Kinetics of OH radical reactions with dibenzo-\(p\)-dioxin and selected chlorinated dibenzo-\(p\)-dioxins

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Abstract

The pulsed laser photolysis/pulsed laser-induced fluorescence (PLP/PLIF) technique has been applied to obtain rate coefficients for OH + dioxin (DD) \((k_1)\), OH + 2-chlorodibenzo-\(p\)-dioxin (2-CDD) \((k_2)\), OH + 2,3-dichlorodibenzo-\(p\)-dioxin (2,3-DCDD) \((k_3)\), OH + 2,7-dichlorodibenzo-\(p\)-dioxin (2,7-DCDD) \((k_4)\), OH + 2,8-dichlorodibenzo-\(p\)-dioxin (2,8-DCDD) \((k_5)\), OH + 1,2,3,4-tetrachlorodibenzo-\(p\)-dioxin (1,2,3,4-TCDD) \((k_6)\), and OH + octachlorodibenzo-\(p\)-dioxin (OCDD) \((k_7)\) over an extended range of temperature. The atmospheric pressure (740 ± 10 Torr) rate measurements are characterized by the following Arrhenius parameters (in units of cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), error limits are 1\(\sigma\)):

\[
\begin{align*}
    k_1(326–907 \text{ K}) &= (1.70 \pm 0.22) \times 10^{-12} \exp(979 \pm 55) / T, \\
    k_2(346–905 \text{ K}) &= (2.79 \pm 0.27) \times 10^{-12} \exp(784 \pm 54) / T, \\
    k_3(400–927 \text{ K}) &= (1.83 \pm 0.19) \times 10^{-12} \exp(742 \pm 67) / T, \\
    k_4(390–769 \text{ K}) &= (1.10 \pm 0.10) \times 10^{-12} \exp(569 \pm 53) / T, \\
    k_5(379–931 \text{ K}) &= (1.02 \pm 0.10) \times 10^{-12} \exp(580 \pm 68) / T, \\
    k_6(409–936 \text{ K}) &= (1.66 \pm 0.38) \times 10^{-12} \exp(713 \pm 114) / T, \\
    k_7(514–928 \text{ K}) &= (3.18 \pm 0.54) \times 10^{-11} \exp(–667 \pm 115) / T.
\end{align*}
\]

The overall uncertainty in the measurements, taking into account systematic errors dominated by uncertainty in the substrate reactor concentration, range from a factor of 2 for DD, 2-CDD, 2,3-DCDD, 2,7-DCDD, and 2,8-DCDD to ± a factor of 4 for 1,2,3,4-TCDD and OCDD. Negative activation energies characteristic of an OH addition mechanism were observed for \(k_1–k_6\); \(k_7\) exhibited a positive activation energy. Cl substitution was found to reduce OH reactivity, as observed in prior studies at lower temperatures. At elevated temperatures (500 K < \(T\) < 500 K), there was no experimental evidence for a change in reaction mechanism from OH addition to H abstraction. Theoretical calculations suggest that H abstraction will dominate OH reactivity for most if not all dioxins (excluding OCDD) at combustion.

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1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDD) are produced by numerous manufacturing and combustion processes and emitted into the atmosphere (US-EPA, 1998; Baker and Hites, 2000). Specific isomers of this class of compounds are considered among the most toxic organic chemicals associated with our industrial society (Kociba and Cabey, 1985). The gas-phase transformation of these chemicals under atmospheric conditions and high-temperature incineration (destruction) conditions is not well understood. Reaction with hydroxyl (OH) radicals is an important pathway in the homogeneous oxidation of organic compounds in the atmosphere (Finlayson-Pitts and Pitts, 1999) and in incineration systems (Senkan, 2000). There have been no previous reports of the OH reactivity of these compounds at elevated temperatures. However, to assist in environmental impacts of PCDD via airborne routes, a few recent studies have determined their atmospheric reactivity (Kwok et al., 1994, 1995; Brubaker and Hites, 1997, 1998).

