SUPERCRITICAL WATER OXIDATION REACTION PATHWAY AND KINETICS OF POLYCHLORINATED BIPHENYLS

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ABSTRACT

Supercritical water oxidation (SCWO) reaction is effective in destruction of polychlorinated biphenyls (PCBs) to mineral products of CO_2, HCl, and H_2O such that 99.95% conversion of Aroclor 1248 is possible in 54.5 seconds residence time at 823 K and 25.3 MPa. Yet to design and operate SCWO reactors to avoid harmful products formation such as polychlorinated dibenzofurans and dioxins, it is necessary to understand the PCB reaction pathway leading to final products. This study shows the dechlorination reaction pathway of 33'44'-Tetrachlorobiphenyl (a surrogate for Aroclor 1248) in methanol solutions. It is suggested that hydrogen species from methanol act as reaction rate enhancers and lead to a series reaction pathway of dechlorination to biphenyl followed by ring-opening oxidation to mineral products. Also, reaction kinetics for this system are presented. These results are of value for reactor design to ensure oxidation of these recalcitrant pollutants in an environmentally safe manner.

Key words: supercritical water oxidation, reaction pathways, reaction kinetics, PCBs

INTRODUCTION

Methods to destroy polychlorinated biphenyls (PCBs) are facing unusually challenging problems due to the very high chemical stability and low water solubility of these compounds (Hutzinger et al., 1983; Bolgar et al., 1995; D. O. Carpenter, 2000). For example, incineration of PCBs generates very harmful products such as polychlorinated dibenzofurans/dioxins (PCDFs/Ds) and because PCBs themselves result from incineration of chlorinated pollutants and have been used as fire retardant, this method is inappropriate for PCB destruction. Supercritical water oxidation (SCWO) of organic compounds is drawing much attention due to attractive features such as cleanness, quickness, and the potential to effectively destroy a large variety of industrial and high-risk wastes. The process is conducted at temperatures and pressures above the critical point of water (647 K and 22.1 MPa) and is considered applicable to aqueous streams containing up to 20% organics (Tester et al., 1993). Detailed reviews of the SCWO process can be found in Modell (1989), Tester et al. (1993), Tester and Cline (1999), Gloyna et al. (1994), Gloyna and Li (1995), Savage et al. (1995), Savage (1999), Schmieder and Abeln (1999), etc.

Different classes of water-soluble organic compounds have been subjected to SCWO conditions, including chlorinated aromatics. However, only few investigations on decomposition of only liquid PCBs in SCW are known (Modell, 1989; Oe, 1998; Hatakeda et al., 1997 and 1999; Crain et al., 2000). These experiments have been focussed on the capability of the SCWO process to achieve high conversions rather than the acquisition of kinetic information, which requires voluntarily accepted incomplete conversions. These studies are quite promising but the reaction pathways through which these results are obtained are not well

established. Some stable products of PCB SCWO such as PCDDs/Fs, formed under certain conditions, are more hazardous than the starting material and their formation is a factor to consider in the design of SCWO reactors. None of the studies cited provides a systematic pathway analysis to determine the nature and concentrations of reaction products. The lack of suitable and comprehensive data on PCB decomposition led us to initiate research work in the field of SCWO. In addition, a two-stage supercritical fluid technology process of PCB extraction from soil/sediments with SC-CO$_2$/ MeOH fluids, followed by SCWO of the extracts, is under investigation at Syracuse University (Tavlarides et al., 2000).

One approach to elucidate the chemistry of PCBs in the SCWO process involves the selection of and experimentation with single congeners that serve as models within the complex PCB mixtures. In this study, the dechlorination/oxidation kinetics of 33'44'- tetrachlorobiphenyl (T$_4$CB) from methanol solutions in SCW is presented and discussed. The solid T$_4$CB is a representative PCB copla-nar congener with a dioxin-like structure and the most toxic component of Aroclor mixtures, providing useful information about meta- and para-chlorine reactivity.

EXPERIMENTAL SECTION

Apparatus and procedure

The experiments are conducted in a high-pressure, isothermal plug-flow tubular reactor with temperature and pressure limits set at 873 K and 69 MPa, respectively. The experimental setup used is described in detail elsewhere (Anitescu and Tavlarides, 2000), so only the most relevant features are given here.

