

# **Development of Jet REMPI as a Research Tool for Toxic Combustion Byproduct Measurement: Research Proposal Planning Activities**

## **Final Report submitted to SRI**

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### **Scope of Work**

The purpose of this work was to explore collaborative opportunities between researchers at Georgia Institute of Technology, Louisiana State University (LSU), the Environmental Protection Agency (EPA), and SRI International for the development of a jet REMPI instrument as a research tool for studying combustion byproduct emissions. A one-year study was proposed for planning a proposal to NSF under the program Biocomplexity in the Environment: Instrumentation Development for Environmental Activities (IDEA). SRI was the lead institution, with subcontracts to Georgia Tech and LSU. Work on this project was conducted over a one-year time period ending December, 2002.

An initial meeting was held at EPA's National Risk Management Research Laboratory in Research Triangle Park, North Carolina in April 2002. Participants observed a jet REMPI instrument already in use for combustion byproduct identification in Brian Gullett's research laboratory. The real-time monitoring of dioxins in combustion stack gas is an application of jet REMPI instrument being explored by Dr. Gullett's research team. Needed for this application are models that can extrapolate from measurements of selected compounds the complete dioxin distribution. Under this project, with support from EPA for a post-doc who assisted in model development, we decided to perform laboratory experiments at Georgia Tech to demonstrate the feasibility of developing these models.

In my laboratory at Georgia Tech, we have been investigating the formation of dioxins from phenol precursors, both in the gas phase and via surface-mediated reactions. To advance this study toward the development of predictive models of dioxin formation from phenol precursors, we conducted experiments and analyses using phenol distributions typical of municipal waste incinerators. Results are presented here which indicate how models might be used to predict dibenzofuran distributions from measurements of phenol precursors.

### **Introduction**

Chlorinated dibenzo-*p*-dioxin (CDD) and dibenzofuran (CDF) byproducts are formed in combustion systems by variety of mechanisms. In combustion exhaust gas prior to the air pollution control equipment, dibenzofuran and CDF concentrations have been found to be greater than CDD concentrations, and less chlorinated congeners, which are most abundant, may be chlorinated on particle surfaces at lower temperatures [1,2]. One likely source of these byproducts is the gas-phase condensation of phenol and chlorinated phenol congeners. CDF

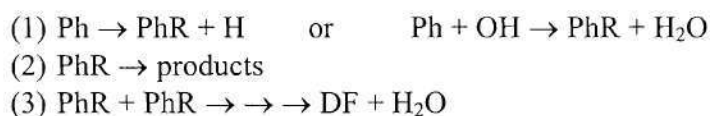
product distributions have been used to infer the formation mechanism [3]. To be of use as fingerprints in this way, a model is needed that predicts the CDF product distribution from a distribution of phenols.

A detailed chemical mechanism of gas-phase CDF formation by condensation of phenols was first proposed by Born *et al.* [4]. 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 CDF product. Factors controlling the relative rate of coupling of phenoxy radicals are electronic, steric, and statistical effects associated with chlorine substitution pattern [5-7]. Maximum CDF product yields occur between 550 and 700 °C.

Presented here is a model that predicts the CDF product distribution from a distribution of phenols, applicable to conditions that favor gas-phase CDF formation. A model framework is developed based on a simplified chemical mechanism. Model parameters are derived from experimental results using single phenols and equal molar mixtures of up to four phenols. The model predictions are then compared with results of experiments using a typical distribution of phenols.

## Methods

*Model framework:* The mechanism for formation of dibenzofuran (DF) from phenol (Ph) in combustion gas exhaust is simplified as follows (PhR = phenoxy radical).



Invoking the pseudo-steady state approximation for phenoxy radical, the overall rate of DF formation ( $R_{\text{DF}}$ ) can be written as follows.

$$(4) R_{\text{DF}} = k_{\text{eff}} [\text{Ph}]^n$$

Here,  $k_{\text{eff}}$  is an effective rate constant and  $[\text{Ph}]$  is the molar concentration of phenol. In the limit that phenoxy radical is consumed by reaction (2), the order  $n$  is 2; in the other limit in which phenoxy radical is consumed by reaction (3), the order  $n$  is 1.

Extending this mechanism to any 135 CDF congener  $i$ , a global rate of formation is written as follows.

$$(5) R_i = k_{\text{eff},i} [\text{Ph1}_i]^{n/2} [\text{Ph2}_i]^{n/2}$$

Here, it is assumed that the rate is same order in each phenol reactant. Each CDF congener is formed from only one pair of phenol precursors.

