Decomposition of Monochlorobiphenyl Isomers in Supercritical Water in the Presence of Methanol

Gheorghe Anitescu and Lawrence L. Tavlarides
Dept. of Chemical Engineering and Materials Science, Syracuse University, Syracuse, NY 13244

Valentin Munteanu
Dept. of Physical Chemistry, Bucharest University, Bucharest 7036, Romania

DOI 10.1002/aic.10154

Comprehensive studies of monochlorobiphenyl (MCB) decomposition in supercritical water in the presence of methanol and other cosolvents, both with and without oxygen, are being conducted to understand the reaction kinetics and pathways of individual PCB isomers and to determine the structure–reactivity relationships. In the present study the disappearance rate of MCBs, delivered in an isothermal plug-flow tubular reactor as methanolic solutions, is investigated at 25 MPa and temperatures of 673, 723, and 773 K. Experiments are conducted at nominal MCB feed concentrations of 1–100 μmol/L (reaction conditions) using MCB/MeOH and H_2O_2/H_2O solutions (1–3 g/L and 0–10 wt. %, respectively). Molar conversions of these isomers vary from 3% (2-CB, 773 K, 2 s) to 30% (4-CB, 773 K, 46 s) without oxygen (SCWT) and from 1% (2-CB, 673 K, 3.8 s) to 97% (4-CB, 773 K, 24.5 s) with oxygen (SCWO). For SCWT the overall conversion follows apparent first order, whereas for SCWO the conversion is second order. The regressed data lead to Arrhenius parameters of frequency factor and activation energy with values of $10^{20.5}$–$10^{21.3}$ s^{-1} and 320–331 kJ/mol for SCWT and $10^{24.1}$–$10^{24.8}$ s^{-1} $(mol/L)^{-1}$ and 281–292 kJ/mol for SCWO, respectively. The reactivity of the MCB isomers increases in the order 2-MCB < 3-MCB < 4-MCB. The positively identified reaction products by GC-MSD and GC-FID/ECD/TCD analyses are mainly biphenyl, open-ring biphenyl compounds such as acetophenone and benzaldehydes, and mineral products (CO, CO_2, and HCl). More studies are in progress regarding the role of the second solvent on reaction rates and reaction mechanisms and pathways. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 1536–1544, 2004

Keywords: supercritical water oxidation/thermolysis, global kinetics, tubular flow reactor, GC-FID/ECD/TCD/MSD, PCBs, methanol

Introduction

Because pollutants exist in a variety of matrices with different chemical and physical characteristics, destruction of toxic organic materials is an overwhelming problem if left for conventional treatment processes. Incineration and supercritical water oxidation (SCWO) are two existing options for a rapid and complete destruction of toxic persistent organic pollutants (POPs) included in adequate feedstock solutions. However, whereas incineration has associated problems such as very high cost (especially associated with dewatering steps) and public resentment, SCWO is a proven method to treat (without high-cost preparation steps) different materials contaminated with POPs. Although SCWO technology takes advantage of the complete miscibility of most organic compounds and oxygen with supercritical water (SCW), eliminating the slow mass-

---

Correspondence concerning this article should be addressed to L. L. Tavlarides at lltavlar@ecs.syr.edu.

transfer process that occurs in multiphase systems, the problem of delivering hydrophobic POPs to a flow reactor has not yet been satisfactory solved. In dealing with such problems, the use of a second solvent for the delivery of water-insoluble organics is a viable alternative, and the best choice to date appears to be methanol (Anitescu and Tavlarides, 2000, 2002). Other major problems challenging the SCWO applications are corrosion, salt deposits on the walls of reactors, and lack of optimum parameters to be used in the design of large-scale reactors. Numerous research groups are executing intense work on these important issues and are showing progress on solving the mentioned problems (Crain et al., 2000; Crooker et al., 2000; Konys et al., 1999; Kritzer and Dinjus, 2001; Macdonald and Kriksunov, 2001; Mitton et al., 2000; Rice and Steeper, 1998; Savage, 1999; Shaw and Dahmen, 2000; Tester and Cline, 1999).

Although the vast majority of organic compounds can be technically destroyed by incineration of nonaqueous solutions, the class of halogenated POPs poses a great challenge even to the most sophisticated modern incinerators. For example, the incineration of polychlorinated biphenyl congeners (PCBs) commonly generates the most harmful known POPs such as polychlorinated dibenzofurans/dioxins (PCDFs/PCDDs) (Hutzinger et al., 1985). To overcome this problem, temperatures of more than 1373 K are required. Moreover, this method is apparently inappropriate for PCB destruction because PCBs themselves result as byproducts from the incineration of chlorinated compounds and these flame retardants scavenge free radicals, which are essential in sustaining the flames in combustion reactions. Furthermore, the undesired precursors of smog and acid rain, $(N/S)O_x$ oxides produced by combustion processes, are not formed under much lower temperatures of SCWO reactions if any compounds containing nitrogen and sulfur are present in the reactor (Savage, 1999).

Different chlorinated aromatic compounds have been studied under SCWO conditions, including a few PCB mixtures and only one congener. Modell (1989) first reported a destruction efficiency of over 99.99% at +783 K, 25.3 MPa, and 3.7 min for a transformer fluid containing PCBs. Hatakeda et al. (1999) reported SCWO of the liquid 3-CB congener and a PCB mixture (Kaneclor KC-300). A 99.99% destruction removal efficiency of trace PCBs in sludge has been reported by Crain et al. (2000). High oxidative destruction rates of PCBs during 15-min treatments under SCWO conditions in a batch reactor are reported by Weber et al. (2002). These experiments have been focused on the ability of the SCWO process to achieve high conversions rather than on the acquisition of kinetic information, which requires studies under conditions of incomplete conversions. Although the results based on the former approach permit one to assess the feasibility of the method under severe conditions, the information gathered from the latter research will permit a design of SCWO reactors to operate under less-severe conditions for comparable performances.

Our previous kinetic studies, conducted over a wide range of conditions for a complex mixture of PCB congeners (Aroclor 1248) and for a tetrachlorobiphenyl as a surrogate for this mixture, were intended to assess the rate of destruction of PCBs using the SCWO technique (Anitescu and Tavlarides, 2000, 2002). The data on the oxidation of 33′44′-PCB and Aroclor 1248 (a mixture of nearly 76 PCB congeners) revealed significant differences among the reactivities of PCB molecules, depending on the number and positions of Cl substituents. However, no systematic and comprehensive study of SCWO of individual PCB congeners, including isomers, has been carried out to date.

