

## Gas-phase Hydroxyl Radical Reactions and Related Atmospheric Removal of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans

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### Abstract

The gas-phase reaction kinetics of five polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) with the hydroxyl radical (OH) have been investigated over temperatures ranging 72-159 °C. OH reaction rate constants were determined experimentally for each PCDD/F and extrapolated by the Arrhenius equation. Rate constants were estimated at 25 °C and found to agree with previous measurements and predictions at room temperature. Predicted rate constants for tetra- through octachlorodibenzo-*p*-dioxin and dibenzofuran isomers were then used in a simple model of the atmospheric removal of PCDD/F. The results of our model indicate that atmospheric removal is a combination of gas-phase removal processes of lower chlorinated dioxins and furans and particle-phase removal processes of higher chlorinated ones.

### Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) are emitted into the atmosphere by numerous combustion processes and can be transported great distances before depositing to other environmental compartments. One would expect the relative PCDD/F homologue concentrations in these sinks to be similar to those of the emissions; however, this is usually not the case.<sup>1</sup> Previous investigations in our laboratory of atmospheric wet and dry deposition of PCDD/F and the photodegradation of particle-bound PCDD/F do not completely explain such differences;<sup>2,3</sup> therefore, we now focus on PCDD/Fs' gas-phase chemistry.

Atmospheric PCDD/F with six or fewer chlorines exist largely in the gas-phase, and in this phase, hydroxyl radical (OH) reactions are likely to be an important PCDD/F removal pathway from the atmosphere.<sup>4</sup> Due to the low vapor pressures of PCDD/F at room temperature, OH reaction rate constants have only been determined experimentally for dibenzo-*p*-dioxin, dibenzofuran,<sup>5</sup> and 1-chlorodibenzo-*p*-dioxin.<sup>6</sup> A system was recently developed in our laboratory measuring OH reaction rate constants for gas-phase semi-volatile organic compounds.<sup>7</sup> This system, consisting of a heated quartz reaction chamber sampled by on-line mass spectrometry, has now been modified with electron capture mass spectrometry (EC-MS) to enhance the sensitivity to higher chlorinated PCDD/F which have lower vapor pressures. OH reaction rate constants were measured for dibenzo-*p*-dioxin (DD), dibenzofuran (DF), 2,7-dichlorodibenzo-*p*-dioxin (2,7-D), 2,8-dichlorodibenzofuran (2,8-F), and 1,2,3,4-dibenzo-*p*-dioxin (1,2,3,4-D). Using Atkinson's OH reaction rate constants for each of the tetra- through octachlorinated dioxin and furan homo-

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logues,<sup>4</sup> a simple model has been developed to evaluate the role of OH reactions in the removal of PCDD/F from the atmosphere.

## Experimental Methods

All experiments were performed at atmospheric pressure in a quartz reaction chamber with a volume of 160-mL, which was mounted in the oven of a gas chromatograph. Helium served as the primary diluent gas, and OH radicals were produced by either the photolysis of O<sub>3</sub> ( $\lambda = 254$  nm) in the presence of water vapor or the photolysis of H<sub>2</sub>O<sub>2</sub> ( $\lambda = 254$  nm). Reactants in the chamber were monitored in real time by a Hewlett-Packard 5985B mass spectrometer, operating in either its electron impact ionization mass spectrometry (EI-MS) or EC-MS mode. EC-MS was used only in 1,2,3,4-D experiments.

PCDD/F-OH reaction rate constants were measured by the relative rate technique, where a reference compound, with a known OH reaction rate constant, was introduced with the test compound. Cyclohexane served as the reference compound for EI-MS, and hexafluorobenzene and 2,3,4,5,6-pentachlorobiphenyl were used for EC-MS. Assuming OH reactions were the primary loss processes during UV irradiation of the chamber, the recorded signal intensities for the two compounds follow the equation:

$$\ln \frac{[\text{test}]_0}{[\text{test}]_t} = \left( \frac{k_{\text{test}}}{k_{\text{ref}}} \right) \ln \frac{[\text{reference}]_0}{[\text{reference}]_t} \quad (1)$$

