

# Prediction of polychlorinated dibenzofuran congener distribution from gas-phase phenol condensation pathways

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## Abstract

A model for predicting the distribution of dibenzofuran and polychlorinated dibenzofuran (PCDF) congeners from a distribution of phenols was developed. The model is based on a simplified chemical mechanism. Relative rate constants and reaction order with respect to phenol precursors were derived from experimental results using single phenols and equal molar mixtures of up to four phenols. For validation, experiments were performed at three temperatures using a distribution of phenol and 19 chlorinated phenols as measured in municipal waste incinerator exhaust gas. Comparison of experimental measurements and model predictions for PCDF isomer distributions and homologue pattern shows agreement within measurement uncertainty. The *R*-squared correlation coefficient exceeds 0.9 for all PCDF isomer distributions and the distribution of PCDF homologues. These results demonstrate that the distribution of dibenzofuran and the 135 PCDF congeners from gas-phase condensation of phenol and chlorinated phenols can be predicted from measurement of the distribution of phenol and the 19 chlorinated phenol congeners.

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**Keywords:** Polychlorinated dibenzofuran; Chlorinated phenols; Gas-phase PCDF formation

## 1. Introduction

Polychlorinated dibenzo-*p*-dioxin (PCDD) and dibenzofuran (PCDF) byproducts are formed in combustion systems by variety of mechanisms. In combustion exhaust gas prior to the air pollution control equipment, dibenzofuran and PCDF concentrations have been found to be greater than PCDD concentrations (Yamamoto et al., 1989; Wikstrom and Marklund, 2000). Less chlorinated PCDF congeners, which are most

abundant, may be chlorinated on particle surfaces at lower temperatures (Weber and Sakurai, 2001; Zimmermann et al., 2001; Yasuhara et al., 2003). In a detailed study of incinerator emissions, approximately 50% of the PCDF found in stack gas were found at the post-combustion chamber outlet in the temperature range 700–900 °C (Blumenstock, 2002). One possible source of these byproducts is the gas-phase condensation of phenol and chlorinated phenol congeners. PCDF product distributions have been used to infer the formation mechanism (Wehrmeier et al., 1998). PCDF distributions from chlorinated phenols depend on the distribution of phenol precursors and on the relative rates of formation from different phenol pairs. To be of use as fingerprints in this way, a model is needed that predicts the PCDF congener distribution from a distribution of phenols. In

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combustion systems, PCDFs can be produced by several different mechanisms. The complete distribution of PCDF congeners provides a rich fingerprint that can be used to identify the formation mechanism. In this paper, a model is developed and tested for predicting the distribution of PCDFs formed by gas-phase phenol condensation pathways. Such a tool is needed to help identify PCDF formation pathways in combustion systems and to develop more effective control strategies. A second motivation for this work is that the development of a predictive model might help to reduce the number of measurements necessary to characterize PCDF emissions. Extensive field monitoring of such a large number of congeners present in very low concentration is extremely time-consuming and expensive.

A detailed chemical mechanism of gas-phase PCDF formation by condensation of phenols was first proposed by Born et al. (1989). The mechanism is shown in Fig. 1 for 3-chlorophenol. Carbon-carbon coupling of phenoxy radicals at unchlorinated *ortho* sites followed by enolization results in the formation of a *o,o*-dihydroxybiphenyl (DOHB) intermediate. Subsequent elimination of water leads to the PCDF product. All direct PCDF products from phenol precursors are shown in Table 1. Note that 2,6 chlorinated phenol precursors are not included as these do not directly produce PCDF products.

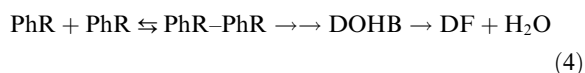
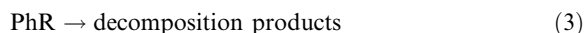
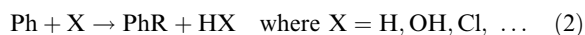
Dibenzofuran and each of the 135 PCDFs are produced by a unique coupling of a phenoxy radical pair. (Note: In this paper, PCDF refers to all chlorinated dibenzofurans, from mono through octa.) Factors controlling the relative rate of coupling of phenoxy radicals, i.e. electronic, steric, and statistical effects associated with chlorine substitution pattern, have been studied in our laboratory (Yang et al., 1998; Nakahata and Mulholland, 2000; Mulholland et al., 2001). Isomer distri-