The experimental system consists of three major subsystems: pumps and preheaters, reactor, and cooling and separation. T$_4$CB/MeOH and H$_2$O$_2$/H$_2$O solutions are delivered to the reactor in separate lines by high-pressure feed pumps. Both the oxidizer and organic preheated high-pressure tubing is Hastelloy C-276. The variation of reactor residence time is achieved either by changing the reactor length (sections of Hastelloy tubing) or by changing the feed rate. The preheated organic feed and supercritical oxidant are mixed in a mixing block and the combined stream then flows through the reactor housed in an isother-mal fluidized sand bath with preheating coils. The temperature is monitored at the both ends of the reactor (± 1.5 K). The pressure ($\pm 1.4\%$) is fixed by manually controlling the total flow rate of the effluent stream using a specially designed micrometric valve. The stream pres-sure is dropped first to ambient conditions and then the hot effluent mixture is cooled, resulting in a separation of gaseous and liquid phases in either one of two separators connected in parallel. During the unsteady state portion of the reaction, the cooled products are collected in the first separator and removed later. Products of the steady state reaction (5-10 min) are depressurized, cooled, and separated in the second separator and further analyzed by chromatographic methods. Steady state is attained after adequate time has transpired for

reactants to flow through both the preheater and reactor, and SCWO conditions (T, P, and flows) are stabilized.

Analytical technique

The gaseous phase is captured into a 250-μL sample loop and analyzed by on-line GC/TCD. A portion of the liquid-phase product is analyzed by off-line capillary GC/ECD, GC/FID, and/or GC/MSD to identify and measure the unreacted PCBs and reaction products. GC separation is achieved on capillary columns HP Ultra-2 (25 m × 0.20 mm i.d., 0.33 μm film thickness), DB-1 (30 m × 0.32 mm i.d., 3 μm film thickness), and HP-5MS (30 m × 0.25 μm i.d., 0.25 mm film thickness), respectively. The GC was calibrated with standard solutions containing certified concentrations of PCB congeners in hexane and methanol. Chromatographic errors for the compounds in the liquid and gas samples are determined by replicate analysis to be 4% and 6%, respectively. A chemical analysis using the NIST library of spectra is performed with the GC/MSD chromatographic technique.

Reactants

The oxidant is O_2, supplied for most of the experiments as a solution of hydrogen peroxide of 6 wt %, prepared from 30 wt % H_2O_2/H_2O solution (purum p.a., Fluka). Under these conditions, an excess of O_2 of approximately 20 mol % is provided. Neat T_4CB solid congener is from AccuStandard. The purity of methanol (Optima, Fisher Scientific) is min. 99.9%, and water is distilled and deionized.

RESULTS AND DISCUSSION

T_4CB/MeOH decomposition/oxidation in SCW

These experiments are conducted in order to characterize the reactivity of this PCB congener in the presence of methanol and to provide the necessary information for global kinetic and reaction pathway analysis. The main variable parameters in SCWO experiments with T_4CB are residence time and temperature. Residence times of the experiments range from 3.11 s at 773 K to 25.6 s at 673 K. The experiments are conducted isothermally at five different temperatures: 673, 698, 723, 748, and 773 K. In addition to replicate runs (two or three for most of the experiments with standard deviations less than 6%), duplicate samples are analyzed by combined chromatographic methods.

The experimental results of the disappearance of T_4CB in supercritical water at 25.3 MPa and the above temperatures for initial T_4CB feed concentration of 2.97-5.48 μmol/L (reaction conditions) in methanol solutions are presented in Figure 1. Overall, conversions range from 20.2% (5.76 s, 673 K) to 99.5% (20.7 s, 773 K), depending on residence time and temperature. Accuracy of these data is determined through propagation error calculations to be within ± 0.04(1-X_1), with the lower errors for the higher conversions ($RD < 1\%$ for $X_1 > 0.8$). The conversion increases rapidly with temperature and is essentially complete at 500 °C and beyond 5 s. This destruction level of T_4CB is very high when one considers the remarkable chemical stability of PCBs.

