Total Organic Carbon Disappearance Kinetics for the Supercritical Water Oxidation of Monosubstituted Phenols

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We oxidized phenols bearing single $-CH_3$, $-C_2H_5$, $-COCH_3$, $-CHO$, $-OH$, $-OCH_3$, and $-NO_2$ substituents in supercritical water at 460 °C and 25.3 MPa. The observed effects of the concentrations of total organic carbon (TOC) and oxygen on the global disappearance rates for TOC were correlated by using power-law rate expressions. This kinetics study revealed that the rate of TOC disappearance is more sensitive to the oxygen concentration than is the rate of reactant disappearance. Additionally, the rate of TOC disappearance is always slower than the rate of reactant disappearance, with the ratio of these rates ranging from 0.10 to 0.65 for the different phenols at the conditions studied. The rates of TOC disappearance during supercritical water oxidation (SCWO) of these substituted phenols varied by nearly 2 orders of magnitude, showing significant effects from both the identity and location of the substituent. These substituent effects are greater for TOC disappearance kinetics than for reactant disappearance kinetics. Additionally, all of the substituted phenols exhibit faster TOC disappearance rates than does phenol. Accordingly, phenol is a good "worst case" model compound for SCWO studies. The pronounced substituent effects for TOC disappearance rates indicate that the oxidation of a common refractory intermediate is not an important feature of the SCWO networks for these phenols at the conditions studied.

Introduction

Supercritical water oxidation (SCWO) is a process technology for destroying organic compounds present in aqueous waste streams. SCWO proceeds by bringing together an oxidant, usually fed as air or oxygen, and organic compounds in the presence of water at a high temperature (450–600 °C) and high pressure (~250 atm). Organic compounds and oxygen can be intimately mixed in a single homogeneous aqueous phase at these supercritical conditions. Thus, the rapid oxidation reactions are unhindered by interphase transport limitations that could occur at subcritical conditions where multiple phases could exist. SCWO can treat a variety of wastes, including hazardous organic compounds (*1*) and sludges (*2*, *3*). The SCWO process, also referred to as hydrothermal oxidation, is a commercial technology, but research continues to resolve fundamentals and to address problems associated with difficult-to-treat or high-risk wastes.

A knowledge of the kinetics of the chemical reactions that occur during SCWO is required to design and analyze SCWO

reactors and processes (*4*). This realization has motivated numerous previous studies of SCWO kinetics, nearly all of which have concentrated on the kinetics of reactant disappearance. Simply making the reactant disappear, however, by converting it into a set of different organic compounds is insufficient for waste treatment by SCWO. Moreover, it is potentially dangerous if the products of incomplete oxidation are more toxic or hazardous than the starting material. It is the oxidation rate of the total organic carbon (TOC) content to CO_2, not the disappearance rate of the initial organic reactant itself, that is of primary applicability to the commercial SCWO process (*5*). Indeed, destruction and removal of TOC is the ultimate goal of SCWO. Thus, the kinetics of TOC disappearance assumes particular significance. There have been only a few previous investigations of the kinetics of TOC disappearance during SCWO. The phenolic compounds for which TOC disappearance rate laws are available are phenol (*6–8*), *o*-chlorophenol (*6*), and *o*-cresol (*9*). In this paper we present the kinetics of TOC disappearance for the SCWO of seven different monosubstituted phenols at 460 °C and 250 atm. The compounds investigated are cresols, hydroxybenzaldehydes, methoxyphenols, nitrophenols, resorcinol, ethylphenols, and hydroxyacetophenones.

Background

This paper is the final one in a series that presents results and analyses for the SCWO of a set of monosubstituted phenols. Our interest was in exploring the reaction networks and relative reactivities for a large number of different phenolic compounds at a single reaction temperature (460 °C) and pressure (25.3 MPa). Our previous work provided reaction networks and the kinetics of reactant disappearance for cresols and hydroxybenzaldehydes (*9–11*), methoxy-, nitro-, and hydroxy-substituted phenols (*12*), and ethylphenols and hydroxyacetophenones (*13*). These previous publications also report the experimental procedures, the reaction conditions explored, and the values of the CO_2 molar yield for each of the experiments with each compound. These previously reported data for CO_2 form the basis for the kinetics analysis presented herein.