butions vary little as a function of temperature, while total product yield and, to a lesser extent, homologue distribution can vary greatly (Schramm et al., 1996; Mulholland and Ryu, 2001). Maximum PCDF product yields of about 1% (phenol conversion) occur between 550 and 700 °C (Nakahata, 2001). Presented here is a model that predicts the PCDF congener distribution from a distribution of phenols, applicable to conditions that favor gas-phase PCDF formation. The model is developed based on a simplified chemical mechanism. Relative rate constants and reaction order are derived from the experimental results cited above in which single phenols and equal molar mixtures of up to four phenols were studied.

## 2. Methods

### 2.1. Model

The formation of dibenzofuran (DF) from phenol (Ph) in combustion gas exhaust is summarized by the following set of reactions:



Phenoxy radicals (PhR) produced by reactions (1) and (2) can either be consumed by decomposition (reaction (3)), such as CO elimination, or by dimerization which leads to the formation of DF via the *o,o*-dihydroxybi-

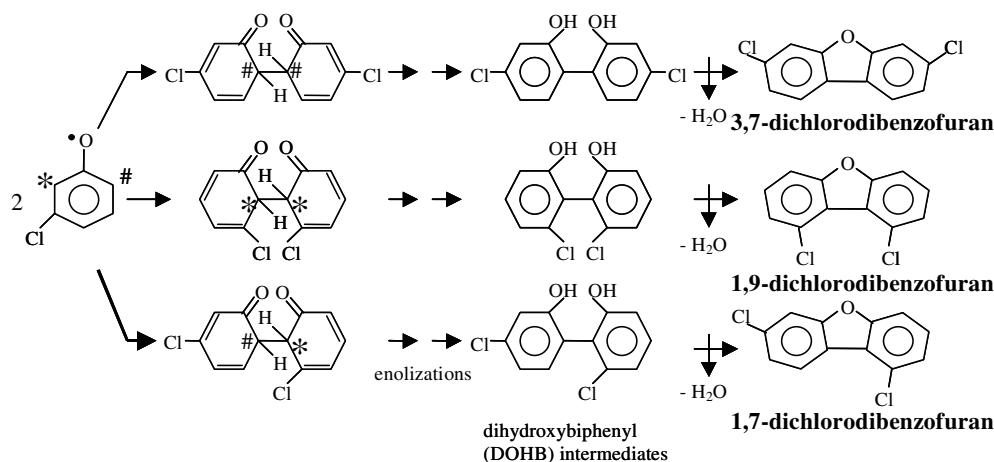


Fig. 1. Gas-phase PCDF formation pathways from 3-chlorophenol.

Table 1  
PCDF congeners from phenol precursors<sup>a</sup>

Precursor	Ph	2-CP	3-CP	4-CP	2,3-DCP	2,4-DCP	2,5-DCP	3,4-DCP	3,5-DCP	2,3,4-T <sub>3</sub> CP	2,3,5-T <sub>3</sub> CP	2,4,5-T <sub>3</sub> CP	3,4,5-T <sub>3</sub> CP	2,3,4,5-T <sub>4</sub> CP
Ph	DF													
2-CP	4	46												
3-CP	1, 3	16, 36	17, 19, 37											
4-CP	2	26	18, 27	28										
2,3-DCP	34	346	347, 349	348	3467									
2,4-DCP	24	246	247, 249	248	2467	2468								
2,5-DCP	14	146	147, 149	148	1467	1468	1469							
3,4-DCP	12, 23	126, 236	127, 129, 237, 239	128, 238	1267, 2367	1268, 2368	1269, 1478	1278, 1289, 2378						
3,5-DCP	13	136	137, 139	138	1367	1368	1369	1279, 1378	1379					
2,3,4-T <sub>3</sub> CP	234	2346	2347, 2349	2348	23467	23468	23469	23478, 23489	23479	234678				
2,3,5-T <sub>3</sub> CP	134	1346	1347, 1349	1348	13467	13468	13469	13478, 13489	13479	134678	134679			
2,4,5-T <sub>3</sub> CP	124	1246	1247, 1249	1248	12467	12468	12469	12478, 12489	12479	124678	124679	124689		
3,4,5-T <sub>3</sub> CP	123	1236	1237, 1239	1238	12367	12368	12369	12378, 12389	12379	123678	123679	123689	123789	
2,3,4,5-T <sub>4</sub> CP	1234	12346	12347, 12349	12348	123467	123468	123469	123478, 123489	123479	1234678	1234679	1234689	1234789	OCDF