To calculate the distribution of CDF products from the distribution of phenol reactants, relative rates are needed. The relative rate of formation of CDF congener i to CDF congener j is given by equation (6).

$$(6) R_{rel,i/j} = [CDF_i] / [CDF_j] = k_{rel,i/j} \{ [Ph1_i] [Ph2_i] / ([Ph1_j] [Ph2_j]) \}^{n/2}$$

Thus, to calculate the mono- through hepta-CDF isomer distributions and the distribution of DF through octa-CDF homologues, values for 135 independent  $k_{rel,i/j}$  parameters are needed, as well as the reaction order n.

*Model Parameters:* Values for the model parameters were obtained from flow reactor experiments performed with single phenol reactants and equal molar mixtures of up to four phenol reactants [5-7]. Over ranges in temperature of 500 to 800 °C, residence time of 0.5 to 10 seconds, and oxygen concentration of 0 to 8 percent, the distribution of CDF products varied little for a given reactant or mixture of reactants, even though the total CDF yield varied by several orders of magnitude. Therefore, to a first approximation, one set of values for relative rate constant parameters and reaction order can be used for these conditions.

*Model validation:* Experiments were performed using the distribution of phenol and 19 chlorinated phenols measured in municipal waste incinerator exhaust gas by Weber and Hagenmaier [8]. Phenol was by far the major reactant, representing over 90 percent of the total phenol input. Of the chlorinated phenols, the major congeners were 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol. Distributions of CDF congeners produced by this mixture of 20 phenols were measured and compared to model predictions.

## Results and Discussion

*Model Parameters:* Published results from flow reactor experiments single phenol reactants and equal molar mixtures of up to four phenol reactants [5-7] were used to assess ratios of approximately 40 CDF congeners. Based on these results, other relative rate constants were estimated based on similarities in molecular structure and reaction pathway.

In addition to CDF products, chlorinated naphthalenes were formed in significant amounts, as well as benzonaphthofurans. Naphthalenes are likely formed via coupling of cyclopentadienyl radicals produced by CO elimination from phenoxy radicals. This is evidence that phenoxy radical decomposition (reaction 3) competes with phenoxy radical dimerization (reaction 4). Thus, we choose an intermediate value of 1.6 for n. We are currently examining this experimentally.

The 135 relative rate constants that were derived from the experimental data are listed in Table 1. In section 1, eight relative rate constants for CDF congeners with different numbers of Cl atoms are presented. Phenol is the most potent CDF precursor. In section 2, six relative rate constants for CDF isomers formed from phenols with different numbers of Cl atoms are presented. In general, CDF isomers formed from phenols with different numbers of Cl atoms are favored over isomers formed from phenols with similar numbers of Cl atoms. In section 3, relative rate

constants for CDF formation from condensation of a phenol pair that includes 3-chlorophenol and/or 3,4-dichlorophenol are presented. These phenol pairs produce multiple isomers due to their lack of symmetry and their having both *ortho* sites unchlorinated. There are 31 of these values. In sections 4, 5, and 6, relative rate constants for formation of CDF isomers from trichlorophenol, dichlorophenol, and monochlorophenol reactants, respectively, are presented. These values demonstrate that CDF isomers from phenols with chlorine at *meta* sites are favored over CDF isomers from phenols with chlorine at *ortho* and *para* sites. Also evidenced by these values are steric effects associated with CDF isomers formed with 1,9 sites chlorinated.

*Model validation:* Mono- through hexa-CDF products were detected in the experiments run at three temperatures (600, 650 and 700 °C). The total CDF yield varied by a factor of 100, with the greatest yield observed at 600 °C. The CDF product distributions for the three experiments, however, were nearly identical. A comparison of experimental measurements and model predictions for CDF isomer distributions and homologue pattern is shown in Figures 1 and 2, respectively. Agreement between experimental measurement and model prediction is quite good. The R-squared correlation coefficient exceeds 0.91 for the six CDF isomer distributions and the distribution of CDF homologues. Agreement was lowest for the hexa-CDF isomers, whose yields were lowest.

These results demonstrate that distribution of dibenzofuran and the 135 CDF byproducts from gas-phase condensation of phenol and chlorinated phenols can be predicted from measurement of the distribution of phenol and 19 chlorinated phenols.