Given that complex PCB mixtures and high chlorinated congeners do not allow a detailed analysis of the reaction kinetics/pathways and structure–reactivity relationships to be determined, we are conducting comprehensive SCWO and thermolysis (SCWT) studies of MCB isomers dissolved in methanol and other solvents. Herein we report the experimental data concerning the conversion of MCB/MeOH solutions and the modeling procedure as global kinetics. More studies are in progress regarding the role of the second solvent on reaction rates and reaction mechanisms and pathways. With appropriate models, this information will permit evaluation of the feasibility and cost of SCWO of PCB extracts from soils and other materials.

Experimental

Apparatus

Experiments of MCB/MeOH decomposition in supercritical water, both with and without oxygen, are conducted in a high-pressure tubular reactor capable of continuous operation at temperatures up to 873 K and pressures up to 70 MPa. Under the operating conditions, calculated Reynolds numbers characterize a turbulent flow, thus confirming the validity of the assumption of a plug-flow reactor.

The experimental apparatus, described in detail elsewhere (Anitescu et al., 1999), consists of three major modules: pumps and preheaters, reactor, and cooling and separation. Several modifications are operated to improve its functionality and the quality of the data. In the pump and preheating subsystem, PCBs/MeOH and oxidant (H_2O_2/H_2O solutions) are delivered in separate lines by three high-pressure feed pumps (ISCO 100-D): one for the organic stream and two for the aqueous solutions. The reactor and oxidizer preheater tubings (1.6 mm ID, 3.2 mm OD) are made from Hastelloy C-276, whereas the organic feed line is stainless steel tubing (0.2 mm ID, 3.2 mm OD). The organic feed is mixed with supercritical oxidant in a mixing tee by flowing from opposite directions. The temperature is monitored near the reactor inlet in the centerline of combined flows in a second tee (connected close to the previous tee), at the middle, and the outlet of the reactor. Because of the low organic concentrations used, temperature does not vary significantly along the reactor (max. ±2 K). The variation of reactor residence time is achieved either by changing the reactor length while maintaining constant feed rates or by changing the feed rates and keeping the same reactor length. The reactor and the preheating coils are immersed in an isothermal fluidized sand bath. The cooling and separation module consists of a special new water-cooled glass separator for steady-state effluents (designed and fabricated at Syracuse University), and a coiled, air-cooled, SS-316 heat-exchanger, connected to a waste collecting bottle for the unsteady-state portion of the reaction.

Procedure

Deionized water for MCB thermolysis and the H_2O_2/H_2O solutions for SCWO experiments are fed to the system by two

ISCO pumps connected in parallel. The oxidizer is thermally decomposed in the preheating section to a high-pressure mixture of oxygen in SCW. The preheated PCB/MeOH and aqueous streams with and without oxygen are pumped in the reactor at the desired temperature, pressure, and flow rates. The temperature and pressure are controlled by three heaters at the bottom of the fluidized sand bath and by a special designed micrometric valve at the end of the reactor, respectively. The stream pressure is dropped to ambient conditions, and the gaseous and liquid phases are then directed in either one of two separators connected in parallel. During the unsteady-state portion of the reaction, the liquid products are collected directly in a waste bottle and removed occasionally while the gases are vented. The products of the steady-state reaction are depressurized, cooled, and separated in the second separator and further analyzed by chromatographic methods. The steady state is assumed to be attained after adequate time has transpired for reactants to flow through both the preheater and reactor and SCWO conditions (temperature, pressure, and flow rates) are stabilized. The conditions at the end of the reactor and in the separator were carefully established such that no significant amount of organic reaction products are lost after the steady-state effluent content is removed for sampling. These include a thorough rinsing of the steady-state separator and both inlet and outlet pipes.

Main experimental parameters

The main reaction parameters considered in the experiments are: the residence time, temperature, and the MCB and oxygen initial concentrations. All the experiments are performed in pairs of replicates and the results show an overall standard deviation less than 10%.

Residence Time. This parameter ranges from 2.0 s at 773 K to 45.5 s at 673 K and is determined by the flow rates of H_2O_2/H_2O and PCB/MeOH liquid solutions (5.0–10.0 and 0.1–0.2 mL/min, respectively). When combined with the two reactors used for these sets of experiments, these flow rates result in five-point isotherms. By assuming a constant volumetric flow rate through the reactor at given low concentration of the organic reactants, residence time (τ) is calculated by dividing reactor volume (V) by the volumetric flow rate at supercritical conditions (v_{SC})

$$\tau = V/v_{SC} \tag{1}$$

Based on the mass balance of the materials in the liquid phase (L) and in the supercritical phase (SC), a simple equation to calculate residence time can be obtained

$$\tau = (\rho_{SC}/\rho_L)V/v_L \tag{2}$$

The residence time is in seconds, the volume of the reactor is in mL, the densities of the both phases are in g/mL, and the total flow rate of the liquid reactants (v_L) is in mL/s. The density of water at reaction conditions is calculated using NBS Steam Tables (Haar et al., 1984). The fluid mixture density is assumed to be that of the bulk water and the assumption is valid when checked with the Peng–Robinson equation of state.

Temperature. The SCWO experiments are conducted isothermally at 25 MPa and three different temperatures (673, 723, and 773 K), whereas most of the SCWT reactions are studied at 773 K. Some SCWT experiments are carried out at lower temperatures of 673 and 723 K. Because at these low temperatures the MCBs barely decompose, the results can be used as a PCB mass balance and closures within the error limits of the overall method are obtained.

Initial Concentrations of the MCB Isomers. These are selected at values of 1–3 g/L in methanol and resulted in different concentrations under the reaction conditions (1–100 μmol/L), attributed to density change with temperature and the flow rates.

Initial Oxygen Concentration. Most of the experiments are conducted at a nominal $[H_2O_2]/[H_2O]$ concentration of 6 wt. %, providing an excess oxygen of 20 mol % (144 mmol/L or 1.59 mol % at the reaction conditions). In the case of 3-CB, experiments at different concentrations of oxidant (substoichiometric, stoichiometric, and with excess oxygen) are also conducted. It is important that H_2O_2 be completely converted to O_2 and H_2O to ensure the reliability of the experimental results (Croiset et al., 1997). Using the maximum oxidizer flow rate for our experiments of 10 mL/min, the residence time in the preheating line is beyond 10 s at 673 K. This high value of the preheating time allows for a complete decomposition of H_2O_2 before the oxidizer and organics are mixed and is helpful to level off the oscillations in the flow rate and pressure throughout the reactor. For lower flow rates and higher temperatures of the experiments, H_2O_2 decomposition is apparently ensured.