<sup>a</sup> Phenols with both *ortho* sites chlorinated do not produce PCDF.

phenyl (DOHB) intermediate (reaction sequence (4)). Assuming pseudo-state state concentrations of intermediates in reaction sequence (4), the rate of DF formation ( $R_{DF}$ ) is given as follows:

$$R_{DF} = k_{4,eff} [PhR]^2 \tag{5}$$

The overall rate of DF formation from phenol is defined as follows:

$$R_{DF} = k_{eff} [Ph]^n \tag{6}$$

Here,  $k_{eff}$  is an effective rate constant and  $n$  is the order of reaction with respect to phenol. The value of  $n$  is expected to lie between 1 and 2, as discussed below.

In the limit that phenoxy radical is consumed predominantly by reaction (3), the pseudo-steady state approximation for PhR yields the following:

$$d[PhR]/dt = 0 = R_1 + R_2 - R_3 \tag{7}$$

$$[PhR] = \{(k_1 + k_2)/k_3\} [Ph] \tag{8}$$

Plugging Eq. (8) into Eq. (5), the order with respect to phenol ( $n$ ) is found to be 2. In the other limit in which the predominant phenoxy radical consumption pathway is reaction (4), the pseudo-steady state approximation for PhR yields the following:

$$d[PhR]/dt = 0 = R_1 + R_2 - 2R_{4,eff} \tag{9}$$

$$[PhR] = \{\frac{1}{2}(k_1 + k_2)/k_{4,eff}\}^{1/2} [Ph]^{1/2} \tag{10}$$

Plugging Eq. (10) into Eq. (5), the order with respect to phenol ( $n$ ) is found to be 1.

Extending Eq. (6) to any of the 135 PCDF congeners, the overall rate of formation of PCDF congener  $i$  is written as follows:

$$R_i = k_{eff,i} [Ph1_i]^{n/2} [Ph2_i]^{n/2} \tag{11}$$

Here, Ph1 and Ph2 are the pair of phenol precursors. For simplicity, we assume that the order with respect to each phenol reactant is the same ( $n/2$ ). Without this simplification, 270 values of  $n$  would be needed; the validity of this assumption will be evaluated.

The relative rate of formation of PCDF congener  $i$  to PCDF congener  $j$  is given as follows:

$$R_{rel,i/j} = [PCDF_i]/[PCDF_j] \\ = k_{rel,i/j} \{ [Ph1_i][Ph2_i]/([Ph1_j][Ph2_j]) \}^{n/2} \tag{12}$$

Each PCDF congener is formed from only one pair of phenol precursors. To calculate the distribution of PCDF congeners produced from a known distribution of phenol reactants, 135 relative rate constants,  $k_{rel,i/j}$ , and the reaction order,  $n$ , are needed. Values for these model parameters are derived from flow reactor experiments performed with single phenol reactants and equal

molar mixtures of up to four phenol reactants (Yang et al., 1998; Nakahata and Mulholland, 2000; Mulholland et al., 2001). Over ranges in temperature of 500–800 °C, residence time of 0.5–10 s, and oxygen concentration of 0–8%, the distribution of PCDF congeners varied little for a given reactant or mixture of reactants, even though the total PCDF yield varied by several orders of magnitude. Therefore, to a first approximation, one set relative rate constants and reaction order can be used for these conditions.

### 3. Experimental

Experiments were performed using a distribution of phenol and the 19 chlorinated phenols typical of municipal waste incinerator exhaust gas to validate our model. For this distribution, the data of Weber and Hagenmaier (1999) were used, as shown in Fig. 2. Phenol is by far the major reactant, representing over 90% of the total phenol input. Of the chlorinated phenols, the major congeners are 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, and pentachlorophenol. This chlorinated phenol congener pattern is typical of that found in incinerators in which the chlorinated phenols are formed by chlorination of phenol.

