

Gas-Phase Oxidation Products of Biphenyl and Polychlorinated Biphenyls

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Our laboratory recently measured the gas-phase reaction rate constants of polychlorinated biphenyls (PCBs) with the hydroxyl radical (OH) and concluded that OH reactions are the primary removal pathway of PCBs from the atmosphere. With the reaction system previously employed for kinetics, we have now investigated the products of these PCB–OH reactions. Experiments were carried out in either air or He as the diluent gas at approximately 1 atm in a 160-mL quartz chamber. Temperatures ranged between 318 and 363 K in order to enhance the vapor pressures of these less volatile compounds. OH was produced in situ by the photolysis of ozone in the presence of H₂O. Reaction products from biphenyl, the three monochlorobiphenyls, and five dichlorobiphenyls were extracted from the chamber, derivatized by diazomethane, and analyzed by gas chromatographic mass spectrometry (GC/MS). Experiments gave benzoic acid and the appropriate chlorinated benzoic acids in significant product yields (8–17%).

Introduction

Polychlorinated biphenyls (PCBs) are industrial pollutants that have become ubiquitous in nearly all environmental compartments, including air, soil, water, sediments, and vegetation. Although PCB production and use were phased out and banned by the mid-1970s in most countries, PCB concentrations in the atmosphere have only decreased slightly, if at all, since that time (1–4). This is possibly due to ongoing inputs from waste sites (5) and to the continuous cycling of PCB between the atmosphere and water or soil (6–8).

In the atmosphere, PCBs are primarily found in the gas phase (9); thus, PCBs react with the hydroxyl radical (OH) (9–11). Our laboratory recently developed a gas-phase system for measuring OH reaction rate constants of semi-volatile organic compounds, such as PCBs, as a function of temperature (12). An investigation with this reaction system determined OH reaction rate constants of 16 PCBs with 0–5 chlorines (13). From these rate constants, it was concluded that OH reactions are the major removal pathway for PCBs in the atmosphere (13). It is now important to identify the products of these reactions because they could pose a greater environmental or health risk than the parent PCB. Identifying products is relatively difficult because PCBs have low vapor pressures (between 10⁻² and 10⁻⁷ Torr) at ambient temperatures. This makes it difficult to both introduce a significant amount of a PCB into the gas phase and to collect its gas-

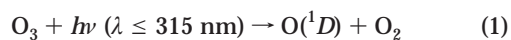
phase reaction products, which could have even lower volatilities.

Due to the small size of its quartz reaction chamber (160 mL), our reaction system provides some advantages over traditional systems that were previously used for OH reaction product studies (14–18). The chamber is mounted in an oven allowing experimental temperature control. Higher temperatures increase the vapor pressures of PCBs and, thus, the amount of these compounds in the gas phase. Also, the chamber is easily isolated and removed from the system. Products (and remaining reactants) can then be extracted from its walls and analyzed.

The research presented here had two goals: First, methods were developed and evaluated so that our reaction system could be used for PCB–OH product studies. This testing was initially done with biphenyl and naphthalene as the reactants. Second, the reaction system was then used to investigate the gas-phase OH reaction products of biphenyl, the three monochlorobiphenyls, and five dichlorobiphenyls as representative PCBs. The products from nine different PCB–OH reactions were extracted from the reaction chamber, derivatized with diazomethane, and analyzed by gas chromatographic mass spectrometry (GC/MS).

Experimental Section

OH reaction product experiments were carried out in a reaction system similar to that described in detail elsewhere for gas-phase OH reaction kinetics studies (12, 13, 19). The present system consisted of a 160-mL quartz reaction chamber mounted in the oven of a Hewlett-Packard (HP) 5890 gas chromatograph (for temperature control) and sampled by an on-line mass spectrometer (see below). Helium or air served as the primary diluent gas for all experiments, and the pressure inside the chamber was held at approximately 1 atm. OH radicals were produced in situ by