Analytical technique

Reaction products containing carbon and HCl are analyzed by gas and ion chromatography (GC and IC), respectively. Three Hewlett–Packard 5890 series II gas chromatographs and a Dionex DX ion chromatograph are used to perform all of the chemical analyses. The gaseous phase is only occasionally captured into a 250-μL sample loop and analyzed by on-line GC-TCD (CROMPACK, 25 m × 0.53 mm ID, 25 μm film thickness). A portion of the liquid phase product is first extracted in hexane and then diluted or concentrated before analysis by off-line capillary GC-FID/ECD and GC-MSD to identify and measure the amount of unreacted MCBs and the reaction products. GC separation is achieved on capillary columns: Ultra 2 (25 m × 0.2 mm ID × 0.33 μm film thickness) for the former techniques and HP-1MS (30 m × 0.25 mm ID × 0.25 μm film thickness) for the latter. The GC response factors are obtained by running standard solutions containing certified concentrations of the MCB isomers and other major reaction intermediates. Chromatographic errors are found to be less than 5% through replicate analysis. To identify the oxidation reaction products of MCBs, the effluent liquid-phase samples were concentrated and analyzed by GC-MSD using both NIST and Wiley libraries of spectra. Portions of the aqueous effluent streams are analyzed for HCl by IC equipped with a CD20 conductivity detector and an IonPac AS14 (4 × 250 mm) column.

Reactants

The oxidant is oxygen, supplied for the experiments as solutions of hydrogen peroxide of 3–15 wt. % concentration

Table 1. Thermolysis Conversions of MCB Isomers in SCW at 773 K and 25 MPa*

Rxn Time τ (s)	2-CB		3-CB		4-CB		Mole Balance
	$(X_2)_{C1}$	$(X_2)_{C2}$	$(X_3)_{C1}$	$(X_3)_{C2}$	$(X_4)_{C1}$	$(X_4)_{C2}$	
24.5	0.156	0.165	0.207	0.230	0.272	0.311	0.973
24.5	0.150	0.182	0.198	0.244	0.258	0.291	0.985
17.5	0.120	0.152	0.151	0.189	0.210	0.260	0.993
17.5	0.109	0.138	0.162	0.178	0.233	0.234	0.994
12.3	0.098	0.114	0.125	0.149	0.174	0.195	1.001
12.3	0.082	0.127	0.135	0.152	0.167	0.181	0.991
4.1	0.047	0.065	0.059	0.074	0.075	0.094	1.011
4.1	0.041	0.062	0.057	0.051	0.085	0.079	1.019
2.0	0.028	0.032	0.032	0.043	0.043	0.048	1.012
2.0	0.029	0.033	0.031	0.046	0.044	0.056	0.997
							Overall: 0.998

*C_1 = 1 g/L and C_2 = 3 g/L MCB/MeOH.

prepared from 30 wt % H_2O_2/H_2O solution (purum p.a., Fluka) by dilution with deionized water. Neat MCBs and standard solutions of both MCB isomers and reaction products were purchased from ChemServe. The purity of methanol (Optima, Fisher Scientific) is minimum 99.9%. All reactants were used with no further purification.

Results

PCB/MeOH decomposition in supercritical water without oxygen (SCWT)

The disappearance of each MCB isomer as molar conversion (X_i) is expressed as the ratio of the reacted to the initial amount (moles) charged for steady-state run time, Δt

$$X_i = ([\mathrm{MCB}]_0 - [\mathrm{MCB}]_\tau)[\mathrm{MCB}]_0 = 1 - V_{\Delta t}C_i/V_0C_{i,0} \quad (3)$$

Here $V_{\Delta t}$ is the measured steady state effluent liquid volume and V_0 is the volume of the PCB/MeOH solution fed during the steady-state run time, Δt. The MCB congener concentrations in the initial MCB/MeOH solutions and the condensed effluent aqueous solutions are $C_{i,0}$ and C_i, respectively. Overall, conversions (Table 1) range from 2.8% (2-CB, 2.0 s, 1 g/L 2-CB/MeOH) to 31.1% (4-CB, 24.5 s, 3 g/L 4-CB/MeOH), strongly depending on residence time. The mean molar balance values for these experiments are shown in the last column of Table 1. All positively identified reaction products (see below) are included in the calculations but mainly unreacted MCB congener and biphenyl contribute significantly.

When compared with MCB reactions in the presence of oxygen (see next section), thermolysis shows a lower conversion dependency on the MCB initial concentration and smaller differences among the three MCB isomers. These results can be interpreted as a lower reaction order in this case, proving that a thermal scission of the MCB molecules takes place mainly by breaking the weaker C—Cl bonds, as expected.

The fitting parameters of the regressed data for SCWT of MCB isomers are presented in Table 2, suggesting a reaction apparent order near unity and very similar values of Arrhenius parameters for the three isomers. The regression method is described below.

PCB/MeOH decomposition in supercritical water with oxygen (SCWO)

The experimental results of the decomposition of all the three MCB isomers in supercritical water with oxygen at 25 MPa and 673, 723, and 773 K are shown in Table 3. They are displayed as molar conversion of each MCB (X_i) calculated with Eq. 3. Overall, conversions range from 1% (2-CB, 3.8 s, 673 K) to 97% (4-CB, 24.5 s, 773 K) depending on residence time, temperature, and position (*ortho*, *meta*, and *para*) of Cl substituent in the MCB molecules. The conversion increases rapidly with temperature and is above 80% at 773 K and 24.5 s. This destruction level of MCB is very high when one considers the remarkable chemical stability of PCBs, but surprisingly lower than that of higher chlorinated PCB congeners (Anitescu and Tavlarides, 2000, 2002). An explanation may be based on similarity with polychlorinated benzenes, where the abstraction of a single H radical is invariably more difficult than that from benzene itself. Conversely, the abstraction of Cl radicals is facilitated by the Cl substituents in almost all cases (exception in 1,4-$C_6H_4Cl_2$) (Cioslowski et al., 1997).

The most reactive MCB isomer is 4-CB, whereas the most stable to decomposition is 2-CB, as we expected from our previous studies. The reactivity of 3-CB is closer to that of 4-CB.