Preliminary experiments were conducted at 600 °C using an equal molar mixture of phenol, 4-chlorophenol, and 2,4-dichlorophenol to assess the reaction order  $n$ . These three phenols were chosen because they are present in high concentration and have unsubstituted *ortho* sites needed for PCDF formation. Experiments were then carried out at 600, 650, and 700 °C using the mixture of phenol and 19 chlorinated phenols described above to validate the model. Distributions of PCDF congeners produced by this mixture of 20 phenols were measured

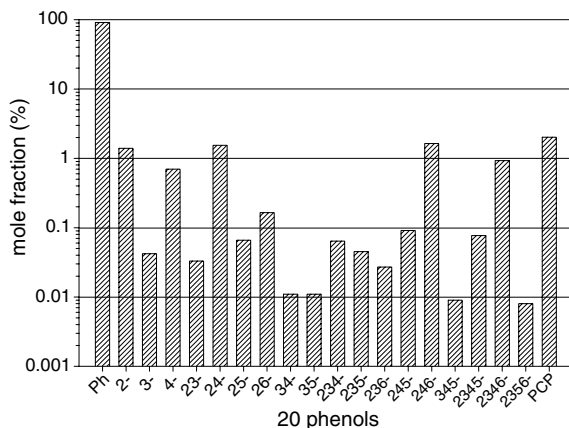


Fig. 2. Distribution of phenol and 19 chlorinated phenols used in this study.

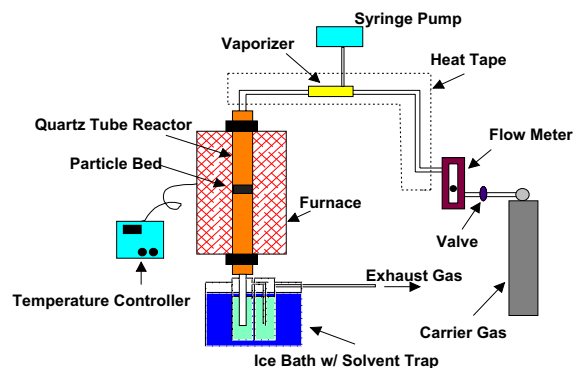


Fig. 3. Experimental apparatus.

and compared to model predictions. The experimental apparatus is shown in Fig. 3. Experiments were conducted in an electrically heated, quartz tube flow reactor, 40 cm in length and 1.7 cm in diameter. The phenols were dissolved in benzene and injected by syringe pump into a heated glass vessel. Reactant vapor was transported to the reactor by 92% nitrogen, 8% oxygen gas stream. Total feed rate of phenol and 19 chlorinated phenols was  $3.18 \times 10^{-5}$  mol/min. This resulted in a reactor feed stream comprised of molar concentrations of  $N_2$ ,  $O_2$ , phenols, and benzene of 91%, 7.9%, 0.7%, and 0.4%, respectively. The total equivalence ratio was 0.9. Reactant vapor was introduced to the isothermal reactor with a total residence time of nominal 4 s. In a baseline experiment with benzene only, a small amount of phenol was formed, but no DF was detected.

Experiments were run for approximately 4 h, with the entire product gas stream rapidly quenched and condensable gases collected in an ice-cooled dichloromethane trap. Sample solutions were filtered and then analyzed by GC/MS (HP 6890 series gas chromatograph with model 5973 mass selective detector) equipped with a HP-5MS capillary column with length 30 m, i.d. 0.25 mm and phase 0.25  $\mu$ m film of crosslinked 5% PH ME siloxane (HP Part No. 19091S-433). The GC analysis was carried out with splitless injection and He as carrier gas with following temperature program: isothermal at 38 °C for 2 min; 3 °C/min ramp to 180 °C and held 2 min; 5 °C/min ramp to 250 °C and held 5 min; 6 °C/min ramp to 280 °C and held 3 min; 2 °C/min ramp to 300 °C. The mass spectrometer was operated in selected ion mode (SIM) for quantification. Preliminary identification of PCDF products was based on published relative retention times for similar columns (Hale et al., 1985; Ryan et al., 1991). Final identification was based on available standards and gas-phase synthesis experiments from single precursors and precursor pairs. All four monochlorodibenzofuran (MCDF) isomers were separated, as were thirteen of sixteen dichlorodibenzofurans (DCDFs), 25 of 28 trichlorodibenzofurans ( $T_3$ CDFs),

34 of 38 tetrachlorodibenzofurans (T<sub>4</sub>CDFs), 22 of 28 pentachlorodibenzofurans (P<sub>5</sub>CDFs), 12 of 16 hexachlorodibenzofurans (H<sub>6</sub>CDFs), all four heptachlorodibenzofurans (H<sub>7</sub>CDFs), and octachlorodibenzofuran (OCDF). A universal response factors was used (DF response factor).