O₃ was produced by flowing O₂ through a 8–12 kV discharge prior to chamber introduction. Water vapor was introduced by bubbling the diluent gas flow through water at about 295 K. UV radiation, centered at 254 nm, was provided by a mercury, Pen-Ray lamp (UVP, Upland, CA). O₃ (and thus OH) concentrations were established by adjusting the gas flows through the chamber and the voltage set on the O₃ generator. The ratio of the primary diluent gas to the combination of O₃ and O₂ varied between 40 and 300, giving approximate O₃ concentrations between 0.3 and 2 × 10¹⁶ cm⁻³. Steady-state OH concentrations during photolysis ranged between 10⁷ and 10⁹ cm⁻³ for all experiments. The OH concentration for a given set of experimental conditions was determined by introducing either biphenyl or naphthalene and monitoring the compound's decay by on-line mass spectrometry. The OH concentration was then calculated using the appropriate OH reaction rate constant (13, 20).

On-Line Analysis. Approximately 100 μg of biphenyl was introduced into the reaction chamber via a heated quartz probe (21). Gas-phase reactants and products were sampled from the center of the quartz chamber by a 100 μm i.d. deactivated fused silica capillary interfaced to the on-line

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mass spectrometer. The capillary (J&W Scientific, Folsom, CA), 60–100 cm in length, was held at about 110 °C. The HP 5985B mass spectrometer was operated with electron impact ionization (EI) and scanned between m/z 50 and m/z 200. We obtained mass spectra every 10 s throughout the experiment, including before and after OH radical reactions had been initiated.

Off-Line Analysis. Two procedures were used to investigate OH reaction products by extracting them from the reaction chamber for GC/MS analysis. With each method, approximately 40–60 μg of reactant was introduced into the chamber by the quartz probe. On-line mass spectrometry was only used to confirm the reactant's introduction and to follow the experiment's progress. The experimental temperature for naphthalene–OH reactions was approximately 300 K. The experimental temperatures for the other reactants were determined by calculation (Clausius–Clapeyron equation) to give the same approximate vapor pressure as that of naphthalene at 298 K (0.29 Torr) (22). The experimental temperatures selected for biphenyl, the monochlorobiphenyls, and the dichlorobiphenyls were 318, 328, and 348 K, respectively. OH radicals were produced by irradiating the reaction chamber with the UV lamp for 20–25 min. Following UV irradiation, 20 μg of biphenyl- d_{10} in 2 μL of acetone was injected into the reaction chamber, which was then cooled to 273–283 K.

With the first extraction method, 6.4 mm i.d. Teflon valves (Cole-Parmer, Vernon Hill, IL) on the reaction chamber's inflow and outflow tubes were opened after the chamber had cooled. The chamber was then flushed with either He or air at 30 mL/min for 10 min. The outflow bubbled through a clean glass tube submerged in 20 mL of CH_2Cl_2 , all of which was held in a dry ice/acetone bath. The chamber itself was then removed from the reaction system's oven, and its inner walls were washed with 20 mL of CH_2Cl_2 . The two CH_2Cl_2 fractions were combined and rotary evaporated to approximately 4 mL.

The second extraction method did not use a cold trap. After the reaction chamber had cooled, it was removed from the oven and spiked with benzoic- d_5 acid, for reasons which will become clear later. The chamber's inner walls were rinsed twice with 20 mL of water at pH 8 and once with 20 mL of CH_2Cl_2 . The water was then acidified with a HCl solution to pH 2. The three fractions were then combined in a separatory funnel, along with 40 mL of additional CH_2Cl_2 . The water was extracted three times with 60 mL of CH_2Cl_2 . The aqueous layer was discarded, and the CH_2Cl_2 was reduced to a volume of about 4 mL.

With both extraction methods, the 4 mL volumes of CH_2Cl_2 were derivatized with diazomethane and then reduced to approximately 400 μL by evaporation under a gentle N_2 stream for analysis by GC/MS. Injections of 1 μL were performed in the splitless mode on a HP 6890 gas chromatograph. Chromatographic separation used a 30 m \times 250 μm i.d. DB-5MS column (J&W Scientific) with He as the carrier gas. The typical temperature program was 40 °C to 170 °C at 3 °C/min, 10 °C/min to 250 °C, and 20 °C/min to 290 °C with a 20-min hold. Experiments with naphthalene used the GC temperature program of Bunce et al. (14). Our mass spectrometer was a HP 5973, operated in the electron impact mode and scanned between m/z 40 and m/z 250.