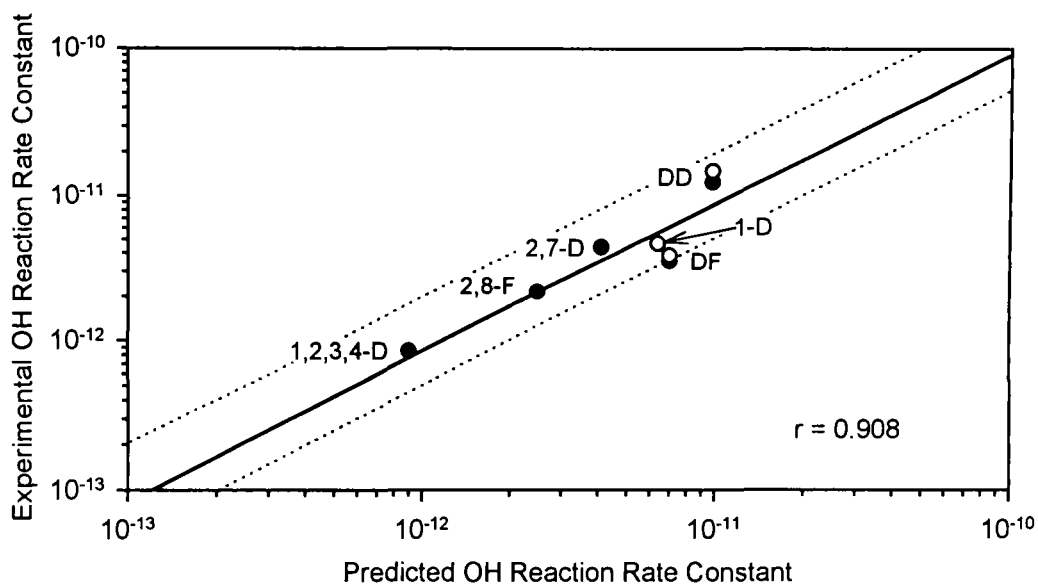
where the signal intensities were measured at time  $t = 0$  and at subsequent times  $t$ . The values  $k_{\text{test}}$  and  $k_{\text{ref}}$  represent the OH reaction rate constants for the test and reference compounds respectively. Values of  $k_{\text{test}}$  were calculated from the slopes of experimental plots of Eqn. 1 and known values of  $k_{\text{ref}}$ .<sup>8,9</sup> Other potential loss processes of the reactants which could interfere with our OH rate constant measurements, such as dark reactions with ozone or losses to the chamber walls, were accounted for by analysis of the pre- and post-UV trends of the signal intensities.

## Results and Discussion

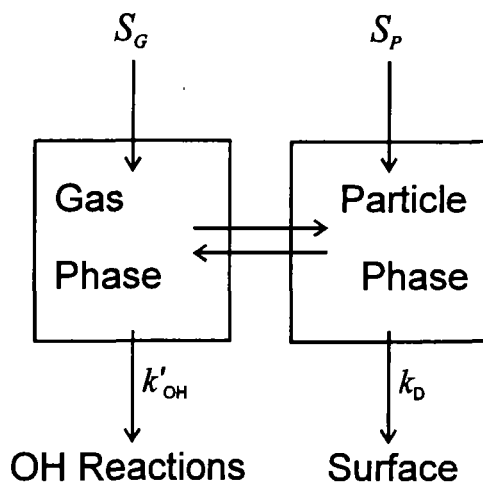
PCDD/F-OH reaction rate constants were measured for DD, DF, 2,7-D, 2,8-F, and 1,2,3,4-D over temperatures ranging 72-159 °C. For each compound, an Arrhenius expression was derived from its rate constants, and an OH reaction rate constant at 25 °C was estimated. These room temperature estimates were then compared to previously measured PCDD/F-OH rate constants and the values predicted by Atkinson.<sup>4</sup> As demonstrated in Fig. 1, the fit between available experimental rate constants and his predictions indicates the structure-activity method is reliable in predicting PCDD/F-OH reaction rate constants.