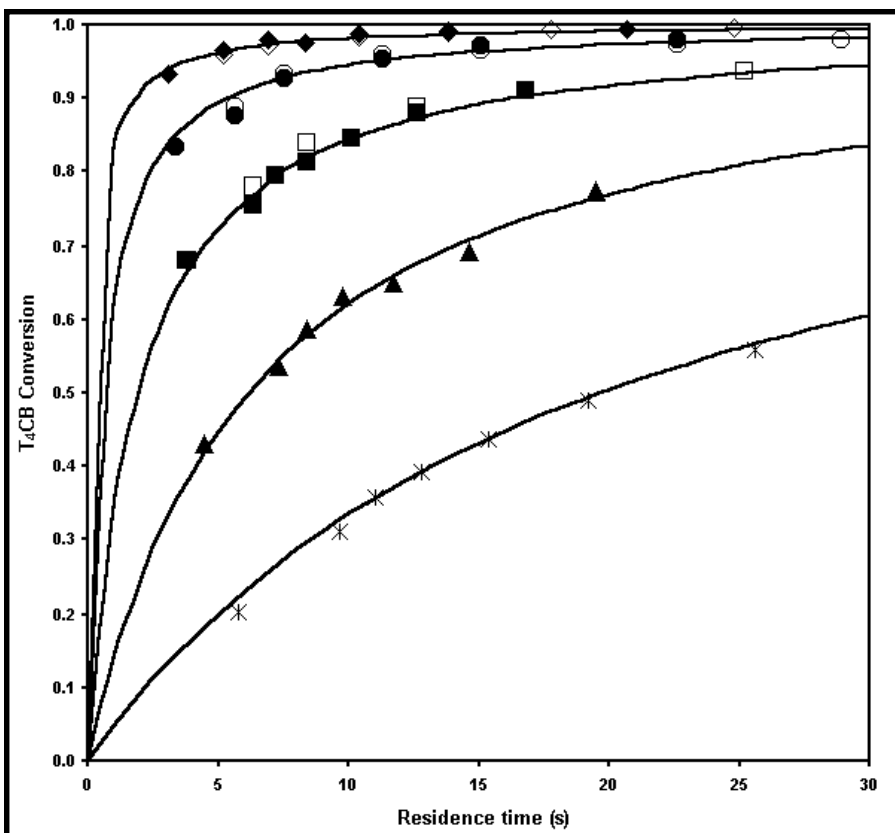**Figure 1.** 33'44'-Tetrachlorobiphenyl (T$_4$CB) conversion versus residence time at 25.3 MPa: calculated by Eq. 2 (——) and experimental for T$_4$CB/MeOH (✳, 673 K; ▲, 698 K; ■, 723 K; ●, 748 K, ◆, 773 K) and for T$_4$CB/Aroclor1248/MeOH (□, 723K; O, 748 K; ◊, 773 K)

It is of interest to compare the T$_4$CB conversions in the Aroclor 1248 (A1248) mixture with those of this work mainly to determine whether significant differences exist between the two cases due to potential interactions and competitive reactions among PCB components of the mixture. A1248/MeOH solution (18.1 mmol/L) has been oxidized previously in SCW at 25.3 MPa and 723, 748, 773, and 823 K (Anitescu and Tavlarides, 2000). T$_4$CB is one of the major components of this mixture (2.73 mol % among 55 congeners in the feed concentration). Both PCBs contain an average of 48.6% chlorine for the same molecular weight (292 g/mol). For an easy comparison, partial results for the common

isotherms of T$_4$CB/A1248/MeOH SCWO are included in Figure 1 (open symbols) and show data to overlap within experimental precision.

Methanol influence on PCB conversion

We have observed that methanol is an attractive co-solvent for SCWO and has an enhancing effect on PCB disappearance kinetics (Anitescu and Tavlarides, 2000). Methanol is easy to oxidize, so it is likely that methanol-derived reactive intermediates are primarily responsible for dechlorination of the PCBs. Our preliminary data on SCWO of PCBs without methanol, compared with the data with methanol, show that the system with methanol is dechlorinated significantly faster and through a different reaction pathway.