Kwok et al. (1994) reported rate constants for the gas-phase reaction of dibenzo-p-dioxin (DD) with OH at 297 ± 2 K and atmospheric pressure of air. Using a relative rate method and two different reference compounds, a rate constant of $1.48 \pm 0.35 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was determined. An OH addition mechanism was suggested based on the magnitude of the observed rate constant and limited product analyses. The initial position of the OH radical addition (1-position vs. the 2-position) could not be determined. Kwok et al. (1995) also reported rate constants for the gas-phase reaction of 1-chlorodibenzo-p-dioxin (1-CDD) under similar conditions. Using a relative rate method with cyclohexane as the reference compound, a rate constant of $4.7 \pm 1.6 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was determined. The factor of 3 lower rate constant for 1-CDD compared to DD was reported to be consistent with the electron-withdrawing nature of the Cl substituent.

Brubaker and Hites (1997) reported rate constants for the reaction of 1,2,3,4-TCDD with OH at 373–432 K in helium atmosphere using a miniature-scale, relative rate technique. An extrapolation of the following experimentally-based Arrhenius fit:

$$k(1,2,3,4-TCDD) = 2.4 \pm 0.3 \times 10^{-10}$$

$$\times \exp\left[\frac{-1680 \pm 270}{T}\right] \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

yielded a rate constant of $8.5 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K. Using the same technique, Brubaker and Hites (1998) also reported rate constant measurements for DD and 2,7-dichlorodibenzo-p-dioxin over a temperature range of ca. 350–390 K. The DD measurements did not exhibit a discernible temperature dependence. Good agreement with the earlier studies of Kwok et al. (1994) was observed upon extrapolation of the rate constants to room temperature ($1.2 \pm 0.3 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$). Rate measurements for 2,7-dichlorodibenzo-p-dioxin exhibited a small, positive, temperature dependence ($A = 6.6 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$). The magnitude of the extrapolated rate constants reported by Brubaker and Hites (1997, 1998) were in good agreement with the recent room temperature structure–activity calculations of Kwok et al. (1995) and Atkinson (1996). The results suggested that increasing chlorine substitution results in a significant reduction in the overall reaction rate, consistent with an OH addition mechanism and the electron-withdrawing nature of the Cl substituent.

This manuscript reports the first extended temperature measurements for the following OH/dioxin reactions:

$$\text{OH} + \text{DD} \rightarrow \text{products} \quad (k_1)$$
$$\text{OH} + 2-\text{CDD} \rightarrow \text{products} \quad (k_2)$$
$$\text{OH} + 2,3-\text{DCDD} \rightarrow \text{products} \quad (k_3)$$
$$\text{OH} + 2,7-\text{DCDD} \rightarrow \text{products} \quad (k_4)$$
$$\text{OH} + 2,8-\text{DCDD} \rightarrow \text{products} \quad (k_5)$$
$$\text{OH} + 1,2,3,4-\text{TCDD} \rightarrow \text{products} \quad (k_6)$$
$$\text{OH} + \text{OCDD} \rightarrow \text{products} \quad (k_7)$$

A labeled molecular structure diagram for the substrates is given in Fig. 1. Our measurements also represent the first measurements of this kind using an absolute rate technique. Our objectives in pursuing this study were the following: (1) to verify the previous low temperature measurements for DD (Kwok et al., 1994; Brubaker and Hites, 1998), 2,7-DCDD (Brubaker and Hites, 1998), and 1,2,3,4-TCDD (Brubaker and Hites, 1997); (2) to
verify that Cl substitution on a single aromatic ring resulted in a significant decrease in the overall reaction rate as reported previously (Kwok et al., 1995; Brubaker and Hites, 1997, 1998); and (3) to determine the Arrhenius behavior of these reactions at temperatures approaching post-combustion conditions.

2. Experimental approach

The experimental procedures developed for pulsed laser photolysis–pulsed laser-induced fluorescence (PLP–PLIF) studies of the reaction of OH radicals with chlorinated dioxins are based on recent studies of chlorinated olefinic compounds (Yamada et al., 2001a,b). The following paragraphs summarize these procedures and discuss modifications to the experimental design that were necessary to perform measurements with halogenated species of much lower vapor pressure.