Before proceeding with the kinetics analysis, we will first briefly summarize the experimental procedure employed. All experiments were done in an isothermal, isobaric, tubular flow reactor operating at a nominal steady state of 460 °C and 25.3 MPa. The reactor feed stream was prepared by mixing an aqueous stream containing the substituted phenol with a separate aqueous stream containing dissolved oxygen. These streams had been preheated separately to the reaction temperature before being mixed at the reactor entrance. The concentrations of the phenolic compounds were $\sim 10^{-4}$ M, and the concentrations of oxygen were $\sim 10^{-2}$ M at the reactor entrance. The reactor residence times were between 0.5 and 13 s, but values of 1–3 s were most common. The reactor effluent was cooled, depressurized, and then separated into gas and liquid streams, which were analyzed chromatographically. The molar flow rates of oxygen and the phenolic reactant in the reactor feed stream were the manipulated variables. The molar flow rates of products and unreacted reactant were the measured dependent variables. From these data we determined the reactant conversion and product molar yields. The molar yield of CO_2, Y_{CO_2}, was calculated as the molar flow rate of CO_2 in the reactor effluent divided by the molar flow rate of carbon atoms into the reactor. This latter quantity is simply the product of the molar flow rate of the phenolic reactant into the reactor and the number of carbon atoms contained in the reactant molecule. The CO_2

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molar yields obtained in these experiments ranged from 1 to 98%. The experimental conditions were such that the lowest CO_2 yield obtained for each compound was typically <10%. The highest CO_2 yields were usually between 40 and 70% for each compound. The exceptions were cresols and ethylphenols, for which the highest CO_2 yields were only ~15%, and m-OH- and m-CHO-substituted phenols, for which CO_2 yields >90% were obtained.

Our previous research with substituted phenols (*11–13*) showed that some of these compounds partially decomposed in supercritical water on the time scales of our experiments even in the absence of added oxygen. Consequently, the material being oxidized in some of the experiments is a mixture of the original compound and lesser amounts of its thermolysis products, which first form in the reactor preheat line and continue to form in the reactor itself. Thus, the TOC disappearance rate we determine in the next section is, in a strict sense, that for the oxidation of the substituted phenol plus its thermolysis products. To be concise, however, we will refer to this oxidation rate simply as the TOC disappearance rate for the substituted phenol itself. The reader should bear in mind that this rate necessarily includes any contribution from thermal and hydrolytic decomposition reactions in the preheat line and in the reactor. The compounds with the fastest thermolysis rates in supercritical water are the hydroxybenzaldehydes, nitrophenols, and methoxyphenols (*11, 12*). Thermolysis alone could result in reactant conversions (but not TOC conversions) of up to 20% for most of these compounds at our experimental conditions. For o-hydroxybenzaldehyde the thermolysis conversion could be as high as 65%. For all other reactants used, thermolysis would produce <10% conversion. Of course, thermolysis of the substituted phenol will not generate CO_2, but it will form reactive intermediates and other molecular products that might affect the global rate of TOC disappearance from the reaction mixture.

Kinetics Analysis

The literature clearly shows that the selectivities to CO_2 from the SCWO of phenolic compounds are less than unity even when the conversion of the phenolic compound itself is close to complete. This observation implies that a significant amount of the converted organic carbon is associated with intermediate products of incomplete oxidation and that the rate of CO_2 formation is slower than the rate of reactant disappearance. In this section we follow the procedure of Li et al. (*6*) to develop global rate laws for the conversion of organic carbon to CO_2 during the SCWO of substituted phenols.

The global disappearance rate (mol/L–s) for organic carbon can be written as a power-law rate expression of the form

$$\text{rate} = -k[\text{TOC}]^a[\text{O}_2]^b \tag{1}$$

where k is the rate constant, the quantities in brackets represent molar concentrations at reaction conditions, and a and b are global reaction orders. The rate of CO_2 formation is simply the rate of TOC destruction in eq 1 multiplied by the number of carbon atoms in the reactant. Note that we include CO within the TOC concentration, so our use of the term TOC could more accurately be defined as total oxidizable carbon.