OH Reaction Kinetics. OH reaction rate constants for 2-hydroxybiphenyl and benzoic acid were measured between 323 and 363 K using our previous techniques (19–21). Measurements were based on the relative rate method (23), and the reference compounds were biphenyl and cyclohexane for the 2-hydroxybiphenyl and benzoic acid experiments, respectively. Reactants introduced into the quartz reaction chamber were monitored in real time by the on-line HP 5985B

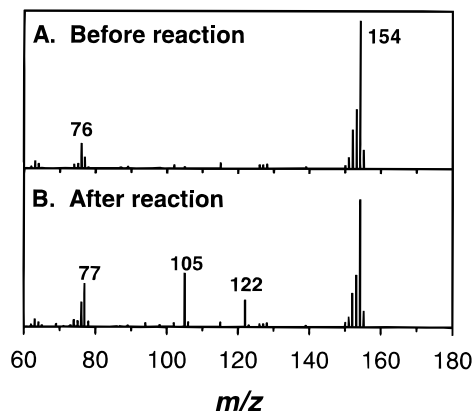


FIGURE 1. Mass spectra acquired on-line (A) before and (B) after reaction of biphenyl with OH radicals.

mass spectrometer operating in electron impact and selected ion monitoring modes.

Assuming OH reactions were the primary loss processes during UV irradiation of the chamber, the recorded signal intensities for the test and reference compounds follow

$$\ln \frac{[\text{test}]_0}{[\text{test}]_t} = \left(\frac{k_{\text{test}}}{k_{\text{ref}}} \right) \ln \frac{[\text{reference}]_0}{[\text{reference}]_t} \quad (3)$$

where the signal intensities were measured at time $t = 0$ and at subsequent times t . The values k_{test} and k_{ref} represent the OH reaction rate constants for the test and reference compounds, respectively. Values of k_{test} were calculated from the slopes of experimental plots of eq 3 and the temperature-dependent expressions of k_{ref} recommended for biphenyl (13) and cyclohexane (24). Other potential loss processes of the reactants that 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 signal intensities before and after the UV light was turned on.

Materials. Gases: He (99.999%), O_2 (99.998%), and air (Gas Tech, Hillside, IL). Solvents: CH_2Cl_2 and HPLC-grade H_2O (EM Science, Gibbstown, NJ). Reactants: naphthalene, biphenyl, and 2-hydroxybiphenyl (Aldrich, Milwaukee); benzoic acid, (Mallinckrodt, Paris, KY); 2-, 3-, and 4-chlorobiphenyls and 2,4-, 2,5-, 2,2'-, 2,3'-, and 2,4'-dichlorobiphenyls (AccuStandard, New Haven, CT). Internal standards: biphenyl- d_{10} and benzoic- d_5 acid (Aldrich). Calibration standards: 2-, 3-, and 4-chlorobenzoic acids, 2,4- and 2,5-dichlorobenzoic acids, methyl benzoate, and methyl 4-chlorobenzoate (Aldrich). Diazomethane generation: Diazald and KOH (Aldrich); diethyl ether (Fisher, Fair Lawn, NJ); methanol (EM Science). Miscellaneous: HCl solution (0.100 N; Fisher); *N,O*-bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane (BSTFA + 1% TMCS; Pierce, Rockford, IL). The stated purities for all compounds were 98% and higher, unless otherwise noted.