Using Atkinson's predicted OH reaction rate constants, a simple model of PCDD/F removal from the atmosphere was developed. This model (see Fig. 2) consists of two atmospheric stocks representing gas-phase and particle-phase PCDD/F, with  $S_G$  and  $S_P$  as the input rates into each compartment, respectively. A fast equilibrium is assumed between the two phases, and the significant loss processes from the gas- and particle-phases are assumed to be OH reactions and wet and dry

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**Figure 1.** Comparison of experimental OH reaction rate constants and predicted OH reaction rate constants.<sup>4</sup> Symbols: ● this study; ○ values of Kwok, *et al.* for dibenzo-*p*-dioxin, dibenzofuran,<sup>5</sup> and 1-chlorodibenzo-*p*-dioxin.<sup>6</sup> Lines: (solid) fit between all experimental data and the predicted values; (dotted) representation of disagreement with predicted values by a factor of 2.



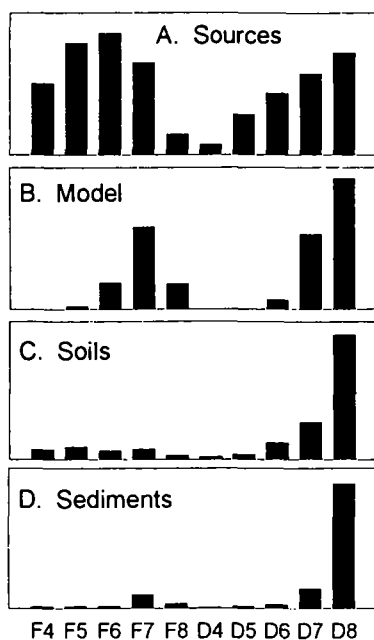
**Figure 2.** Model for the atmospheric removal of PCDD/F (see text for details). Variables:  $S_G$ , rate of input to the gas phase from sources;  $S_P$ , rate of input to the particle phase from sources;  $k'_{OH}$ , pseudo-first order rate constant of gas phase OH reactions;  $k_D$ , first order rate constant of deposition to the Earth's surface from the particle phase.

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deposition, respectively. Using steady state approximations for the two compartments, we find that for any PCDD/F isomer,

$$S_P = S_T \left( \frac{k_D \phi}{k'_{OH} (1 - \phi) + k_D \phi} \right) \quad (2)$$

where  $S_T = [S_G + S_P]$ ,  $k_D$  is a first order deposition rate constant,  $\phi$  is the fraction of the isomer in the particle-phase, and  $k'_{OH}$  is a product of the predicted OH rate constant for the isomer and the global concentration of OH averaged over 24 h.<sup>4, 10</sup>  $S_P$  under steady state conditions would be equal to the deposition rate to environmental sinks of the PCDD/F isomer bound to atmospheric particles. To compare our model to relative PCDD/F concentrations in sources and sinks (see Fig. 3), values of  $S_P$  were found for each of the tetra- through octadioxin and furan homologues by using relative  $S_T$  values (A in Fig. 3) and average values of  $k'_{OH}$  and  $\phi$  for each homologue.<sup>4, 11</sup> We assumed  $k_D = 10^{-8} \text{ s}^{-1}$  for all PCDD/F. Note the results of this model (B in Fig. 3) show reasonable agreement to environmental sink profiles (C and D in Fig. 3). While the model and sinks are not in perfect agreement, we conclude the mismatch between homologue profiles for environmental sources and sinks can be attributed to the combination of the gas-phase removal processes (OH reactions in particular) of the lower chlorinated dioxins and furans and the particle-phase removal processes of the higher chlorinated ones.



**Figure 3.** Comparison of our model to environmental sources and sinks of PCDD/F: (A) relative concentrations in municipal incinerator emissions,<sup>1</sup> (B) relative deposition rates from the atmosphere (see model in text), (C, D) relative concentrations in soils and sediments, respectively.<sup>1, 12</sup> The letters F and D designate furans and dioxins respectively, while the numbers indicate chlorination levels.

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