Three precursors, nitrous oxide/water (N\(_2\)O/H\(_2\)O) mixtures, hydrogen peroxide (HOOH), and nitrous acid (HONO), were employed to generate OH radicals. N\(_2\)O/H\(_2\)O mixtures (193 nm) represent the cleanest overall source of OH radicals. This precursor combination can also be used to generate OH radicals over a fairly wide temperature range (up to ca. 1000 K). Measurements at lower temperatures were conducted with HOOH (248 nm) and HONO (for DD and 2-CDD) (351 nm) to investigate the effect of photolysis wavelength on the rate measurements. The N\(_2\)O/H\(_2\)O precursor system was used predominantly at elevated temperatures. To minimize potential photolysis of the substrate, low photolysis energies (0.15–0.3 mJ/cm\(^2\) @ 193 nm and 2.5–5.0 mJ/cm\(^2\) @ 248 nm and 351 nm) were used in all experiments.

A pulsed, 10 Hz, ArF excimer laser (Lamba Physik Compex Model 102) was used as the photodissociation source for the N\(_2\)O/H\(_2\)O experiments. Initial [OH]\(_0\) ranged from ca. 6–12 \(	imes\) \(10^{10}\) molecules cm\(^{-3}\), and was determined based on the measured pump laser fluence (2.5–5.0 mJ cm\(^{-2}\)), the absorption cross-section for HOOH (9.1 \(	imes\) \(10^{-20}\) cm\(^2\) molecule\(^{-1}\) at 248 nm) (DeMore et al., 1997), a quantum yield of two (DeMore et al., 1997), and measured values of the HOOH volumetric flow rate into the reactor (ca. 1.1 \(	imes\) \(10^{14}\) molecules cm\(^{-3}\)). A pulsed, 10 Hz, XeF excimer laser (Lamba Physik Compex Model 102) was also used as the photodissociation source for the HONO experiments. Pure HONO (>99%) was generated as described by Febo et al. (1995) and Brust et al. (2000). HONO primarily dissociates into OH and NO when exposed to near-UV radiation of 351 nm. Production of NO\(_2\) and H atoms is a competing dissociation channel and has been observed to be negligible under similar experimental conditions (Wollenhaupt et al., 2000). Initial [OH]\(_0\) ranged from ca. 1.5–3.0 \(	imes\) \(10^{11}\) molecules cm\(^{-3}\), and was determined based on the measured pump laser fluence (2.5–5.0 mJ cm\(^{-2}\)), the most recent published value of the absorption cross-section for HONO (1.54 \(	imes\) \(10^{-19}\) cm\(^2\) molecule\(^{-1}\) at 351 nm) (Brust et al., 2000), a quantum yield of unity (Cox, 1974; DeMore et al., 1997), and measured values of [NO\(_2\)] taken to represent [HONO] determined using ion chromatography (~2 \(	imes\) \(10^{14}\) molecules cm\(^{-3}\)).

Detection of OH radicals was achieved by PLIF, exciting the (1,0) band of the OH (\(A^2\Sigma^-\rightarrow X^2\Pi\)) system at 282.2 nm using a pulsed (10 Hz) Nd:YAG pumped-dye laser (Quanta Ray DCR-1/PDL-2). The laser fluence at the entrance of the reactor was ca. 200 \(\mu\)J/pulse. Broadband fluorescence at 306 nm was collected using a PMT/narrow band-pass filter combination (Yamada et al., 2001a,b).

A modified fused silica optical reactor was designed and constructed for this study as illustrated in Fig. 2. Two significant changes to our previous reactor designs (Yamada et al., 2001a,b) were made to transport part per million concentrations of chlorinated dioxins in the gas phase from the point of sample introduction to the reaction volume (intersection of pump and probe laser beams). The unheated Brewster windows attached to the arms of the previous reactor were replaced with fused silica windows installed ca. 2.2 cm from the reaction volume. The windows were heated to temperatures approaching the gas-phase reactor temperature to minimize condensation of the substrate on the optical
The second change involved the design and construction of a fused silica sample inlet and probe located immediately beneath the cylindrical reactor to provide a means for rapid and efficient introduction of the substrate vapors to the reaction volume while minimizing condensation of the sample during transport. Quartz heating tape was used to uniformly control the temperature of the cylindrical reactor and the sample inlet. The temperatures of the cylindrical reactor and sample inlet were independently controlled using separate voltage regulators.

The gas temperature in the reaction volume was monitored with a chromel–alumel thermocouple positioned ~1 cm outside the body of the main cylindrical reactor.