Results and Discussion

On-Line Analysis of the Biphenyl–OH Reaction. Our first goal was to acquire on-line mass spectra of biphenyl–OH reaction products while making minimal changes to the reaction system previously used for OH reaction kinetics (19, 20). Figure 1 gives mass spectra for such an on-line analysis. Spectrum A is that of the analyte biphenyl, just prior to the generation of OH radicals. The reaction chamber was filled with He and held at 363 K, and the maximum gas-phase concentration of biphenyl was $2.4 \times 10^{15} \text{ cm}^{-3}$. Spectrum B was taken after irradiating the chamber for 2.6 min, generating steady-state OH concentrations between 4 and

TABLE 1. Experimental Conditions, Rate Constant Ratios, and Rate Constants for OH Radical Reactions of 2-Hydroxybiphenyl and Benzoic Acid

<i>T</i> (K)	<i>k</i> _{test} / <i>k</i> _{ref} ^a	rate constant (× 10 ⁻¹² cm ³ s ⁻¹)	<i>T</i> (K)	<i>k</i> _{test} / <i>k</i> _{ref} ^a	rate constant (× 10 ⁻¹² cm ³ s ⁻¹)
	2-hydroxybiphenyl ^b			benzoic acid ^c	
323	3.35 ± 0.73	23 ± 6	333	0.051 ± 0.016	0.42 ± 0.11
323	2.68 ± 0.58	18 ± 5	333	0.079 ± 0.025	0.66 ± 0.16
323	2.61 ± 0.56	18 ± 4	343	0.099 ± 0.031	0.84 ± 0.21
323	1.95 ± 0.42	13 ± 3	363	0.081 ± 0.002	0.73 ± 0.18
363	3.18 ± 0.20	22 ± 5	363	0.081 ± 0.002	0.73 ± 0.18
363	2.77 ± 0.17	19 ± 5	363	0.078 ± 0.002	0.71 ± 0.18
363	3.03 ± 0.19	21 ± 5			
363	2.87 ± 0.18	20 ± 5			

^a Stated uncertainties of the rate constant ratios are based on two relative standard deviations of the measurements at a given temperature.

^b Biphenyl was the reference compound. Stated uncertainties of the experimental rate constants reflect the estimated overall uncertainty recommended for biphenyl's rate constants ±25% (37). ^c Cyclohexane was the reference compound. Stated uncertainties of the experimental rate constants reflect the estimated overall uncertainty recommended for cyclohexane's rate constants ±25% (24).

8 × 10⁸ cm⁻³. A comparison of the absolute intensities of the *m/z* 154 signals for spectra A and B indicates that approximately 70% of the gas-phase biphenyl had reacted during this particular experiment.

There are two interesting things to note by comparing the mass spectra in Figure 1. First, spectrum B had very little signal at *m/z* 170, the molecular ion of hydroxylated biphenyls. Although spectra from this experiment and others definitely showed the generation of *m/z* 170 from OH reactions with biphenyl, the *m/z* 170 signal was rarely above those of background ions. This low yield of hydroxylated biphenyls is interesting because they were expected to be the primary products of the biphenyl–OH reaction. For example, Atkinson et al. showed yields of 20 ± 8% for hydroxylated products in their investigation of this gas-phase reaction (15), and Sedlak and Andren reported seven different hydroxychlorobiphenyls as products of 2-chlorobiphenyl's reaction with OH radicals in the aqueous phase (25). The relative absence of hydroxylated biphenyls in our experiments was curious and unanticipated.

Note also that spectrum B in Figure 1 is relatively "clean". In addition to hydroxylated biphenyls, we also anticipated several other aromatic and ring-opened products from secondary reactions (15), resulting in overlapping mass spectra of several compounds. Clearly, this was not the case. The only new ions, relative to those for biphenyl, were *m/z* 77, 105, and 122, ions that indicated the unexpected production of benzoic acid.

There are two possible explanations for the lack of the expected biphenyl–OH reaction products. First, they might be less volatile than the parent compound and more apt to sorb from the gas phase onto the chamber's walls, and these products would not be detected by on-line mass spectrometry. Second, the reaction products would also be expected to have polar functionalities that would limit their ability to transverse the capillary tube between the reaction chamber and the mass spectrometer's ion source. Even though the capillary tube is deactivated, past experience with this reaction system suggests that the presence of O₃ may tend to reactivate the capillary toward certain compounds (21). Therefore, off-line methods were pursued as an alternative approach for the identification of reaction products.