## 4. Results and discussion

### 4.1. Derivation of reaction order and relative rate constants

Preliminary experiments were performed at 600 °C using an equal molar mixture of phenol, 4-chlorophenol (4-CP), and 2,4-dichlorophenol (2,4-DCP) in benzene at four dilutions to estimate reaction order *n*. The expected products from these phenols (see Table 1) were formed. In all experiments, DF was produced in greatest amount, indicating that chlorine substitution decreases the rate of phenoxy radical coupling. Reaction orders for PCDF product formation obtained from these experiments ranged from 1.2 to 2.0, as shown in Table 2. Here, we use an average value of 1.6 for the model. This compares with a reaction order of PCDD formation from 2,4,6-T<sub>3</sub>CP of 1.3 measured by Sidhu et al. (1995). Overall, the reaction order increases as phenol chlorine content increases, suggesting that suppression of phenoxy radical coupling (Eq. (4)) due to chlorine substitution results in phenoxy radical decomposition (Eq. (3)) becoming the dominant phenoxy radical consumption channel.

Published results from flow reactor experiments single phenol reactants and equal molar mixtures of up to four phenol reactants (Yang et al., 1998; Nakahata and Mulholland, 2000; Mulholland et al., 2001) were used to obtain 40 independent relative rate constants for determining ratios of PCDF products (Eq. (12)). The other 95 relative rate constants are determined from similarities in the molecular structure, considering reaction pathway factors such as steric, statistical, and electronic factors. The relative rate constants and reaction groupings are listed in Table 3. For the rows in which more than one set of reactions are represented, the PCDF products are

not listed. The reader should refer to Table 1 for these products. The basis for these groupings is discussed next, and then an example calculation is provided.

The relative rate constants in Table 3 are listed in six groups. In group 1, eight relative rate constants measured for PCDF congeners with different numbers of Cl atoms are presented. Phenol is the most potent PCDF precursor. Overall, two conclusions can be drawn. First, PCDF formation is favored from less chlorinated phenols. Steric and electronic effects associated with chlorine substitution suppress phenoxy radical dimerization. Second, PCDF formation is favored from phenols with chlorine substitution at *meta* (3 and 5) positions rather than *ortho* (2) and *para* (4) positions, likely due to an electronic effect that favors phenoxy radical dimerization at sites *ortho/para* to chlorine substitution.

In group 2, six relative rate constants measured for PCDF isomers formed from phenols with different numbers of Cl atoms are presented. In general, PCDF isomers formed from phenols with different numbers of Cl atoms are favored over isomers formed from phenols with similar numbers of Cl atoms. This may be due to steric effects associated with a parallel plane approach geometry of reacting phenoxy radicals, as proposed by Nakahata and Mulholland (2000). As in group 1, phenols with chlorine at *meta* positions are observed to produce higher PCDF yields than phenols with chlorine at *ortho* and *para* positions.

In group 3, relative rate constants for different PCDF isomers formed from condensation of the same phenol pairs are presented. 3-Chlorophenol and/or 3,4-dichlorophenol produce multiple isomers due to their having both *ortho* sites unchlorinated and their lack of symmetry. There are relative rate constants for 31 PCDF formation reactions represented in group 3. For example, the relative rate constant for PCDF formation reactions of 3-chlorophenol at its 2 versus 6 positions with phenol, 2- and 4-chlorophenol, 2,3- and 2,4-dichlorophenol, and 2,3,4-trichlorophenol are all estimated to be 0.8. This result is based on experimental data with the three monochlorophenol reactants. Reaction at the 6 position of 3-chlorophenol is favored over reaction at the 2 position, whereas reaction at the 2 position of 3,4-dichlorophenol is favored over reaction at the 6 position except when 1,9 CDF isomers are formed.

In groups 4, 5, and 6, relative rate constants are presented for formation of various PCDF isomers from trichlorophenol, dichlorophenol, and monochlorophenol reactants, respectively. Again, these values demonstrate that PCDF isomers from phenols with chlorine at *meta* sites are favored over PCDF isomers from phenols with chlorine at *ortho* and *para* sites, and that formation PCDF isomers with 1,9 sites chlorinated is suppressed.