In the experiments with MCB/MeOH (+99 mol % MeOH/<1 mol % MCB), as the bulk amount of methanol is oxidized, it is difficult to obtain a carbon mass balance for MCBs because the final oxidation gas products are the same. Further, another reason we cannot obtain a carbon mass balance is that some of the effluent products such as unreacted methanol, formaldehyde, CO, CH_4, and/or organic acids were not measured. Nevertheless, we have verified the reliability of our technique with some SCWT runs at 673 K where no significant reactions occur. One of the other options to verify whether any loses occur in the reaction system is to account for the initial and reaction products containing Cl species (such as HCl), or to perform a chlorine mass balance. We used this option occasionally by ion chromatography analysis and we found similar conversion values as those calculated by Eq. 3, confirming that MCB (initial and unreacted) has been accounted for within the limits of experimental precision.

Thermal decomposition of MCBs may occur during the

Table 2. Fitting Parameters for SCWT Data

MCB Isomer	α (reaction order)	log A (A = the frequency factor)	E_a (activation energy, kJ/mol)
2-CB	1.19 ± 0.06	21.3 ± 0.9	331 ± 16
3-CB	1.17 ± 0.05	21.1 ± 0.6	327 ± 10
4-CB	1.12 ± 0.05	20.5 ± 0.5	320 ± 8

Table 3. Conversions of MCB Isomers in SCW at 673–773 K and 25 MPa with 20% Molar Excess Oxygen*

	2-CB		3-CB		4-CB	
τ (s)	$(X_2)_{C1}$	$(X_2)_{C2}$	$(X_3)_{C1}$	$(X_3)_{C2}$	$(X_4)_{C1}$	$(X_4)_{C2}$
			T = 673 K			
45.5	0.092	0.162	0.153	0.228	0.204	0.275
45.5	0.072	0.152	0.148	0.232	0.192	0.287
32.5	0.062	0.128	0.118	0.188	0.145	0.209
32.5	0.066	0.134	0.125	0.173	0.157	0.227
22.7	0.052	0.098	0.109	0.125	0.126	0.163
22.7	0.048	0.084	0.102	0.141	0.122	0.172
7.6	0.026	0.039	0.047	0.066	0.056	0.068
7.6	0.019	0.048	0.050	0.056	0.049	0.063
3.8	0.012	0.022	0.022	0.043	0.036	0.044
3.8	0.010	0.027	0.027	0.031	0.027	0.039
			T = 723 K			
29.8	0.299	0.390	0.458	0.504	0.486	0.599
29.8	0.311	0.379	0.450	0.515	0.471	0.590
21.3	0.258	0.325	0.370	0.426	0.416	0.506
21.3	0.236	0.314	0.364	0.439	0.410	0.511
14.9	0.213	0.280	0.311	0.384	0.344	0.435
14.9	0.199	0.261	0.302	0.377	0.350	0.428
5.0	0.101	0.153	0.160	0.204	0.175	0.248
5.0	0.106	0.145	0.153	0.190	0.166	0.230
2.5	0.053	0.096	0.101	0.125	0.113	0.153
2.5	0.044	0.084	0.103	0.134	0.106	0.147
			T = 773 K			
24.5	0.793	0.855	0.861	0.915	0.928	0.970
24.5	0.804	0.851	0.853	0.910	0.939	0.966
17.5	0.775	0.838	0.837	0.888	0.904	0.942
17.5	0.769	0.832	0.834	0.897	0.916	0.944
12.3	0.748	0.799	0.805	0.857	0.874	0.919
12.3	0.734	0.803	0.804	0.851	0.866	0.930
4.1	0.645	0.704	0.700	0.751	0.773	0.834
4.1	0.633	0.711	0.688	0.746	0.762	0.843
2.0	0.571	0.616	0.628	0.682	0.704	0.749
2.0	0.556	0.603	0.616	0.693	0.711	0.736

*C_1 = 1 g/L and C_2 = 3 g/L MCB/MeOH.

reactions in the presence of oxygen and its contribution is included in the global kinetics of the SCWO process. However, we note that this contribution to the overall decomposition is smaller in the presence of oxygen as MCB isomers react faster with hydrogen free radicals provided by methanol oxidation than the scission of C—Cl bonds occurring in the reactions without oxygen. This observation is supported by the lower values of activation energy in the case of SCWO compared to those of SCWT.

Global Kinetics of PCB Decomposition

PCB congeners exhibit complex chemical structures undergoing competitive, multistep reactions for which detailed reaction mechanisms are not yet feasible to be determined. Further, when the intermediate reaction products are free radicals, it may not be possible to perform independent experiments to determine the rate law parameters. Consequently, these parameters can be deduced from changes in the distribution of the reaction products with feed conditions. Under these circumstances, the analysis turns into a parameter-optimization problem and the information to be obtained from these PCB SCWO studies is global kinetics, reaction networks, and the identities and yields of the products of incomplete oxidation.

For a global kinetic analysis, the dependency of the reaction rate on the initial reactant concentrations has to be established. Regarding this dependency on the initial oxidant concentration, $[O_2]_0$, our previous and the present experiments with different $[H_2O_2]/[H_2O]$ concentrations (0–10 wt %) show that conversion of PCBs/MeOH is only slightly dependent on initial excess oxygen used to oxidize both PCBs and the bulk methanol to CO_2. The 3-CB conversion as a function of the oxidant/organic equivalence ratio, Φ, is shown in Figure 1, where

$$\Phi = ([O_2]/[\text{organic}])_{\text{actual}}/([O_2]/[\text{organic}])_{\text{stoichiometric}} \qquad (4)$$

Diminishing amplitude of this dependency is apparent for equivalence ratios higher than the stoichiometric value of 1. A possible explanation of this behavior could be that increasing oxygen concentrations up to stoichiometric amounts enhance the overall PCB dechlorination by increasing the generation rate of free radicals in the reaction with methanol. Additional increase in oxygen has a marginal effect as it competitively reacts with hydrogen free radicals, which are the most active participants in the dechlorination reactions (Senkan et al., 1992). The PCB SCWO reactions proceeding by free radicals released from methanol oxidation are faster than direct reac-

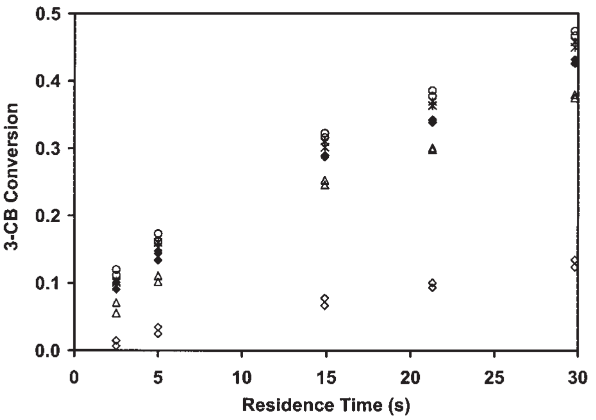

Figure 1. Conversion dependency on residence time and initial oxygen concentration for 3-CB/MeOH solutions (1 g/L): ◇, $\Phi = 0$; △, $\Phi = 0.6$; ◆, $\Phi = 1.0$; $\ast$, $\Phi = 1.2$; ○, $\Phi = 2.0$.