A comparison of model predictions from this work with reported data for kinetic experiments executed without methanol, shows that similar performance can be achieved under less severe conditions or in a significantly shorter reaction time. For example, under Modell's conditions (Modell, 1989), essentially a complete destruction is achieved for the T_4CB/MeOH system under the above conditions or the temperature can be dropped to near the critical value (647 K), respectively. Also, SCWO is much faster than photodechlorination and is effective at much higher concentrations of PCBs in SCW: 99% conversion of 33'44'-TetraCB is achieved through the former technique in 10 s at 500 °C, while through the latter in 30 min (Yao et al., 1997). The MeOH-enhanced rates of these reactions as a function of reactor operating variables provide information for design and operation of SCWO units under the least severe conditions.

Global kinetics of T_4CB disappearance

The kinetics for SCWO of T_4CB may be conveniently examined by assuming that the global rate of the disappearance reaction is proportional to the T_4CB concentration in the reactor at a given time and independent of the concentrations of water, methanol, and oxygen:

$$-r_1 = kC_1^{\alpha} \tag{1}$$

Combining the rate law of Eq.1 with the definition of conversion and the design equation for a constant-volume, plug-flow reactor (Fogler, 1999), followed by analytical integration, leads to

$$X_1 = 1-(1+(\alpha-1)10^b\exp(-E_a/RT)[T_4CB]^{\alpha-1}\tau)^{1/(1-\alpha)} \tag{2}$$

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 global reaction order α. These parameters are determined over all temperatures by best fit of the experimental data. For both T_4CB/MeOH and T_4CB/A1248/MeOH sets of SCWO experiments, the values of α are found to be very close to a second-order reaction: 1.94 ± 0.02. Also, the values of the Arrhenius parameters, $A = 10^{20.7\pm0.1}\,s^{-1}(mol/L)^{-0.94}$ and $E_a = 219 \pm 2$ kJ/mol for the first case and $A = 10^{20.1\pm0.3}\,s^{-1}(mol/L)^{-0.94}$ and $E_a = 204 \pm 4$ kJ/mol for the second case, are nearly the same. The overall absolute average relative deviations ($AARD = \Sigma|RD_i|/\Sigma i$) are 1.4% and 0.4%, respectively, showing a good agreement between the calculated values and experimental data.

REACTION PRODUCTS AND PATHWAYS

Reaction of intermediate compounds

One of the focal points of this study is the identification and quantification of the yields of the stable products from experiments in which incomplete oxidation is programmed to occur in order to examine whether any harmful stable products can be formed. Positively identified reaction products are all the lower chlorinated PCB congeners (33'4- and 344'-TriCB, 33'-, 34-, 34'-, and 44'-DiCB, 3- and 4-CB), biphenyl, CO, and CO_2. Moreover, no PCDFs/

Ds and other aromatic derivatives among reaction products have been identified at the level of GC limit of detection (~0.1 ppb). Although one rationally would expect single-ring aromatics and oxygen-containing compounds should be produced in this reaction, the potential unstable intermediates compared to PCBs undergo fast reactions and become undetectable in the effluent streams. However, recent preliminary experiments we conducted with ~10 times higher concentrated solutions of biphenyl/ MeOH (5 wt %) compared to T_4CB/MeOH (0.5 wt %) as starting reactant show numerous reaction intermediates: acetophenone, phenol, benzaldehyde, 1-phenyl-1,2-propandione, benzoic acid methyl ester, 1-phenyl 2-propen-1-one, hydroxybiphenyl isomers, benzene, acetic acid, oxiacetic acid, and acetaldehyde. Also, some experiments with neat PCBs show chlorinated benzenes, hydroxylated PCBs, PDDFs, and PCB oligomers/polymers, suggesting competitive reaction pathways occur during PCB SCWO without methanol.