The experiments were performed in a reactor that can be modeled as an isothermal, isobaric plug-flow reactor with a constant volumetric flow rate. The design equation for such a reactor is

$$\text{d[TOC]}/\text{d}\tau = \text{rate} \tag{2}$$

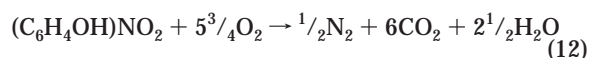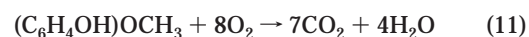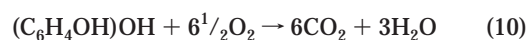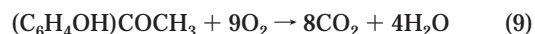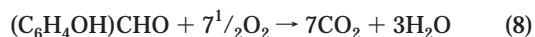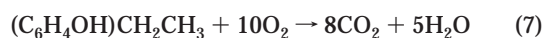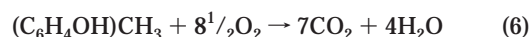where, τ, the residence time, is the ratio of the reactor volume to the volumetric flow rate. We next write the TOC concentration as a function of the TOC conversion, X, which is also equal to the molar yield of CO_2.

$$[\text{TOC}] = [\text{TOC}]_o(1 - X) \tag{3}$$

The subscript, o, denotes a quantity at the reactor entrance.
Combining eqs 1–3 leads to

$$\text{d}X/\text{d}\tau = k(1 - X)^a[\text{TOC}]_o^{a-1}[\text{O}_2]^b \tag{4}$$

Equation 4 can be integrated provided the concentration of O_2 can be written as a function of the TOC conversion. One might be tempted to use the stoichiometric relationship between the concentration of O_2 and that of each phenolic compound based on the total oxidation reactions presented in eqs 5–12.

$$C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O \tag{5}$$

$$(C_6H_4OH)CH_3 + 8^1/_2O_2 \rightarrow 7CO_2 + 4H_2O \tag{6}$$

$$(C_6H_4OH)CH_2CH_3 + 10O_2 \rightarrow 8CO_2 + 5H_2O \tag{7}$$

$$(C_6H_4OH)CHO + 7^1/_2O_2 \rightarrow 7CO_2 + 3H_2O \tag{8}$$

$$(C_6H_4OH)COCH_3 + 9O_2 \rightarrow 8CO_2 + 4H_2O \tag{9}$$

$$(C_6H_4OH)OH + 6^1/_2O_2 \rightarrow 6CO_2 + 3H_2O \tag{10}$$

$$(C_6H_4OH)OCH_3 + 8O_2 \rightarrow 7CO_2 + 4H_2O \tag{11}$$

$$(C_6H_4OH)NO_2 + 5^3/_4O_2 \rightarrow {}^1/_2N_2 + 6CO_2 + 2^1/_2H_2O \tag{12}$$

This stoichiometric relationship is of the form

$$[\text{O}_2] = [\text{O}_2]_o - \nu_{o_2}X[\text{TOC}]_o \tag{13}$$

where ν_{o_2} is the stoichiometric coefficient for O_2 in each of the reactions above. Although these stoichiometric relationships have been used in some previous kinetics analyses of SCWO data (*14*), they are strictly correct only when CO_2 is the sole carbon-containing product. The amount of O_2 consumed will be less than that implied by the eqs 5–12 if carbon-containing products other than CO_2 appear. The literature (*7, 9, 12, 15–17*) clearly shows that SCWO of complex organic compounds produces numerous products of incomplete oxidation and that the reactions do not proceed to CO_2 in a single step. Consequently, the stoichiometric relations between the oxidant and the organic compounds are not known a priori for complex organic compounds. The effective stoichiometric coefficients for oxygen likely increase with conversion and reach the ultimate values implied in eqs 5–12 only as an upper bound. Because the effective stoichiometry for incomplete oxidation is unknown, this approach cannot be used to calculate with any certainty the oxygen concentration as a function of the total organic carbon conversion.