Off-Line Analysis of OH Reaction Products. On the basis of the work of Bunce et al. (14), naphthalene was used as a model compound to test our procedures. Naphthalene was first reacted for 20 min with OH concentrations between 0.9–2 × 10⁷ cm⁻³, air was the diluent gas, and the temperature was about 300 K. From our GC/MS results, we were able to identify many of the same reaction products as Bunce et al. (14): phthalaldehyde, phthalic anhydride, phthalide, 1,4-naphthoquinone, 2-formylcinnamaldehyde (both *cis* and

trans), and 2,3-epoxy-1,4-naphthoquinone. Similar product mixtures were found when we varied the OH concentrations and reaction times. The nitrated products reported by Bunce et al. were not found in our study because these workers generated OH radicals by the photolysis of isopropyl nitrite in the presence of air and NO (14), a process which involves extensive NO_x chemistry.

The same techniques were then used to identify products of the biphenyl–OH reaction. These reactions, however, were carried out at 318 K, and the product mixtures were derivatized with diazomethane. OH concentrations were widely varied between 0.06 and 7 × 10⁹ cm⁻³. In this case, the only major reaction product that was identified by GC/MS was the methylated derivative of benzoic acid, methyl benzoate. Hydroxylated biphenyls were found only inconsistently and only in trace amounts, in contrast with Atkinson et al. (15). 2-Hydroxybiphenyl predominated among the three isomers, and 4- and 3-hydroxybiphenyl, when they were found at all, were present in decreasing amounts, respectively. All observed hydroxybiphenyls were unmethylated. There were no indications that these compounds were derivatized by our diazomethane procedures, and attempts to derivatize a known solution of 2-hydroxybiphenyl with diazomethane were unsuccessful. 2-Hydroxybiphenyl, on the other hand, was easily silylated with BSTFA + 1% TMCS; however, silylation of archived samples still did not reveal any significant amounts of hydroxybiphenyls. Control experiments also revealed that 2-hydroxybiphenyl could be extracted from the reaction chamber and detected as efficiently as biphenyl and benzoic acid. Other identified products were benzaldehyde and salicylic acid (methylated at its carboxylic group); however, both of these compounds represented only minor traces relative to methyl benzoate.

OH Reaction Kinetics for 2-Hydroxybiphenyl and Benzoic Acid. To determine why benzoic acid and not the expected hydroxybiphenyls was the major product of the biphenyl–OH reaction, a comparison was made between their OH reaction rate constants. Because these rate constants were not available in the literature, we measured OH reaction rate constants for 2-hydroxybiphenyl and benzoic acid. These rate constants are presented in Table 1, and the Arrhenius plot is given in Figure 2. Note in Figure 2 that the OH reaction rate constants for 2-hydroxybiphenyl are about a factor of 3 higher than those reported for biphenyl (13). Therefore, under our relatively high OH concentrations, hydroxybiphenyls were probably consumed as soon as they were produced by the initial biphenyl–OH reaction. Benzoic acid, on the other hand, gave measured OH reaction rate constants that were approximately a factor of 10 lower than those of biphenyl, allowing benzoic acid to accumulate in the reaction chamber. This situation is analogous to the one

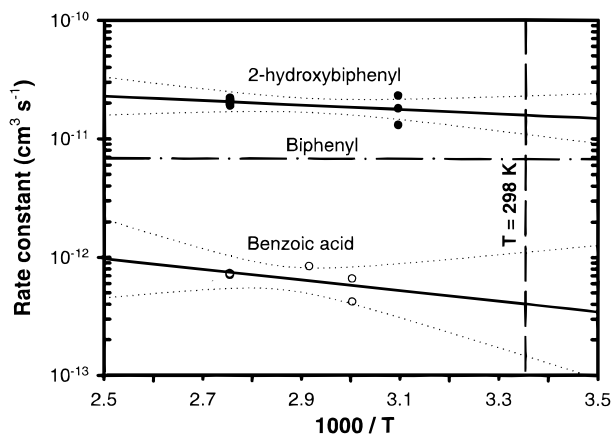


FIGURE 2. Arrhenius plot for the OH reactions of 2-hydroxybiphenyl and benzoic acid. Symbols: ●, 2-hydroxybiphenyl-OH reaction rate constants; ○, benzoic acid-OH reaction rate constants. Lines: (solid), fits to each data set; (dotted), 95% confidence limits of each fit; (dashed), expression reported by Anderson and Hites for the biphenyl-OH reaction (13).