(SCWO/SCWT experiments are conducted at 723 K and 25 MPa and the oxidant/organic equivalence ratio is defined as $\Phi = \{[O_2]/[\text{organic}])_{\text{actual}}/([O_2]/[\text{organic}])_{\text{stoichiometric}}\}$.

tions with oxidative species and the reaction rate can be assumed to be quasi-independent of excess O_2 concentration. Regarding a potential dependency of MCB conversion on methanol concentration, even though it appears that the SCWO of PCB congeners proceeds through free radicals from methanol oxidation, we are not able at this stage of the research to explicitly account for the effect of $[\text{MeOH}]_0$ in the reaction rate, given that the reaction mechanism is still unknown.

Accordingly, the global kinetics for SCWO of PCBs may be conveniently examined by assuming that the global rate of this reaction network ($-r_i$) is proportional to the congener concentration in the reactor at a given time (1–100 μmol/L at $\tau = 0$) and independent of the water, methanol, and O_2 concentrations (8.8 mol/L or 97.5%, 0.08 mol/L or 0.9%, and 0.14 mol/L or 1.6%, respectively, at $\tau = 0$). Therefore, the reaction rate can be written

$$-r_i = -dC_i/dt = kC_i^{\alpha} \tag{5}$$

Here, the global reaction rate constant can be expressed in terms of Arrhenius frequency factor A and the energy of activation E_a

$$k = A\,\exp(-E_a/RT) \tag{6}$$

To examine a power-low dependency of the conversion, the integrated form of Eq. 5 can be obtained for the case of the plug-flow reactor (Fogler, 1999) and for a reaction order higher than unity

$$X_i = 1 - \{1 + (\alpha - 1)10^b\exp(-E_a/RT)[\text{MCB}]^{\alpha-1}\tau\}^{1/1-\alpha} \tag{7}$$

Here $10^b\exp(-E_a/RT)$ represents the rate constant (k) with the Arrhenius frequency factor ($A = 10^b$) and the energy of activation (E_a) as fitting parameters along with the order of the reaction ($\alpha > 1$).

These parameters are determined over all temperatures and MCB concentrations by best fit of the experimental data. The regression technique is performed with the Microcal Origin.6.0 software package by minimizing the objective function defined as the sum of squares of the difference between the experimental and predicted conversions (Eq. 7). The values of the fitted parameters are listed in Table 4. The reaction order α is found to be close to a second-order reaction for all three of the isomers. Also, the Arrhenius parameters A and E_a are found to be higher than those of the 3,3′,4,4′-tetrachlorobiphenyl ($A = 10^{17}$ s^{-1}(mol/L)$^{-1}$; $E_a = 186$ kJ/mol) studied previously (Anitescu and Tavlarides, 2002), showing higher conditions of temperature must be used in the case of MCBs for comparable conversions. This is indeed what we expected based on the accumulation of MCBs when PCBs were reacted and can be also explained through lower effectiveness of the molecular collisions in the case of MCBs (collision probability to target a single Cl substituent by reacting species is lower compared to multitarget PCBs).

An observation can be made regarding the generality of the above rate law. If the oxygen initial concentration is to be considered, when working with the constant initial feed concentration of an excess of oxidant, the fitting procedure cannot meaningfully discriminate between A and $[O_2]^b$ because both are constant. For $\beta = 0$, the expression is obviously valid. If $\beta > 0$, the value of $[O_2]^b$ is lumped together with A.

The calculated MCB conversion values considering the fitting parameters in Eq. 7 are presented in Figure 2a–2c. A good agreement between the calculated values and experimental data is observed except for the two low residence times of each isotherm. This aspect suggests a strong dependency of the reaction rates, especially at the early stages of the reactions, on the free radicals produced by methanol oxidation along with the dependency on MCB initial concentrations. Unfortunately, this dependency is yet unclear and it is obviously determined by the reaction mechanism. A comparison of experimental and calculated (by Eq. 7) conversions is shown in Figure 3. Most of the matching points are within ±5% of the perfect match line, indicating that fitting parameters in Eq. 7 are appropriate to represent the SCWO process of MCB decomposition. Slight underprediction and overprediction of data are observed for the lowest and highest conversions, respectively. Also, four pairs of points are outside of the mentioned interval for the lowest residence times where, other dependency $X_i - \tau$ should be more appropriate.

Main Reaction Products and Possible Pathways

Reaction products analysis is in progress, although the main components have been identified in an attempt to explain the overall reaction trends and whether the more toxic PCDFs/PCDDs are formed under specific conditions. There are many potentially competitive reactions of MCB isomers with different species of free radicals such as H and OH. In the oxidation

Table 4. Fitting Parameters for SCWO Data

MCB Isomer	α (reaction order)	log A (A = the frequency factor)	E_a (activation energy, kJ/mol)
2-CB	2.09 ± 0.08	24.8 ± 0.3	292 ± 8
3-CB	2.14 ± 0.07	24.5 ± 0.2	282 ± 6
4-CB	2.04 ± 0.04	24.1 ± 0.4	281 ± 5