Competitive SCWO pathways

The above findings show a complex reaction pathway network toward complete oxidation to CO_2 and H_2O: (1) dechlorination to lower chlorinated congeners which undergo further dechlorination to biphenyl followed by oxidation to open-ring products; (2) reaction with OH radicals to form PCB-hydroxylated intermediates; (3) cleavage of 1-1' C-C bond leading to chlorinated benzene compounds and thereafter to open-ring and final products; and (4) formation of PCB oligomers. Pathways (1) and (2)-(4) largely appear to occur in the presence and absence of methanol, respectively, with (4) favored by insufficient O_2. If pathway (1) is largely dominant in the presence of methanol and "crosstalk" with other pathways is minimal, it can be considered independent under particular SCWO conditions and analyzed as follows. In the presence of methanol (route 1), the main reaction pathway for these systems appears to involve a successive dechlorination of congeners to biphenyl which then serially reacts to open-ring products leading to CO_2. In the absence of methanol, PCBs undergo parallel, competing reaction pathways (routes 2-4).

Dechlorination networks

Since chlorinated compounds typically have chlorine atoms removed under reductive conditions such as in photodechlorination (Yao et al., 1997), anaerobic biodechlorination (Cho et al., 2000), and SCWO in presence of methanol (Anitescu and Tavlarides, 2000), the global reaction network for SCWO of T_4CB/ MeOH can be written in the broadest sense as consecutive dechlorination and oxidation reactions involving at least 10 main species (Figure 2A). The dechlorination step of the reactions may be due to hydrogen species produced by methanol oxidation, including the water-gas shift reaction. Also, a similar network for T_4CB in 2-propanol is proposed for a photodechlorination process which implies a similar free-radical reaction mechanism (Yao et al., 1997). To characterize in a simpler way the dechlorination step of T_4CB/MeOH, a three-level lumping strategy is also proposed (Fig. 2B-D).
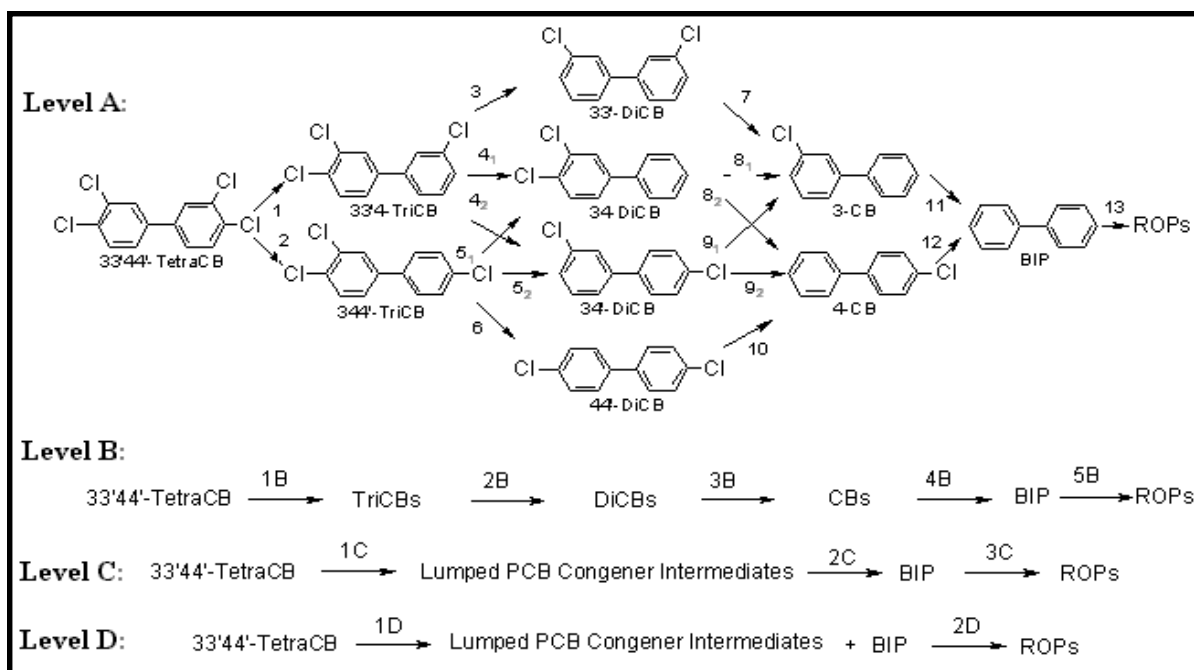
Figure 2. Proposed reaction pathways for dechlorination of 33'44'-TetraCB (delivered in methanol solutions) in supercritical water: level A, detailed reaction network; levels B-D, successively lumped reaction networks.

