calculated thermochemical parameters were input to the CHEMKIN kinetic modeling code which calculated reaction energies and reverse rate parameters using the forward rate parameters that were provided as a separate input to CHEMKIN.

For numerical solution the REACT Kinetic program was used¹³.

Results and Discussion

Comparison of modeling calculations with experimental work Sidhu and Dellinger, 1997

Input conditions for the homogeneous oxidation of 2,4,6-TCP were; [2,4,6-TCP] = 15 ppm, [O₂]=4% in N₂ as carrier gas and a reaction time of 2.0 sec in the presence of hexane (300 ppm)¹¹. Modeling calculations were performed in the temperature range of 850-1200 K in 50 K temperature increments.

A satisfactory agreement between calculated and experimental yields of TCDD can be achieved by regulating the concentration of 2,4,6-TCP through reasonable assignments of the rate parameters for homogeneous initiation, propagation, and termination reactions (Fig.1).

The results of our model are not effected by inclusion of the reaction phenoxy + O₂ ($k \sim 1.2 \times 10^6 \text{ cm}^3/\text{mol}\cdot\text{s}$). Increasing the rate coefficient by two orders of magnitude only slightly decreases the TCDD yield, and it is not until the value of $10^{11} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ is used that the yields of TCDD decrease to the four orders of magnitude lower yield predicted by the ST-model. The reaction of 2,4,6 TCP with O₂ was an important sink of 2,4,6 TCP in this early model, and the higher rate of consumption of 2,4,6 TCP gave unrealistically low prediction of the yields of PCDD via gas-phase pathways.

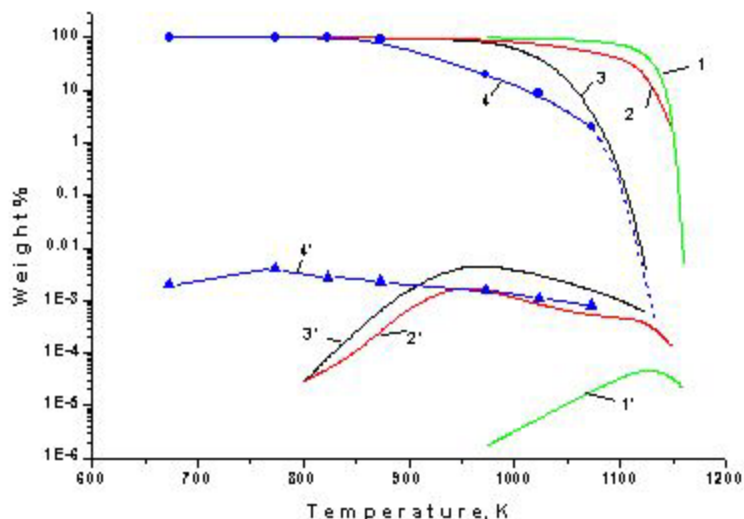


Fig.1. Comparison of gas phase modeling and experimental results for the oxidation of 15 ppm 2, 4, 6 - trichlorophenol in 4% O₂ in N₂, and 300 ppm hexane in a 1.0 cm i.d. fused silica flow reactor for a reaction time of 2.0 s¹¹

Curves 1 and 1'; Model results for 2, 4, 6 - TCP decomposition and 1, 3, 6, 8 TCDD formation via homogeneous, gas-phase reactions *without* hexane. (Reactions 1-45, excluding reaction 1').

Curves 2 and 2'; Model results for 2, 4, 6 - TCP decomposition and 1, 3, 6, 8 TCDD formation via homogeneous, gas-phase reactions *with* hexane. (Reactions 1-70, excluding reaction 1').

Curves 3 and 3'; Model results for 2, 4, 6 - TCP decomposition and 1, 3, 6, 8 TCDD formation via homogeneous, gas-phase reactions *with* hexane and *with* a low energy initiation. (Reactions 1-70, including reaction 1').

Curves 4 and 4'; Experimental results for 2, 4, 6 - TCP and 1, 3, 6, 8 TCDD, respectively¹¹.

Comparison of modeling calculations with experimental work Sidhu and Dellinger, 1995.