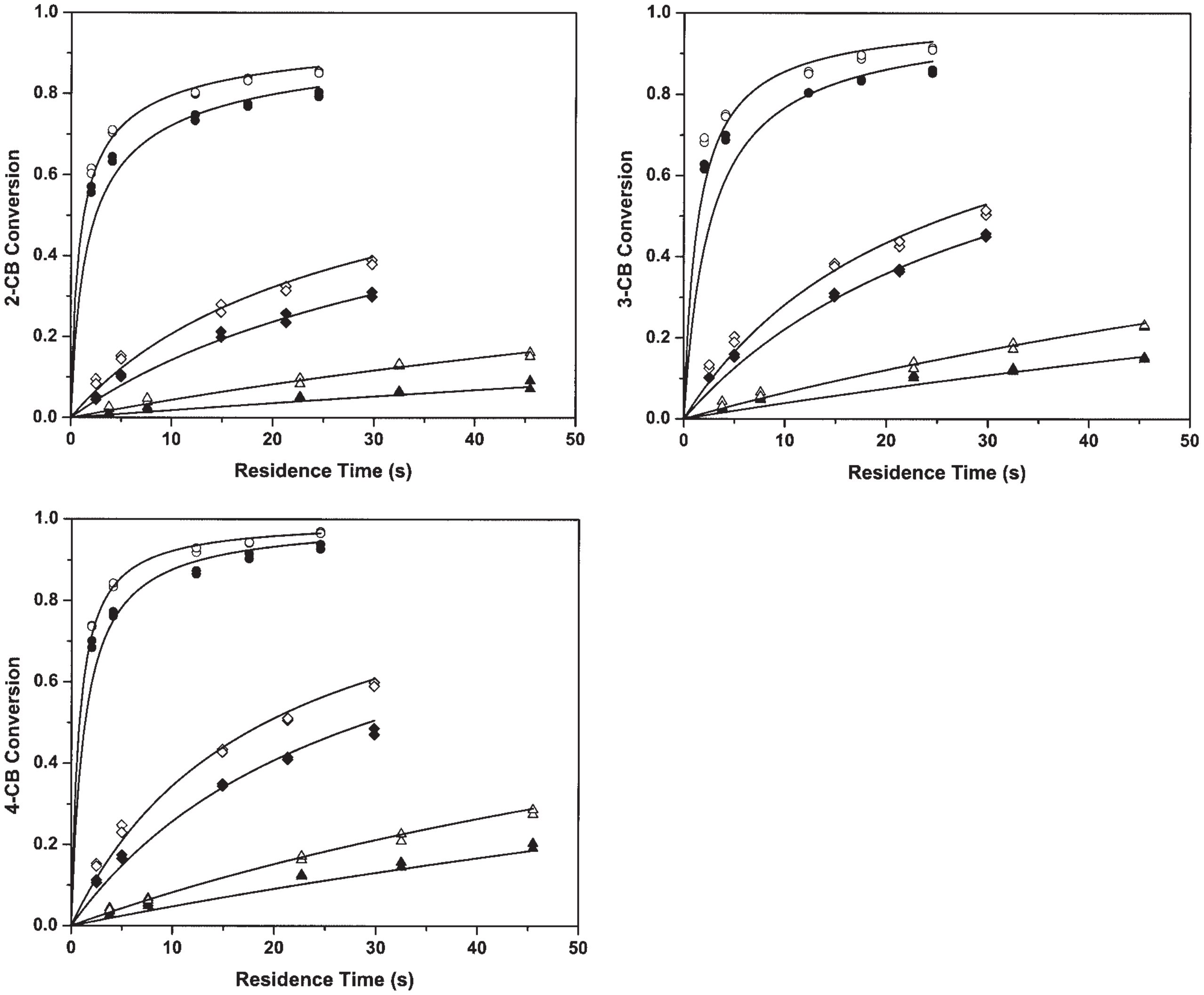

Figure 2. MCB/MeOH conversion as a function of residence time and $[MCB]_0$ at 673 K (triangles), 723 K (diamonds), and 773 K (circles): (a) 2-CB; (b) 3-CB; (c) 4-CB.

(The solid and open symbols are for MCB/MeOH solutions of 1 and 3 g/L, respectively, and the lines represent the calculated conversions with Eq. 7.)

reactions, chlorinated compounds typically react with OH-dominant free radicals through a first step of H abstraction under SCWO conditions, followed by open-ring oxidative reactions. Alternatively, our preliminary observations suggest that in the presence of H free radicals released through methanol oxidation, reactions leading to Cl elimination are dominant when methanol is present in the reactor. We reported this Cl elimination earlier in these systems, wherein 3,3′,4,4′-PCB undergoes stepwise successive dechlorination from tetra- to tri-, to di-, to mono-chlorinated molecules (Figure 4) followed by open-ring intermediates leading to mineral products (Anitescu and Tavlarides, 2002). Accordingly, based on experimental data herein, the global reaction network for SCWO of a MCB/MeOH can be written in the broadest sense as a dechlorination step followed by oxidation

$$C_{12}H_9C1 \rightarrow C_{12}H_{10} \rightarrow \text{ROPs} \rightarrow n\text{CO} + (12 - n)\text{CO}_2 + 5\text{H}_2\text{O} \quad (8)$$

where ROPs are ring-opened products that result from the oxidation of biphenyl and subsequent oxidation intermediates. CO/CO_2 ratios can vary because CO is further oxidized at different levels to CO_2, depending on reaction conditions. There is an indication of the competing phenomena of production and decomposition of intermediate products with the former dominant in the earlier stage of the reaction and the latter dominant at the more advanced stages of the oxidation process. Based on the dominant phenomenon, several trends can be distinguished: reaction of the Cl substituents of MCB molecules with hydrogen free radicals provided by methanol oxidation (a reductive pathway); reaction of MCBs with OH radicals (an oxidative pathway); reaction of Cl free radicals produced in the first pathway with unreacted MCBs and other reaction intermediates.

SCWT

The main thermolysis reaction product along with unreacted MCBs is biphenyl. Other identified products are 2-, 3-, and

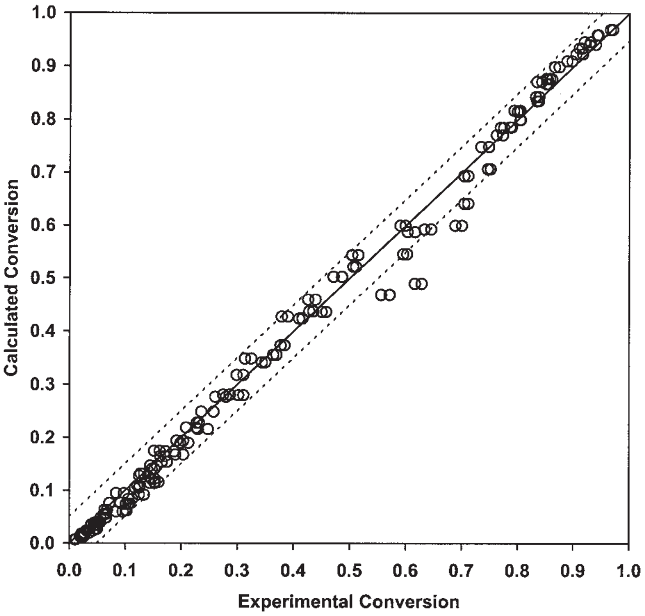

Figure 3. Calculated vs. experimental conversions for all MCB/MeOH SCWO experiments at 673–773 K and 25 MPa.