Reaction rate constants

More conveniently for the case of the reaction pathway analysis, dimensionless yields of the reactants/products defined as moles of compound i in the effluent stream per mole of initial reactant feed into reactor are employed ($Y_i = C_i/C_{1,0}$). Assuming the reaction rates are independent of the oxygen and water concentrations for a given initial concentration of methanol, a set of ordinary differential equations (ODEs) can be conveniently written for the second-order reaction network proposed in Fig.2A in the form

$$dY_1/dt = -(K_1+K_2)Y_1^2$$
$$dY_2/dt = K_1Y_1^2-(K_3+K_{4/1}+K_{4/2})Y_2^2$$
$$...$$ (3)
$$dY_{10}/dt = K_{11}Y_8^2+K_{12}Y_9^2-K_{13}Y_{10}^2$$
$$dY_{11}/dt = K_{13}Y_{10}^2$$

with $K_i = k_i(C_{1,0})$ in s^{-1} as pseudo-rate constants. Since analytical solutions only exist for first and limited second-order Riccati-type equations (Gosoniu, 2000), numerical integration techniques (Runge-Kutta) with parameter optimization by a non-linear least-squares method was employed for the above system to determine K_i parameters. Figure 3, with the ordinate truncated at $Y_i = 0.2$ to amplify the details, provides the molar yields of seven identified PCB intermediate products and biphenyl at different residence times for the five temperatures of the SCWO experiments.

Although yields of each of the individual products are always low (typically less than 10%), the data are sufficiently accurate to execute a complete pathway analysis of all the intermediates (34- and 34'-CB lumped due to the GC co-elution) along with kinetic param-
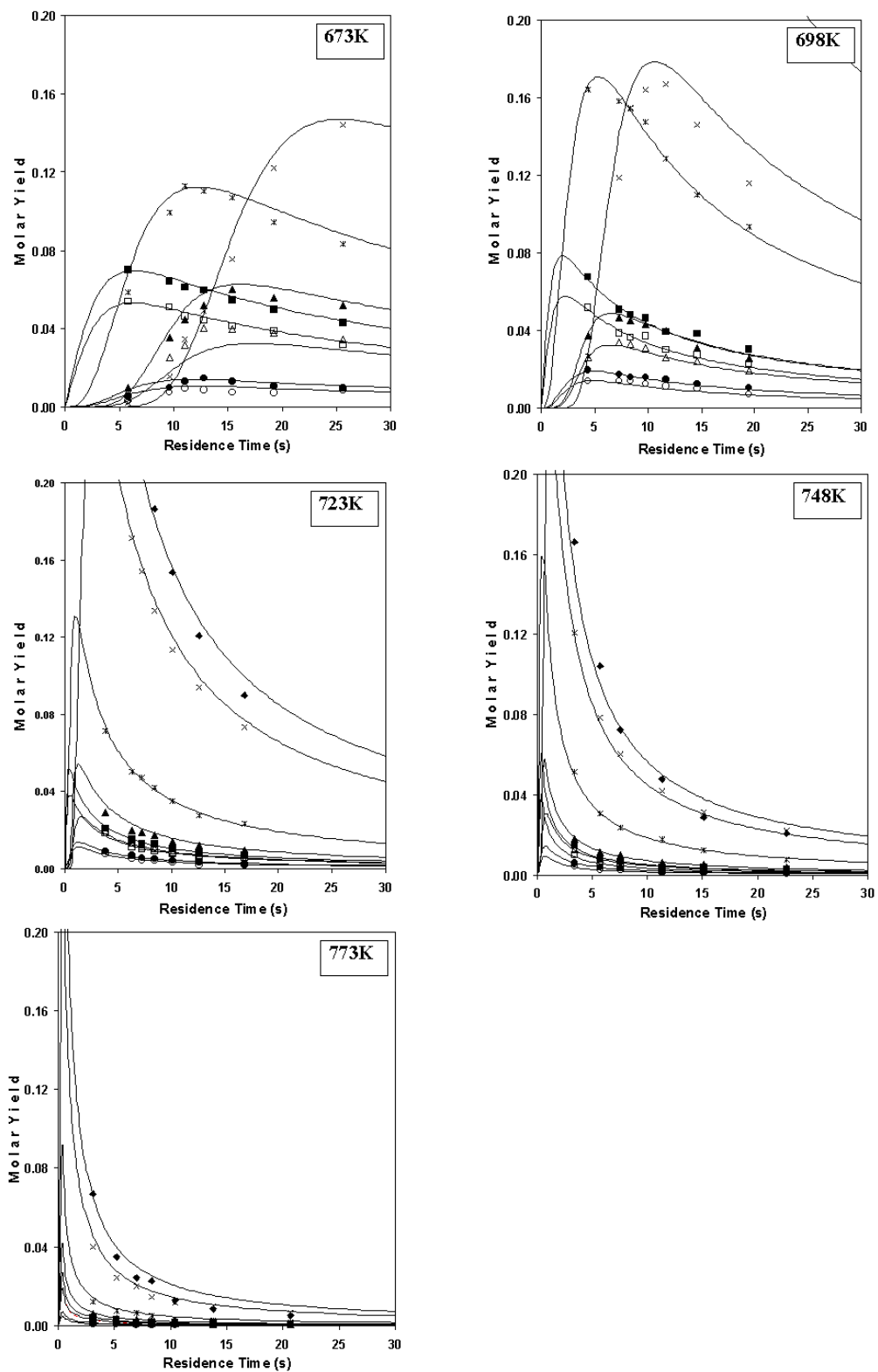
Figure 3. Dechlorination of 33'44'-TetraCB: comparison of predicted (—) and measured (symbols) yields of T4CB (◆), 33'4-(■) and 344'-(□) TriCBs, 33'-(●), (34- + 34')- (✳) and 44'-(○) DiCBs, 3- (▲) and 4- (△) CBs, and biphenyl (✕) as function of time at 673 K, 698 K, 723 K, 748 K, and 773 K.