Bunce et al. reported for the naphthalene-OH reaction (14). They noted that 1- and 2-naphthols were only observed sporadically and in low yields and concluded that the primary reaction products were more reactive toward OH than the initial reactant itself (14).

Benzoic Acids as Products of PCB-OH Reactions. Given that benzoic acid was the major product in our biphenyl-OH reaction mixtures, this study's focus was shifted toward benzoic acids as PCB-OH reaction products. The previous off-line method was modified in order to optimize the extraction of benzoic acids from the reaction chamber (see the second method above). This method gave yields for the benzoic acids resulting from OH reactions from biphenyl, the three monochlorobiphenyls, and five dichlorobiphenyls. The method was comparable to the first off-line method based on results for biphenyl. Experiments were carried out in air at the temperatures given in Table 2. The reaction chamber was irradiated 20–25 min each time, giving approximate OH concentrations of $1-3 \times 10^8 \text{ cm}^{-3}$. Most of the PCBs gave significant yields of benzoic acid and the appropriate

chlorinated isomer(s); see Table 2. 2,3'- and 2,4'-dichlorobiphenyls, with chlorines on different rings, produced significant amounts of 2-chlorobenzoic acid and either 3- or 4-chlorobenzoic acid, respectively. 2-Chlorobenzoic acid was the only significant reaction product of 2,2'-dichlorobiphenyl, which has its two chlorines in the same position on opposite rings. For those PCBs producing two isomers, the yields were generally about even between the two products, indicating no major effect from the chlorine positioning on the initial reactant. The total benzoic acid yields for all the PCB isomers ranged between 15 and 17%, with the exception of the dichlorobiphenyls with chlorines on opposite rings. In this case, the total benzoic acid yields dropped to 8–10%, possibly due to lower vapor pressures and/or lower OH reaction rates under our experimental conditions.

Benzoic acids were also quantitated as a percentage of total PCB-OH reaction products, based on the amount of the initial compound that reacted. Benzoic acids represented approximately 17–33% of the reaction products from PCBs with at least one unsubstituted ring and 11–19% from PCBs with a chlorine on each ring. It is not clear what reaction products represent the remaining 70–90% in each case. Besides hydroxylated biphenyls, trace levels of benzaldehydes, acetophenones, and similar compounds containing a carbonyl linked to an aromatic ring were also identified by GC/MS. These compounds contained 0–2 chlorines (depending on the parent PCB) and, given their low yields, would only represent a very small fraction of the remaining products. Other products could have been small, fragmented compounds that resulted from the ring cleavage of reactants and intermediates and were unamenable to our extraction methods and/or to GC/MS analysis.

In control experiments with biphenyl and the monochlorobiphenyls, we found that the benzoic acids were also formed when reactants were held in the chamber for 20 min under typical experimental conditions but with the UV lamp left off. Therefore, we also measured benzoic acid yields by varying the oxidative conditions for the experiments (see Table 3). Experimental conditions differed by the choice of diluent gas (He or air) and the presence of O_3 and/or UV irradiation. The yields under dark conditions with O_3 present were lower but still significant as compared to the usual conditions using UV light. Only in one instance with

TABLE 2. Yields (in %) for Benzoic Acids as Products of PCB-OH Reactions

initial reactant	rxn temp (K)	product yields, ^a individual benzoic acid isomers ^b					av of total
		Unchl	2-Cl	3-Cl	4-Cl	2,4-Cl	
biphenyl	318	18 17 ^c					17
2-chlorobiphenyl	328	9 7	10 8				17
3-chlorobiphenyl	328	8 8		8 8			16
4-chlorobiphenyl	328	7 8			8 10		16
2,4-dichlorobiphenyl	348	8 8				6 10	16
2,5-dichlorobiphenyl	348	6 6					11 8
2,2'-dichlorobiphenyl	348	0.3 0.2	8 8				8
2,3'-dichlorobiphenyl	348	0.2 0.3	3 5	4 6			9
2,4'-dichlorobiphenyl	348	0.5 0.3	5 3		7 5		10

^a Yield = [(mol of product)/(mol of initial reactant)] × 100%. ^b Benzoic acids were analyzed as methyl benzoates following diazomethane derivatization. ^c Duplicate experiments.