Model calculations were carried out in the temperature range 750-1200 K with the same model reactions discussed briefly above without hexane sub-model oxidation scheme (reactions 46-70). The input conditions for CHEMKIN modeling were: [TCP] = 3.478 x 10⁻⁷ mol/l, [O₂] = 20% in dry air, with a reaction time of 2 sec². Solution of the scheme leads to relatively good agreement between experimental and calculated yields analogous to the picture in Fig.1.

REACT Solution of the Core Model

We next reduced and analyzed a core, ST-like kinetic model with new reactions and rate parameters (Table 1). The goal was straightforward: to determine whether a simple ST like model can predict the yields of gas-phase formation of PCDD concerning the results². A simple ordinary differential equation system solver - REACT Kinetic Program¹³ was used.

Table 1.
Core Reaction Kinetic Model for Formation of PCDD from TCP

No	Reaction Step	Rate Constant*	Units
0	$P \rightarrow P + H$	$3.2 \cdot 10^{15} \exp(-86500/RT)^a$	s^{-1}
1	$P + O_2 \rightarrow P \cdot + H_2O$	$2 \cdot 0 \cdot 10^{12} \exp(-41400/RT)^b$	$cm^3 \cdot mol^{-1} \cdot s^{-1}$
2	$P \cdot + P \rightarrow PD + Cl$	$10^{12} \exp(-26000/RT)^a$	$cm^3 \cdot mol^{-1} \cdot s^{-1}$
3	$P + OH \rightarrow P \cdot + H_2O$	$10^{12} \cdot a$	$cm^3 \cdot mol^{-1} \cdot s^{-1}$
4	$PD \rightarrow D + HCl$	$10^{14} \exp(-45000/RT)^a$	s^{-1}
5	$PD + OH \rightarrow PD \cdot + H_2O$	$10^{12} \cdot a$	$cm^3 \cdot mol^{-1} \cdot s^{-1}$
6	$P \cdot \rightarrow Pr$	$2.5 \cdot 10^{12} \exp(-45000/RT)^c$	s^{-1}
7	$P \cdot + OH \rightarrow Pr$	$10^{12} \cdot a$	$cm^3 \cdot mol^{-1} \cdot s^{-1}$
8	$P \cdot + P \cdot \leftrightarrow P-P$	$k_8 = 8.64 \cdot 10^{11} \exp(1254/RT)^d$ $k_{-8} = 3.16 \cdot 10^{15} \exp(-51000/RT)^c$	$cm^3 \cdot mol^{-1} \cdot s^{-1}$ s^{-1}
9	$P-P \rightarrow PD \cdot + Cl \cdot$	$10^{15} \exp(-44500/RT)^c$	s^{-1}
10	$PD \cdot \rightarrow D + Cl$	$10^{12} \exp(-36500/RT)^c$	s^{-1}
11	$D + OH \rightarrow Pr$	$10^{12} \cdot a, e$	$cm^3 \cdot mol^{-1} \cdot s^{-1}$
12	$D \rightarrow Pr$	$10^{15.5} \exp(-80000/RT)^a$	s^{-1}
13	$P \cdot + O_2 \rightarrow Pr$	$1.2 \cdot 10^{6 \cdot 1}$	$cm^3 \cdot mol^{-1} \cdot s^{-1}$

* - Rate Constants $k = A \exp[-E_a \text{ (cal/mol)}] / RT]$, Symbols denoted P, P·, PD, D as in ref. ¹, P-P – recombination product (ether type) of P· radicals.

^a – ref. ¹, ^{b-f} – see ⁹, The concentration of hydroxyl radicals (mole/l) was calculated by: $[OH] = 10^{-1.7} \exp(-35.0 \text{ kcal/mol} / RT)^1$

The modeling calculations of the core model using REACT yielded similar results to that of CHEMKIN for the extended model. The dioxin yield decreases slowly at temperatures range from 850 to 1000 K, and the average yield (~0.03 weight %) is actually closer to the experimental yield of dioxin (~0.05 weight %).

The results of this study indicate that high-temperature, gas-phase reactions of chlorinated phenols that contain an ortho-chlorine will form polychlorinated dibenzo-p-dioxins (PCDDs) in yields ~ 4 -5 orders of magnitude greater than believed based on the previous modeling results.

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