The temperature of the solid substrate was monitored continuously with a chromel–alumel thermocouple positioned at the location of the substrate within the sample inlet probe. Temperature profile measurements were performed periodically between the sample inlet probe and the reaction volume. A steady, gradual increase in temperature was observed from the point of sample introduction to the reaction volume, indicating that substrate condensation was minimized during sample transit from the point of sample introduction to the reaction volume. The uncertainty in the thermocouple used to measure the temperature of the solid substrate was ±1 K, as determined based on measurements with a NIST calibration thermocouple.

Solid substrates were introduced with a fused silica sample inlet probe, 16.4 mm long × 4 mm i.d. During a typical experiment, ca. 5 mg of sample was loaded in the probe, and fixed in place with quartz wool. A sample gas flow (argon or helium), controllable from 1.7 to 10.6 cm³ min⁻¹, provided a means for varying the substrate concentration in the reactor. Substrate concentrations were periodically checked when feasible (for DD, 2-CDD, and 1,2,3,4-TCDD) using integrated sampling at the exit of the reactor with Tenax® adsorbent and subsequent GC–MS analysis. The reactor concentrations for 2-CDD (± factor of 2) and 1,2,3,4-TCDD (± factor of 4) were consistent with the most recently determined Kirchhoff equation coefficients for chlorinated dioxin congeners reported by Mader and Pankow (2003). The earlier temperature-dependent data (Rordorf, 1985a,b; Rordorf et al., 1986) as reviewed by Shiu and Ma (2000) severely under-predicted the 2-CDD and 1,2,3,4-TCDD concentrations in the reactor. As a result, all chlorinated dioxin rate coefficients presented in this manuscript were determined based on the Kirchhoff equation coefficients reported by Mader and Pankow (2003). In the case of DD, reactor concentrations were consistent (± factor of 2) with the earlier temperature-dependent coefficients reported by Shiu and Ma (2000). Mader and Pankow (2003) did not report Kirchhoff equation coefficients for DD. Thus, for DD, the rate coefficients presented here were determined based on the vapor pressure recommendations of Shiu and Ma (2000).

The buildup of reaction products was minimized by conducting experiments under slow flow conditions. Both helium and argon were used as the carrier gas for the kinetic experiments. Total gas flows ranged from 220 ± 6 to 775 ± 23 cm³ min⁻¹; linear gas velocities based on the plug flow assumption ranged from 12.9 to 37.6 cm s⁻¹. All experiments were performed at a total pressure of 740 ± 10 Torr. The dioxin and chlorinated dioxin substrates were purchased from Ultra Scientific, 98+% purity, and used as-received. GC–MS analysis was used to verify purity.

The reactor exhaust from all experiments was delivered to a laboratory hood designed specifically for capture and treatment of halogenated materials. The reactor exhaust was periodically examined for potential
cross-contamination from the various congeners studied using Tenax® traps and GC/MS analysis. No evidence for cross-contamination was observed. The reactor was heated to 1000 °C in flowing air between studies of different congeners to ensure a contaminant free system.

3. Data reduction

All experiments were performed under pseudo-first order conditions. The rate of disappearance of the OH may be represented as

\[-d[OH]/dt = k_{bi}[A_0][OH] + k_d[OH]\]

where \(k_{bi}\) is the bimolecular rate constant, \(A_0\) the substrate concentration, and \(k_d\) is the model first-order rate coefficient for the reaction of OH with impurities and includes diffusion of OH out of the reaction volume. This relationship holds in the absence of any secondary reactions that may form or deplete OH. Solution of this equation yields \([OH] = [OH]_0 \exp(-k' t)\), where \(k' = k_{bi}[A_0] + k_d\). For all experiments, reactive and diffusive OH radical decay profiles exhibited exponential behavior and were satisfactorily fitted by the following nonlinear expression:

\([OH] = [OH]_0 \exp(-k' t) + \gamma\]

where \(\gamma\) is the (constant) background signal level from the probe laser and \(t\) is the time delay between the pump and probe lasers. Pseudo-first order exponential OH decays were observed, confirming that the substrate concentration was in large excess of \([OH]\) (at least a factor of 50 larger). OH decays were observed over two to three decay lifetimes over a time interval of 0.5–30.0 ms. The bimolecular rate coefficient, \(k_{bi}\), was separated from the diffusive rate coefficient, \(k_d\), by fitting a weighted least-squares line \((\omega_x = 1/\sigma_x^2)\) through the (substrate), \(k'\) data points. Initial chlorinated dioxin concentrations for a kinetic rate determination were typically varied by factors of 5–7, with lower and upper concentration limits of \(1 \times 10^{13}\) molecules cm\(^{-3}\) and \(1 \times 10^{14}\) molecules cm\(^{-3}\), respectively. Fig. 3 presents a plot of \(k'\) versus \(A_0\) at selected temperatures for dibenzo-p-dioxin.