(The dashed lines are for ±5% conversion compared to the perfect 45°-match line of 100%.)

4-substituted methoxy, methanol, and hydroxy biphenyl, and very small amounts of mono- and di-chlorinated biphenyl isomers. The former isomers show that MCBs react with methanolic free radicals (CH_3O and CH_2OH), whereas the latter products show that chlorine free radicals, produced by MCB dechlorination, react further with both biphenyl and MCB molecules. Very low amounts of hydroxylated biphenyls suggest that MCBs also react with OH free radicals, but at a low level.

SCWO

A thorough investigation is being conducted to identify the oxidation reaction products of MCBs. The major products of the SCWO of MCB/MeOH are biphenyl, CO, CO_2, H_2O, and HCl. Some smaller amounts of oxidation products from biphenyl such as hydroxy-biphenyls, acetophenone, benzaldehydes, and their chlorinated derivatives have also been produced mainly as a function of temperature and residence time. However, there are no dioxins among them at the level of GC/MS limit of detection (~1 ppb). Small amounts of dibenzofurane and chlorodibenzofurane have been detected only for 2-CB decomposition, indicating a reaction pathway via hydroxylated biphenyl or 2-CB. However, the data analysis shows that PCDFs formed in the early stage of the SCWO reaction can be minimized and finally destroyed by choosing appropriate reaction conditions. The positive identification and quantification of these compounds by further concentration of the hexane extracts of aqueous solutions are currently in progress.

In accordance with the above results, a general observation about the reaction pathway can be made. The *ortho*-chlorinated position for 2-CB isomer is the most resistant to SCWO. Similar resistance to reaction in biodechlorination is known for these types of congeners (Rhee et al., 1993). PCB congeners 2-CB and both 22′- and 26-DCBs constitute over 65% of the biodechlorination products transported by waters of the Upper Hudson River (Bush et al., 1985). One possible explanation here may be attributed to differences in reactivity resulting from the two different steric conformations of MCB congeners: *ortho*-substituted congeners exhibit a non-coplanar conformation, whereas the non-*ortho*-substituted congeners exhibit a dioxin-like coplanar conformation (Carpenter, 1998). The latter isomers expose the Cl substituent to free-radical attacks from many directions, whereas the former partially hinders the chlorine from such attacks. Further, the electronic dynamic distributions in the MCB molecules may also play an important role (Cioslowski, 1997). Accordingly, the *meta*- and *para*-chlorines from non-coplanar congeners appear to be removed first in the early stage of the reactions, resulting in an increase of lower *ortho*-chlorinated congeners in the case of the decomposition of polychlorinated congeners at different molecular positions. Therefore, the observed shift in the congener pattern of Aroclor 1248, occurring between the feed material and the product, can be explained based on different reactivities of the Cl atoms existing at different positions. Work on the mechanism of PCB decomposition and the reaction pathways is in progress and the findings will be published shortly. An insight into the reactive behavior of more harmful related POPs, such as PCDDs and PCDFs, may also be connected to the results of PCB decomposition.

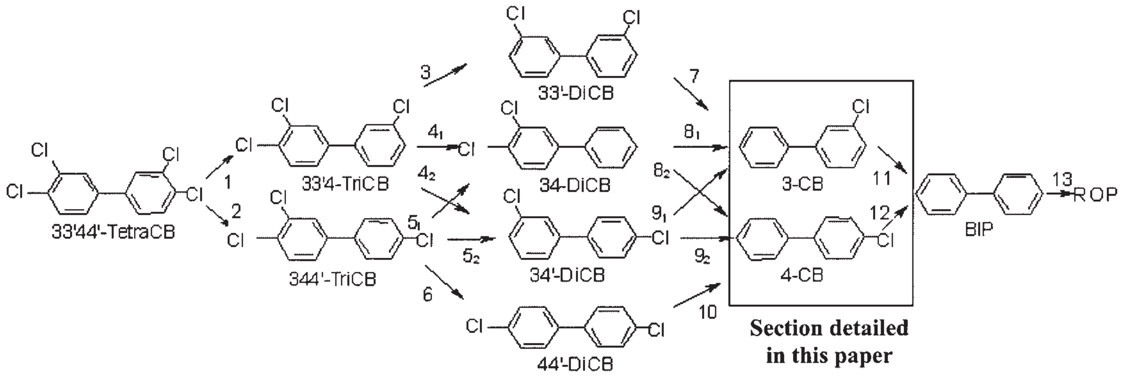

Figure 4. Reaction network section detailed in this article from the proposed dechlorination pathways of 33′44′-TetraCB (delivered in methanolic solutions) in SCW with oxygen.

Summary and Conclusions

The oxidation and thermolysis of monochlorinated biphenyl isomers were studied over a temperature range of 673–773 K and at 773 K, respectively, and residence times from 2.0 to 45.5 s at 25 MPa. The disappearance conversions of all three MCB isomers in methanolic solutions were determined for excess oxygen of 20 mol %. The reaction kinetics is quasi-independent on the O_2 concentration higher than the stoichiometric value.

The experimental results were correlated with overall first- and second-order kinetic models for SCWT and SCWO sets of data, respectively, over the temperature and initial MCB concentration ranges studied.

Complex reaction pathways of these systems were observed in a qualitative fashion. The global reaction network for SCWO of MCB/methanol is based on the consecutive reactions of dechlorination and oxidation with biphenyl, CO, CO_2, H_2O, and HCl as ultimately the main products of the process. Competing phenomena of production and decomposition of intermediate products occurred, with the former dominant in the earlier stage of the reaction and the latter dominant at the more advanced stages of the oxidation process. The use of methanol with oxygen as a free-radical promoter during SCWO enhanced the efficiency of the treatment by lowering the activation energy of the process to 280–292 kJ/mol, from 320–330 kJ/mol (SCWT, MeOH without oxygen), for Cl elimination.