TABLE 3. Total Benzoic Acid Yields (in %) under Different Oxidative Conditions

initial reactant	total benzoic acid yields, ^a increasing oxidative conditions →							
	He only	air only	air, H ₂ O	air, UV	air, H ₂ O, UV	He, O ₃	air, O ₃	air, O ₃ , UV
biphenyl	0.3	0.5	0.7	0.5 0.5 ^b	0.8 0.5	2.0 6.1	1.1 0.4	18 17
2-chlorobiphenyl			0.3				5.4	19 15
3-chlorobiphenyl	0.2		0.3			21 5.9	11	17 16
4-chlorobiphenyl			0.3				6.7	14 18

^a Yield = [(mol of product)/(mol of initial reactant)] × 100%. ^b Duplicate experiments.

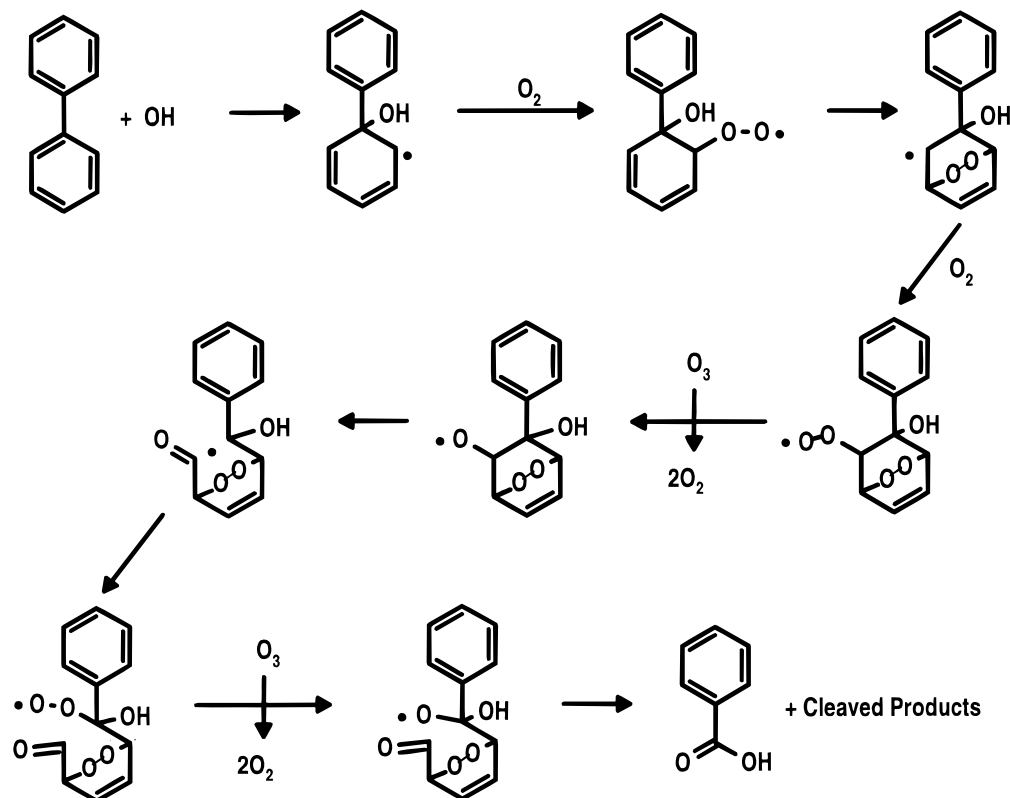


FIGURE 3. Possible reaction scheme leading to benzoic acid from the OH radical-initiated reaction of biphenyl.