eters determination (Table 1). The Arrhenius plots of $\ln(k_i)$ versus $1000/T$ correlate the data quite well and provide the base to calculate the energies of activation and frequency factors in Table 1. However, at the higher temperatures, the problem of multiple optima for K_i occurred for this detailed network and it has been solved by imposing some restrictions in the K_i ranges based on the values obtained by a lumped strategy as described below and where this problem did not occur. At all temperatures, yields of the intermediates decrease with increasing residence time after reaching a maximum. This observation suggests that these products undergo further dechlorination.

Lumped strategy

This method can be useful when applied to numerous products formed through similar pathways with similar kinetics, shrinking their number to representative pseudoproducts. Consequently, in the first lumped network derived from the detailed network (level A), Tri-, Di-, and Mono-CB congeners are lumped separately (level B). In the next lumping steps, all PCB intermediates are lumped together (level C), with biphenyl (level D) as a global pseudo intermediate. All further ring-open products (ROPs) of biphenyl oxidation are lumped as a pseudo final product, which is assumed to have the same molar mass as biphenyl and is calculated by difference using a material balance.

Table 1. Rate constants ($k_i \times 10^{-6}\,\text{L} \times \text{mol}^{-1} \times \text{s}^{-1}$) and Arrhenius parameters for the detailed (level A) and lumped (levels B, C, and D) reaction* networks (Figure 2) of 33'44'-TetraCB SCWO at 25.3 MPa.