The reactivity among the MCB isomers increases in the order 2-MCB $<$ 3-MCB $<$ 4-MCB.

This study of the SCWO of MCB isomers provides both an understanding of the kinetics of PCBs themselves and an insight into the reactive behavior of more harmful related POPs such as PCDDs and PCDFs.

Acknowledgments

The financial support from the National Science Foundation, Grant CTS-0115650, is acknowledged. Dr. Valentin Munteanu has been supported by Fulbright Grant No. 245 for C.I.E.S. by The Romanian–U.S. Fulbright Commission.

Literature Cited

Anitescu, G., and L. L. Tavlarides, “Oxidation of Aroclor 1248 in Supercritical Water: A Global Kinetic Study,” *Ind. Eng. Chem. Res.*, **39**, 583 (2000).

Anitescu, G., and L. L. Tavlarides, “Methanol as a Cosolvent and Rate-Enhancer for the Oxidation Kinetics of 3,3′,4,4′-Tetrachlorobiphenyl Decomposition in Supercritical Water,” *Ind. Eng. Chem. Res.*, **41**, 9 (2002).

Anitescu, G., Z. Zhang, and L. L. Tavlarides, “A Kinetic Study of Methanol Oxidation in Supercritical Water,” *Ind. Eng. Chem. Res.*, **38**, 2231 (1999).

Bush, B., K. Simpson, L. Shane, and R. Koblintz, “PCB Congener Analysis of Water and Caddisfly larvae (*Insecta Trichoptera*) in the Upper Hudson River by Glass Capillary Chromatography,” *Bull. Environ. Contam. Toxicol.*, **34**, 96 (1985).

Carpenter, D. O., “PCBs: What They Are, How They Behave, and Uncertainties That Exist,” *Improved Communications Workshop: Remediation of PCB-Contaminated Sites in New York and Massachusetts*, School of Public Health, Albany, NY, October (1998).

Cioslowski, J., G. Liu, and D. Moncrieff, “Energetics of the Homolitic C—H and C—Cl Bond Cleavages in Polychlorobenzenes: The Role of Electronic and Steric Effects,” *J. Phys. Chem.*, **101**, 957 (1997).

Crain, N., A. Shanableh, and E. F. Gloyna, “Supercritical Water Oxidation of Sludges Contaminated with Toxic Organic Chemicals,” *Water Sci. Technol.*, **42**, 363 (2000).

Croiset, E., S. F. Rice, and R. G. Hanush, “Hydrogen Peroxide Decomposition in Supercritical Water,” *AIChE J.*, **43**, 2343 (1997).

Crooker, P. J., K. S. Ahluwalia, Z. Fan, and J. Prince, “Operating Results from Supercritical Water Oxidation Plants,” *Ind. Eng. Chem. Res.*, **39**, 4865 (2000).

Fogler, H. S., *Elements of Chemical Reaction Engineering*, Prentice-Hall, Upper Saddle River, NJ (1999).

Haar, L., J. S. Gallagher, and G. S. Kell, *NBS/NRC Steam Tables: Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI Units*, Hemisphere, New York (1984).

Hatakeda, K., Y. Ikushima, O. Sato, T. Aizawa, and N. Saito, “Supercritical Water Oxidation of Polychlorinated Biphenyls Using Hydrogen Peroxide,” *Chem. Eng. Sci.,* **54**, 3079 (1999).

Hutzinger, O., G. G. Choudhry, B. G. Chittim, and L. E. Johnston, “Formation of Polychlorinated Dibenzofurans and Dioxins during Combustion, Electrical Equipment Fires and PCB Incineration,” *Environ. Health Perspect.*, **60**, 3 (1985).

Konys, J., S. Fodi, J. Hausselt, H. Schmidt, and V. Casal, “Corrosion of High-Temperature Alloys in Chloride-Containing Supercritical Water Oxidation Systems,” *Corrosion*, **55**, 45 (1999).

Kritzer, P., and E. Dinjus, “An Assessment of Supercritical Water Oxidation (SCWO). Existing Problems, Possible Solutions and New Reactor Concepts,” *Chem. Eng. J.*, **83**, 207 (2001).

Macdonald, D. D., and L. B. Kriksunov, “Probing the Chemical and Electrochemical Properties of SCWO Systems,” *Electrochim. Acta*, **47**, 775 (2001).

Mitton, D. B., J.-H. Yoon, J. A. Cline, H.-S. Kim, N. Eliaz, and R. M. Latanision, “Corrosion Behavior of Nickel-Based Alloys in Supercritical Water Oxidation Systems,” *Ind. Eng. Chem. Res.*, **39**, 4689 (2000).

Modell, M., “Supercritical Water Oxidation,” *Standard Handbook of Hazardous Waste Treatment and Disposal*, H. M. Freeman, ed., McGraw-Hill, New York, p. 8.153 (1989).

Rhee, G. Y., R. C. Sokol, C. M. Bethoney, and B. Bush, “Dechlorination of PCBs by Hudson River Sediment Organisms: Specificity to the Chlorination Pattern of Congeners,” *Environ. Sci. Technol.*, **27**, 1190 (1993).

Rice, S. F., and R. R. Steeper, “Oxidation Rates of Common Organic Compounds in Supercritical Water,” *J. Hazard. Mater.*, **59**, 261 (1998).

Savage, P. E., “Organic Chemical Reactions in Supercritical Water,” *Chem. Rev.*, **99**, 603 (1999).

Senkan, S. M., S. Sethuraman, and D. Gutman, “An Experimental Study of the Gas Phase Oxidation of C_6H_5Cl in a Flow Reactor,” *Combust. Sci. Technol.*, **82**, 13 (1992).

Shaw, R. W., and N. Dahmen, “Destruction of Toxic Organic Materials Using Supercritical Water Oxidation: Current State of the Technology,” *NATO Sci. Ser., Ser. E Supercrit. Fluids*, **366**, 425 (2000).

Tester, J. W., and J. A. Cline, “Hydrolysis and Oxidation in Subcritical and Supercritical Water: Connecting Process Engineering Science to Molecular Interactions,” *Corrosion*, **55**, 1088 (1999).

Weber, R., S. Yoshida, and K. Miwa, “PCB Destruction in Subcritical and Supercritical Water—Evaluation of PCDF Formation and Initial Steps of Degradation Mechanisms,” *Environ. Sci. Technol.*, **36**, 1839 (2002).

Manuscript received July 1, 2003, and final revision received Oct. 10, 2003.