As an example of how to use Table 3, consider the distribution of the 28 T<sub>3</sub>CDF isomers. A total of 28

Table 2  
Reaction order *n* from a mixture of phenol, 4-chlorophenol, and 2,4-dichlorophenol

Phenol reactants	PCDF products	Reaction order <i>n</i>
Phenol + phenol	DF	1.2
Phenol + 4-CP	2-MCDF	1.6
Phenol + 2,4-DCP	2,4-DCDF	1.5
4-CP + 4-CP	2,8-DCDF	1.8
4-CP + 2,4-DCP	2,4,8-T3CDF	1.9
2,4-DCP + 2,4-DCP	2,4,6,8-T4CDF	2

Table 3  
Relative rate constants used in Eq. (12)

Phenol reactant pairs ( $1i + 2i/1j + 2j$ )	PCDF products ( $i/j$ ) <sup>a</sup>	$k_{rel,i/j}$
<i>1. PCDF congeners with different numbers of Cl atoms</i>		
Ph + 2/Ph + Ph	4/DF	0.3
Ph + 23/Ph + 2	34/4	1.9
Ph + 234/Ph + 23	234/34	0.6
Ph + 2345/Ph + 234	1234/234	1.8
2 + 2345/Ph + 2345	12346/1234	0.15
23 + 2345/2 + 2345	123467/12346	1.2
234 + 2345/23 + 2345	1234678/123467	0.1
2345 + 2345/234 + 2345	OCDF/1234678	0.1
<i>2. PCDF isomers from precursors with different numbers of Cl atoms</i>		
2 + 2/Ph + 23	46/34	0.05
2 + 23/Ph + 234	346/234	0.3
2 + 234/Ph + 2345	2346/1234	0.05
23 + 23/2 + 234	3467/2346	1.5
23 + 234/2 + 2345	23467/12346	0.5
234 + 234/23 + 2345	234678/123467	0.2
<i>3. PCDF isomers from same phenol pair</i>		
3 + 3	17/37	2
	19/37	0.4
34 + 34	1278/2378	2
	1289/2378	0.4
3 + 34	127/237	2
	239/237	2
	129/237	0.4
3 + x, where x = Ph, 2, 4, 23, 24, 234	rxn at 2- vs. 6-site of 3-CP	0.8
3 + x, where x = 25, 35, 235, 245, 345, 2345	rxn at 2- vs. 6-site of 3-CP	0.2
34 + x, where x = Ph, 2, 4	rxn at 2- vs. 6-site of 3,4-DCP	3
34 + x, where x = 23, 24, 234	rxn at 2- vs. 6-site of 3,4-DCP	1.5
34 + x, where x = 25, 35, 235, 245, 345, 2345	rxn at 2- vs. 6-site of 3,4-DCP	0.4
<i>4. PCDF isomers from trichlorophenols</i>		
345 + x/245 + x, where x = Ph, 2, 3, 4, 23, 24, 25, 34, 35, 234, 235, 245, 345, 2345		4
245 + x/235 + x, where x = Ph, 2, 3, 4, 23, 24, 25, 34, 35, 234, 235, 245, 2345		0.5
235 + x/234 + x, where x = Ph, 2, 3, 4, 23, 24, 34, 234		2
235 + x/234 + x, where x = 25, 35, 235, 2345		0.4
<i>5. PCDF isomers from dichlorophenols</i>		
35 + x/25 + x, where x = Ph, 2, 3, 4, 23, 24, 25, 34, 35, 234, 2345		3
34 + x/23 + x, where x = Ph, 2, 3, 4, 23, 24, 25, 34, 234, 2345	rxn at 6-site of 3,4-DCP	1.2
25 + Ph/23 + Ph	14/34	1
25 + x/23 + x, where x = 2, 3, 4, 23, 24, 234		0.7
25 + x/23 + x, where x = 25, 2345		0.2
24 + Ph/23 + Ph	24/34	0.5
24 + x/23 + x, where x = 2, 3, 4, 23, 24, 234		0.3
24 + 2345/23 + 2345	123468/123467	0.1
<i>6. PCDF isomers from monochlorophenols</i>		
4 + x/2 + x, where x = Ph, 2, 3, 4, 23, 234, 2345		3
3 + x/2 + x, where x = Ph, 2, 3, 23, 234, 2345	rxn at 6-site of 3-CP	3