3-chlorobiphenyl was the yield with and without UV about the same. Experiments without any O₃ in the reaction chamber gave much lower amounts of *only* the unchlorinated benzoic acid. This resulted from background contamination, because extraction of the reaction system without any reactants present gave the same levels of benzoic acid.

It has been widely known that chlorinated benzoic acids are produced by PCB-degrading bacterial strains (26–28); however, no gas-phase biphenyl-to-benzoic acid link has been reported in the literature. We suggest a possible gas-phase mechanism initiated by OH radicals (see Figure 3). This scheme is unusual in that OH first attacks the ipso position on one of the two phenyl rings. One would expect OH initiation at either the ortho, para, or meta position (14, 24, 29), but such pathways, which are not well-known past their first step, would not likely lead to benzoic acid. The pathway in Figure 3 only suggests a role for O₃ as an O-atom scavenger from dioxy radicals, but our dark reaction results imply that other significant roles may also exist for O₃. It is unlikely that O₃ reactions with biphenyl actually initiate the benzoic acid production pathway. Toluene, an aromatic structurally similar to biphenyl, has a relatively slow O₃

reaction rate constant of $1.6 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1}$ at 318 K (30). Assuming that biphenyl has approximately the same O₃ reaction rate, its lifetimes under our experimental conditions with regard to OH and O₃ reactions would be about 20 min and 20 h, respectively; thus, OH would most likely initiate a reaction with biphenyl. However, once aromaticity is broken along an OH-initiated pathway, there is a greater probability that O₃ will become a significant reactant in the overall reaction pathway. For example, the O₃ reaction rate constant for 1,4-cyclohexadiene is $4.6 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ at 296 K (31) as compared to $1.4 \times 10^{-22} \text{ cm}^3 \text{ s}^{-1}$ for benzene at the same temperature (30). It is also interesting to note that O₃ itself could have been generating significant OH concentrations during our dark experiments. Finlayson-Pitts et al. reported OH relative rate constant measurements for simple alkanes and toluene using O₃/O₂ as a dark source for OH and experimental conditions similar to ours (32). While there was no clear explanation as to how this source produced OH, the authors suggested that OH radicals (at approximate concentrations of 10^8 cm^{-3}) may have resulted from slow reactions of O₃ with the analytes, catalyzed by the surfaces of their quartz reaction vessel. This may have been possible

with our system. Our quartz chamber was approximately the same size, and the kinetics of such slow reactions could have been enhanced by our higher experimental temperatures.

Atmospheric Implications. Results presented in this study indicate that the gas-phase oxidation of PCBs can result in relatively high yields of chlorinated benzoic acids. The same processes could also occur in the atmosphere. Clearly, evidence of chlorinated benzoic acids in the atmosphere, presumably in the vicinity of PCB sources, is needed in order to support this hypothesis. The literature currently contains no reports of chlorinated benzoic acids in the environment, with the exception of a very few indications related to either biodegradation (33) or waste incineration (34). This scarcity of information may be due to a lack of proper analytical techniques or research interest in these compounds.

Besides environmental data, additional product studies are needed for the gas-phase OH reactions of PCBs. No single reaction system can simulate what actually occurs in the atmosphere, and investigations by several research groups would complement each other, and together they might be able to deduce the actual atmospheric reaction pathways and their products. As shown here, our system and conditions may not be optimal for the formation or accumulation of primary PCB-OH reaction products, just as those in other studies may or may not recover chlorinated benzoic acids. Our study also suggests that OH reaction product analyses with our reaction system may be susceptible to dark and/or heterogeneous surface reactions related to O₃, our OH source. Additional studies, especially those using different types of OH sources and reaction chambers, would help in further evaluating our system's results and understanding the actual gas-phase oxidation of atmospheric PCBs.

Acknowledgments

The U.S. Environmental Protection Agency (Grant R82-5377) provided financial support. The authors also thank Philip Stevens (Indiana University, School of Public and Environmental Affairs) for helpful discussions regarding reaction pathways.

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Received for review May 18, 1998. Revised manuscript received September 8, 1998. Accepted September 17, 1998.

ES9805021