### References

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Table 1. Relative rate constants (135) used in model.

phenol precursors	CDF products	krel	number	other phenols
1. CDF congeners with different numbers of Cl atoms:				
Ph+2/Ph+Ph	4/DF	0.33	1	
Ph+23/Ph+2	34/4	1.9	1	
Ph+234/Ph+23	234/34	0.6	1	
Ph+2345/Ph+234	1234/234	1.8	1	
2+2345/Ph+2345	12346/1234	0.15	1	
23+2345/2+2345	123467/12346	1.2	1	
234+2345/23+2345	1234678/123467	0.1	1	
2345+2345/234+2345	OCDF/1234678	0.1	1	
2. CDF isomers from precursors with different numbers of Cl atoms:				
2+2/Ph+23	46/34	0.05	1	
2+23/Ph+234	346/234	0.32	1	
2+234/Ph+2345	2346/1234	0.05	1	
23+23/2+234	3467/2346	1.5	1	
23+234/2+2345	23467/12346	0.5	1	
234+234/23+2345	234678/123467	0.2	1	
3. CDF isomers from same phenol pair:				
3+3	17/37	2	1	
	19/37	0.4	1	
34+34	1278/2378	2	1	
	1289/2378	0.4	1	
3+34	127/237	2	1	
	239/237	2	1	
	129/237	0.4	1	
3+x	rxn at 2- vs. 6- site of 3-CP	0.8	6	x = Ph, 2, 4, 23, 24, 234
3+x	rxn at 2- vs. 6- site of 3-CP	0.2	6	x = 25, 35, 235, 245, 345, 2345
34+x	rxn at 2- vs. 6- site of 34-DCP	3	3	x = Ph, 2, 4
34+x	rxn at 2- vs. 6- site of 34-DCP	1.5	3	x = 23, 24, 234
34+x	rxn at 2- vs. 6- site of 34-DCP	0.4	6	x = 25, 35, 235, 245, 345, 2345
4. CDF isomers from trichlorophenols:				
345+x/245+x		4	14	x = Ph, 2, 3, 4, 23, 24, 25, 34, 35, 234, 235, 245, 345, 2345
245+x/235+x		0.5	13	x = Ph, 2, 3, 4, 23, 24, 25, 34, 35, 234, 235, 245, 2345
235+x/234+x		2	8	x = Ph, 2, 3, 4, 23, 24, 34, 234
235+x/234+x		0.4	4	x = 25, 35, 235, 2345
5. CDF isomers from dichlorophenols:				
35+x/25+x		3	11	x = Ph, 2, 3, 4, 23, 24, 25, 34, 35, 234, 2345
34+x/23+x	rxn at 6- site of 34-DCP	1.2	10	x = Ph, 2, 3, 4, 23, 24, 25, 34, 234, 2345
25+P/23+P		1	1	
25+x/23+x		0.7	6	x = 2, 3, 4, 23, 24, 234
25+x/23+x		0.2	2	x = 25, 2345
24+P/23+P		0.5	1	
24+x/23+x		0.3	6	x = 2, 3, 4, 23, 24, 234
24+2345/23+2345		0.1	1	
6. CDF isomers from monochlorophenols:				
4+x/2+x		3	7	x = Ph, 2, 3, 4, 23, 234, 2345
3+x/2+x	rxn at 6- site of 3-CP	3	6	x = Ph, 2, 3, 23, 234, 2345