Rxn	T=673 K	T=698 K	T=723 K	T=748 K	T=773 K	E_a(kJ/mol)	Log(A)
1A	0.005	0.023	0.090	0.300	1.020	229	21.5
2A	0.004	0.015	0.059	0.550	0.550	218	20.5
3A	0.115	0.339	2.460	8.840	8.840	192	20.0
4A	0.482	1.770	17.20	236.0	236.0	266	26.3
5A	0.665	1.897	21.60	307.0	307.0	273	26.9
6A	0.136	0.507	2.770	12.10	12.10	197	20.5
7A	1.696	3.664	20.00	237.0	237.0	210	22.4
8A	0.187	0.696	2.780	35.30	35.30	217	22.1
9A	0.073	0.142	0.775	6.060	6.060	189	19.5
10A	1.823	5.856	26.10	260.0	260.0	208	22.4
11A	0.652	3.127	16.60	169.0	169.0	233	24.0
12A	1.008	4.713	20.10	249.0	249.0	233	24.1
13A	0.130	0.285	0.579	7.120	7.120	172	18.4
1B	0.009	0.037	0.149	1.840	1.840	229	21.7
2B	0.342	1.128	11.90	164.0	164.0	270	26.4
3B	0.258	0.465	2.760	39.00	39.00	214	21.8
4B	0.396	1.882	12.20	111.0	111.0	237	24.0
5B	0.130	0.403	0.752	7.120	7.120	167	18.0
1C	0.009	0.038	0.150	1.840	1.840	227	21.6
2C	0.028	0.076	0.777	13.70	13.70	267	25.1
3C	0.109	0.351	0.593	7.510	7.510	177	18.7
1D	0.009	0.039	0.151	1.550	1.550	228	21.6
2D	0.014	0.043	0.180	2.730	2.730	242	22.7

Based on our previous study (Anitescu and Tavlarides, 2000) and the present work, we assume that a simplified successive global reaction network with second-order kinetics represents the main features of this system. The molar yields obtained from the above lumped-reaction networks (levels B-D) are favorably compared with results from the above detailed-reaction network (level A). The rate constants and the Arrhenius parameters for these reaction networks (Figure 2B-D) are also presented in Table 1. The similarity between the values of the Arhenius parameters for both unlumped and lumped PCB intermediates suggests the dechlorination step of the process is essentially the same for all of the PCB congeners.

SUMMARY AND CONCLUSIONS

A kinetic study of the dechlorination/oxidation of T_4CB in SCW in the presence of methanol is conducted over a temperature range of 673-773 K at 25.3 MPa and residence times of 3.11 to 25.6 s. The disappearance kinetics of T_4CB under experimental conditions is shown to follow a second-order decomposition which is independent of excess oxygen concentration. The kinetic model is confirmed by comparison with the oxidation kinetics of T_4CB in A1248 mixture, and the values of the reaction rate coefficients (Arhenius pre-exponential factor and energy of activation) are essentially the same. The formulated rate expression is a useful tool to use in assessing optimum operating conditions for destroying PCBs or for reactor design purpose.

Results of this study demonstrate that use of methanol as a second solvent to deliver water-insoluble chlorinated compounds provides the benefit of a significantly enhanced reaction rate. Indeed, the experimental results show that the presence of methanol in the reactor feed stream significantly accelerates the rate of T_4CB disappearance through a free-radical dechlorination step. This result is contrary to conventional wisdom that the addition of other organic compounds along with a given reactant in SCW makes the SCWO process less effective.

The reaction pathway of T_4CB, in the presence of methanol, proceeds through consecutive dechlorinations involving all lower chlorinated congeners leading to biphenyl, which undergoes oxidation resulting in products of which CO and CO_2 are observed. Competing phenomena of production and decomposition of the reaction intermediates (all tri-, di-, and mono-CB isomers, and biphenyl) occur in the SCWO process. Cl-abstraction from PCB molecules by hydrogen species, produced through methanol oxidation, avoids the reported formation of PCDDs/Fs. These compounds, which are more harmful than PCBs and form through OH radical addition mechanisms in the absence of methanol, are not detected in our experiments within the analytical limits (~0.1 ppb). In the absence of methanol, PCBs undergo parallel, competing reaction pathways through hydroxylated compounds, chlorinated benzenes, and dimers as primary SCWO products.

A global reaction network of 13 coupled reactions with second-order kinetics is shown to capture the detailed step mechanism of successive dechlorination of PCB congeners followed

by ring-opening oxidation of biphenyl leading to mineral products. Successively simplified global reaction networks are shown to represent the main features of this reaction process by using lumped pseudo-reaction products.

A comparison of our model predictions with the reported conversions of PCBs in the literature shows that similar performance can be achieved under less severe conditions or in a significantly shorter reaction time. For example, at 500 °C and 20.7 s, the high value of 99.5% conversion for $T_4CB/MeOH$ (1.71 mmol/L) is obtained. This conversion value is very high when one considers the remarkable chemical stability of PCBs.

ACKNOWLEDGMENTS

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