4. Results

Prior to conducting the measurements, calibration tests were performed to examine the accuracy of our experimental method. The very low vapor pressures of the substrates did not permit room temperature calibration measurements using this technique. As a result, verification of this sample introduction procedure was obtained by conducting room temperature rate measurements for a structurally similar, solid-phase sample with a higher vapor pressure, phenol. A rate of \(2.1 \pm 0.14 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) was measured at 296 K using HOOH as the OH precursor, in satisfactory agreement with the previous measurements by Semadeni et al. (1995) and Rinke and Zetzsch (1984) (2.32 ± 0.20 × 10\(^{-11}\) and 2.81 ± 0.58 × 10\(^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), respectively). This agreement with previous measurements using different experimental methods validated the accuracy of our experimental approach.

Absolute rate measurements for \(k_1–k_7\) are presented in Figs. 4–10. 95% confidence intervals \((\pm 2\sigma)\) representing random statistical errors in the data ranged from 5% to 25%, with most rate coefficients exhibiting \(\pm 2\sigma\) values between 10% and 15%. Changes in carrier gas (helium or argon) had no impact on the rate measurements within
statistical uncertainties. Variation in photolysis wavelength (193 and 248 nm (and 351 nm for DD and 2-CDD)), photolysis energy (factor of 3), total flow rate (factor of 3), substrate concentration (factor of 2) and initial OH concentration (factor of 2) also had no impact on the rate measurements within statistical uncertainties. The overall uncertainty in the measurements, taking into account systematic errors dominated by uncertainty in the substrate reactor concentration, range from ± a factor of 2 for DD, 2-CDD, 2,3-DCDD, 2,7-DCDD, and 2,8-DCDD to ± a factor of 4 for 1,2,3,4-TCDD and OCDD.

Rate measurements spanned a temperature range of ca. 400 to ca. 900 K. Measurements at lower temperatures (room temperature for DD) were not possible due to the inability to establish pseudo-first order conditions in the reactor because of the low substrate concentrations. Measurements at elevated temperatures were limited by the onset of thermal decomposition of N₂O, the photochemical precursor to OH radical generation and by the onset of thermal decomposition of the substrate (Rordorf and Marti, 1985). For our reaction conditions, this limiting temperature is ~1000 K (for both N₂O and substrate decomposition). An Arrhenius fit of our extended temperature data for $k_1$–$k_7$ yielded the
following expressions (in units of cm$^3$ molecule$^{-1}$ s$^{-1}$, error bars are 1σ):

\[
\begin{align*}
k_1(326-907\text{ K}) &= (1.70 \pm 0.22) \times 10^{-12}\exp(979 \pm 55)/T, \\
k_2(346-905\text{ K}) &= (2.79 \pm 0.27) \times 10^{-12}\exp(784 \pm 54)/T, \\
k_3(400-927\text{ K}) &= (1.83 \pm 0.19) \times 10^{-12}\exp(742 \pm 67)/T, \\
k_4(390-769\text{ K}) &= (1.10 \pm 0.10) \times 10^{-12}\exp(569 \pm 53)/T, \\
k_5(379-931\text{ K}) &= (1.02 \pm 0.10) \times 10^{-12}\exp(580 \pm 68)/T, \\
k_6(409-936\text{ K}) &= (1.66 \pm 0.38) \times 10^{-12}\exp(713 \pm 114)/T, \\
k_7(514-928\text{ K}) &= (3.18 \pm 0.54) \times 10^{-11}\exp(-667 \pm 115)/T.
\end{align*}
\]