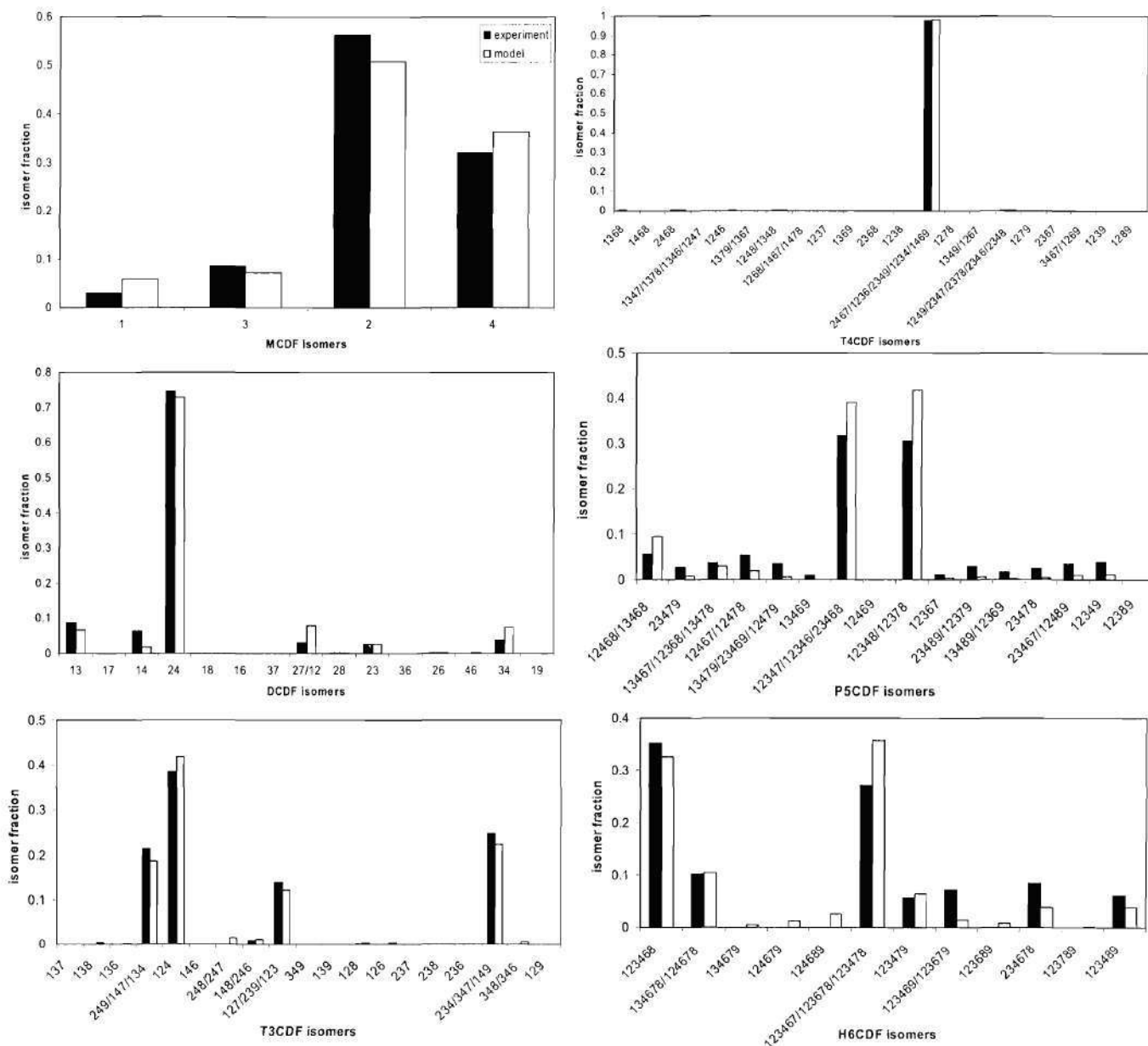


Figure 1. Comparison of CDF isomer patterns.

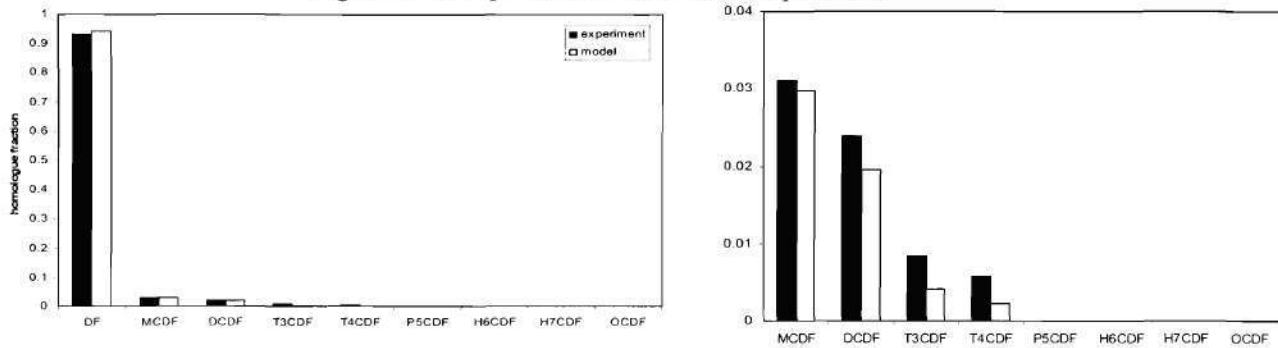


Figure 2. Comparison of CDF homologue pattern.