<sup>a</sup> In rows in which more than one reaction pathway are represented, refer to Table 1 for PCDF products.

relative rate constants are needed. From group 1, the rate constant of 2,3,4-T<sub>3</sub>CDF formation relative to 3,4-DCDF is shown to be 0.6. This provides a link to

congeners in other homologues From group 2, the rate constant for 3,4,6-T<sub>3</sub>CDF formation relative to 2,3,4-T<sub>3</sub>CDF formation is given as 0.3. This provides a link

between isomers with three chlorine substituents on one ring to isomers with two chlorine substituents on one ring and one on the other. From group 3, ratios of the 1,2,7-, 2,3,9-, and 1,2,9-T<sub>3</sub>CDF rate constants to the 2,3,7-T<sub>3</sub>CDF rate constant are given as 2, 2, and 0.4, respectively. Also in group 3, rate constants for combination of 3-CP at the 2-carbon site relative to those for combination at the 6-carbon site are given for combinations of 3-CP with 2,3-, 2,4-, 2,5-, and 3,5-DCP. Similarly, rate constants for combination of 3,4-DCP at the 2-carbon site relative to those for combination at the 6-carbon site are given for combinations of 3,4-DCP with 2- and 4-CP. These group 3 values represent relationships between isomers from the same phenol pair. Of the remaining 17 relative rate constants that are needed,

three come from group 4, 12 come from group 5, and two from group 6. These involve combinations that include T<sub>3</sub>CP, DCP, and CP precursors.

A simple, algebraic model was developed that uses these relative rate constants, the reaction order of 1.6, and the distribution of phenol and the chlorinated phenols as inputs to predict the distribution of PCDF congeners. The total PCDF yield is not predicted, but the addition of one absolute rate constant would allow for total PCDF yield to be calculated.

**4.2. Model validation**

DF and MCDF through HCDF products were measured in validation experiments run at three