5. Discussion

A comparison of our absolute rate measurements for DD, 2,7-DD, and 1,2,3,4-TCDD with previous relative rate measurements are presented in Figs. 4, 7, and 9, respectively. Our rate measurements for DD, when extrapolated to room temperature, are a factor of three larger than a single prior room temperature measurement (Kwok et al., 1994). This disparity decreases to less than a factor of 2 at higher temperatures (385 K) (Brubaker and Hites, 1998). Our rate measurements for 2,7-DCDD between 350 and 400 K are within a factor of two of the single previous measurement (Brubaker and Hites, 1998), which is larger than that reported here. Our rate measurements for 1,2,3,4-TCDD between 350 and 450 K are within a factor of 4 of the single prior measurement (Brubaker and Hites, 1997) with the disparity decreasing to less than a factor of 2 at the upper end of this temperature range. Although better agreement between kinetic rate determinations is clearly desirable, given the difficulty in the measurements and the uncertainty in the substrate concentration, this level of agreement is acceptable.

The higher rates we observed for DD and 1,2,3,4-TCDD compared to previous relative rate measurements suggest that systematic errors may be present in our measurements. However, a detailed check has not identified a major source of error. Purity levels of the substrates (Ultra Scientific, Inc.), as determined by GC–MS analysis, ranged from 96.0% to 99.9%. With the exception of 1,2,3,4-TCDD, measured purities were consistent with stated purities (98.0–99.9%). The relatively high purity of the substrates and the very fast reaction rate observed indicate that fast reacting impurities are a very unlikely source of error in the measurements. None of the impurities detected from 1,2,3,4-TCDD (96% purity) were other chlorinated dioxin congeners or fast reacting olefinic or aromatic compounds, indicating that impurities were not a source of error in the 1,2,3,4-TCDD measurements. As discussed previously, our rate measurements were not influenced by changes in photolysis wavelength, photolysis energy, flow rate, initial substrate concentration, and initial OH concentration. A possible explanation for our higher rate measurements for DD and 1,2,3,4-TCDD involves sampling and analysis errors during the calibration tests. It is plausible that a portion of the substrate was lost during thermal desorption of the Tenax$^\text{®}$ adsorbent, thus resulting in a low bias for the substrate reactor concentration.

It is difficult to identify potential sources of error in the prior relative rate measurements (Kwok et al., 1994, 1995; Brubaker and Hites, 1997, 1998). The dioxin substrate and reference compound, as opposed to the OH radical, were measured directly in the prior studies.
Potential errors due to substrate vapor pressure uncertainty as identified in this work do not apply to the prior studies. The rate measurements of Kwok et al. (1994, 1995) were static measurements with a very large reactor volume (6400–6900 l). The rate measurements of Brubaker and Hites (1997, 1998) were made with a much smaller reactor volume (160 ml) under slow flow conditions. Kwok et al. (1995) reported large amounts of dark losses in studies of the 1-CDD substrate (26–63%), suggesting that possible wall absorption was occurring. Brubaker and Hites (1997) also reported the observation of wall effects in some of their measurements, particularly at lower temperatures.

As for other aromatic compounds at low temperatures, the gas-phase reactions of OH with DD, 2-CDD, 2,3-DCDD, 2,7-DCDD, 2,8-DCDD, and 1,2,3,4-Tetrachlorodibenzo-p-dioxin likely proceed by initial addition of the OH radical to the aromatic rings to form a hydroxychlorohexadienyl-type radical that is subsequently stabilized by collisions with the bath gas (Kwok et al., 1994, 1995; Atkinson, 1989, 1996). The magnitude and negative temperature dependence of our measurements are consistent with this mechanism. The position on the aromatic ring where OH addition occurs has not been elucidated. Quantum RRK calculations discussed below suggest that OH addition preferentially occurs at the H-substituted carbon site. OH addition at the Cl-substituted carbon site is highly unlikely with the exception of the OH + OCDD reaction.

At elevated temperatures (1000 K > T > 500 K) relevant to post-combustion conditions, our data does not exhibit any evidence for a change in reaction mechanism from formation of a stabilized OH addition adduct to H abstraction (large decrease in observed rate with a reversal in temperature dependence) as has been observed in our laboratories for chlorinated substrates containing a double bond (Yamada et al., 2001a,b). Theoretical estimates of the rate of H abstraction for $k_1$ using density functional theory (Becke, 1993) and transition state theory (Benson, 1976) calculations are consistent with our experimental observations and suggest that this reaction does not contribute to the observed rate at temperatures below 1000 K (see Fig. 4). This result leads us to conclude that H abstraction is not a significant pathway below 1000 K for all chlorinated congeners investigated. It is possible that at higher temperatures H abstraction may be a significant if not dominant mechanism of OH attack for all dioxin congeners excluding OCDD.

Our results are generally consistent with previous results at low temperatures, indicating a decrease in reactivity with increasing Cl substitution (Kwok et al., 1995; Brubaker and Hites, 1997, 1998). Table 1 illustrates extrapolated rates at room temperature ($k_{298}$) for all dioxin congeners examined in this study. We observed a similar rate coefficient for DD and 2-CDD at room temperature. Multiple Cl substitution on a single aromatic ring resulted in a measurable (factor of 2) decrease in OH reactivity. Cl substitution on both aromatic rings resulted in a much larger (factor of 5–13) decrease in room temperature reactivity. These results are generally consistent with the OH addition mechanism and indicate a significant stereoelectronic effect when Cl atoms are present on both aromatic rings.

The reaction rate and temperature dependence of the OCDD + OH reaction was different from all other chlorinated dioxin congeners that were examined in this study. OCDD exhibited a much slower reaction rate and positive temperature dependence throughout the temperature range investigated. The measured activation energy (5.4 ± 0.8 kJ/mol) is similar to that measured for OH + C2Cl4 (6.3 ± 0.8 kJ/mol) (Tichenor et al., 2000). Quantum RRK modeling of the OH + C2Cl4 reaction indicated that OH addition followed by Cl elimination was the dominant reaction pathway at all temperatures (Tichenor et al., 2000). A similar mechanism is plausible for the reaction of OH with OCDD. The electronic structure calculation using Density Functional Theory (DFT) for this size of molecule (12 carbons) is not feasible.

Table 1
Extrapolated room temperature rate coefficients for dioxin and chlorinated dioxins

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$10^{12} \cdot k_{298}$ (\text{(cm}^{-3}\text{molecule}^{-1}\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibenzodioxin</td>
<td>45.8</td>
</tr>
<tr>
<td>2-Chlorodibenzodioxin</td>
<td>38.9</td>
</tr>
<tr>
<td>2,3-Dichlorodibenzodioxin</td>
<td>22.1</td>
</tr>
<tr>
<td>2,7-Dichlorodibenzodioxin</td>
<td>7.4</td>
</tr>
<tr>
<td>2,8-Dichlorodibenzodioxin</td>
<td>7.1</td>
</tr>
<tr>
<td>1,2,3,4-Tetrachlorodibenzo-p-dioxin</td>
<td>18.2</td>
</tr>
<tr>
<td>Octachlorodibenzodioxin</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Fig. 11. Quantum RRK results for the OH addition to the ipso position of monochlorobenzene. $P = 1$ atm.
The calculation for the

**Table 2**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A$ (s$^{-1}$ or cm$^3$/molecule s)</th>
<th>$n$</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_6\text{H}_5\text{Cl} + \text{H} \rightarrow \text{C}_6\text{H}_5\text{Cl}-\text{OH}$</td>
<td>3.06E+04</td>
<td>2.27</td>
<td>29.7</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_5\text{Cl}-\text{OH} \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{OH}$</td>
<td>3.22E+06</td>
<td>2.27</td>
<td>166.5</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_5\text{Cl}+\text{OH} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{Cl}$</td>
<td>3.90E+13</td>
<td>0.00</td>
<td>69.4</td>
</tr>
</tbody>
</table>

Grouped geometric mean frequencies of the adduct with effective degeneracies: $436.8$ cm$^{-1}$ (13.25), $1245.0$ cm$^{-1}$ (16.44), $3238.3$ cm$^{-1}$ (6.31). Lennard-Jones parameters for $\text{C}_6\text{H}_5\text{Cl}-\text{OH}$ adduct, $\sigma = 7.529$ Å, $\epsilon = 813.0$ K.

A rate was estimated based on forward rate constant and principle of microscopic reversibility.

Arrhenius $A$ factor for Cl elimination reaction was adopted from the reaction: $\text{C}_2\text{H}_4\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{Cl}$, Barat and Bozelli (1992).

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References