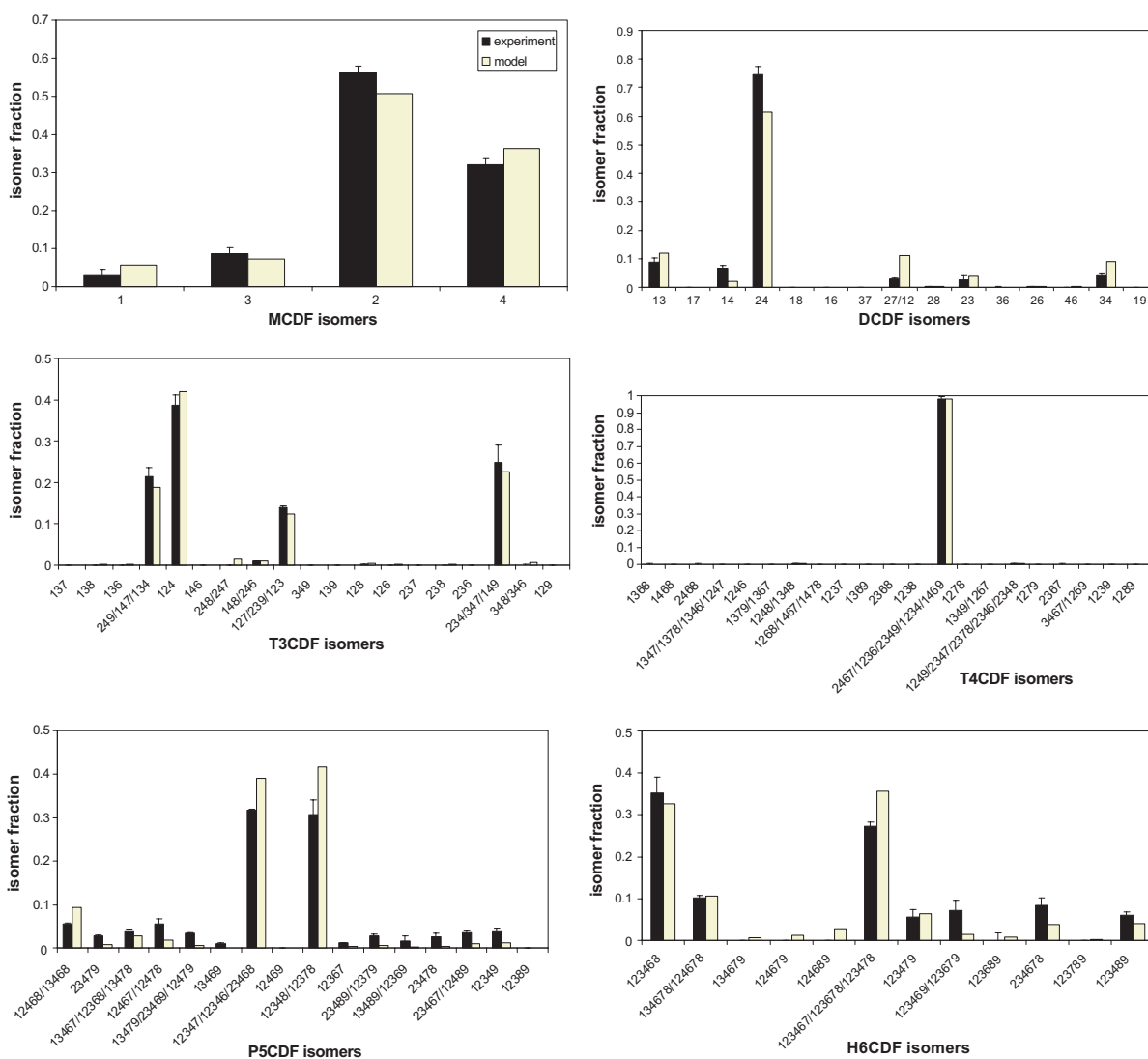


Fig. 4. Comparison of measured and predicted PCDF isomer patterns.

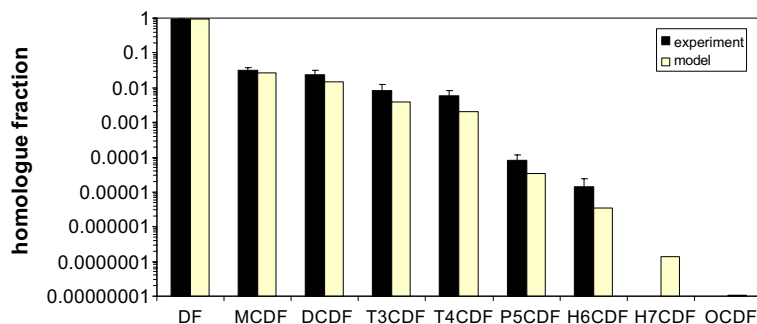


Fig. 5. Comparison of measured and predicted PCDF homologue pattern.

temperatures (600, 650, and 700 °C). In addition to PCDF products, chlorinated naphthalenes were formed in significant amounts, as well as benzonaphthofurans. These results will be presented elsewhere. The total PCDF yield varied by a factor of 100, with the greatest yield observed at 600 °C. PCDF congener distributions (both isomer and homologue) for the three experiments, however, were nearly identical. Comparisons of experimental measurements and model predictions for PCDF isomer distributions and homologue pattern are shown in Figs. 4 and 5, respectively. Agreement between experimental measurement and model prediction is quite good. The *R*-squared correlation coefficient exceeds 0.9 for all PCDF isomer distributions and the distribution of PCDF homologues. Agreement was lowest for the H<sub>6</sub>CDF isomers, whose yields were lowest. H<sub>7</sub>CDF isomer yields were too low to be quantified. Thus, divergence between model predictions and the measurements are likely due to experimental limitation (i.e. detection limit) as much as model limitations (e.g. use of single reaction order).

## 5. Conclusion

The results presented in this paper demonstrate that distribution of dibenzofuran and the 135 PCDF congeners from gas-phase condensation of phenol and chlorinated phenols can be predicted with reasonable accuracy. Relative rate constants and an average reaction order are provided that can be incorporated into a simple, algebraic model for predicting the distribution of PCDF congeners from a distribution of phenol and 19 chlorinated phenols. Distributions of PCDF congeners and known precursors have been used to qualitatively assess the role of alternative PCDF formation mechanisms. This work provides a quantitative model for making the assessment of the role of phenol condensation pathways in PCDF formation.

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