This consideration led us to use excess oxygen in all of the SCWO kinetics experiments. Oxygen was always present in the feed in >200% stoichiometric excess with respect to the organic reactant. On the basis of product analyses presented previously (*9, 10, 12, 13*), we estimate that the O_2 concentration changed at most by 20% during any experiment. Thus, the oxygen concentration can be taken to be essentially constant during an experimental run and equal to its concentration at the reactor entrance. With this approximation, eq 4 can now be solved analytically to give
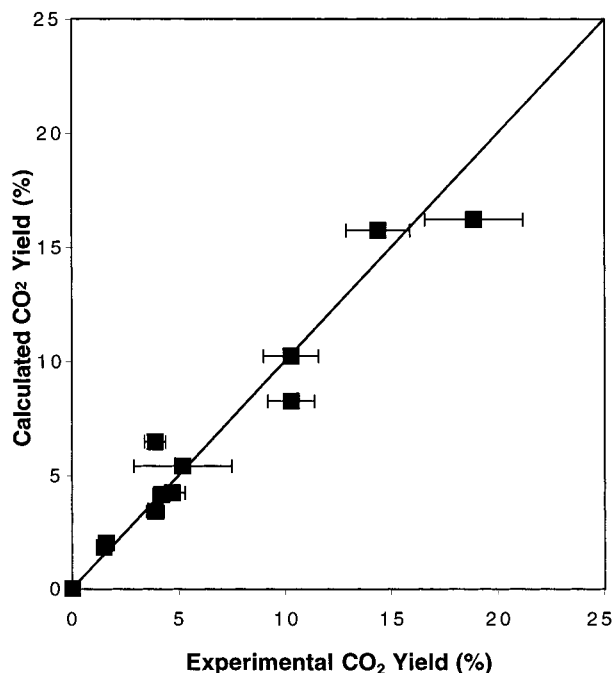
FIGURE 1. Parity plot for TOC conversion from the SCWO of *p*-ethylphenol.

the algebraic relationship below between the TOC conversion, the process variables, and the parameters in the rate law. Note that we rewrite the rate constant k as $10^{k'}$.

$$X = Y_{CO_2} = 1 - (1 + (a-1)10^{k'}[TOC]_0^{a-1}[O_2]_0^b\tau)^{1/1-a}$$
$$\text{for } a \neq 1 \quad (14)$$

The parameters in the rate law for each phenolic reactant were determined by fitting the respective experimental CO_2 molar yields to eq 14. We used SimuSolv (*18*), a software package developed by Dow Chemical Co., to perform the nonlinear regression analysis and thereby determine the optimal values for the parameters a, b, and k' in eq 14. We performed a maximum likelihood parameter estimation with the sum of the squared differences between the experimental and calculated CO_2 yields serving as the objective function. We made residual and parity plots to evaluate the goodness of fit provided by the rate parameters and to determine whether the deviation of the model from the experimental observations exhibits any systematic errors. Parity plots display the Y_{CO_2} values calculated from the rate expression (eq 14) versus the Y_{CO_2} values determined experimentally. Figure 1 provides an example for the case of *p*-ethylphenol. A perfect fit of the data to the model would place all points on the diagonal line, where the calculated and experimental yields are equal. Most of the data in Figure 1, within the 95% confidence intervals shown, do intersect with the diagonal line, indicating a reasonably good fit of the data to the model. Moreover, the deviation from the diagonal line appears to be random rather than systematic, which lends additional support to the model.

Tables 1 and 2 provide the results of this parameter estimation procedure. Table 1 lists numerical values and 95% confidence intervals for k', a, and b. These parameters are simply the values that best described the experimental data. They contain no mechanistic significance. The uncertainties (95% confidence intervals) in Table 1 sometimes exceed the value of the parameter. If desired, the uncertainties could be reduced by acquiring additional experimental data over a wider range of reactant concentrations. Our main goal, however, was not to obtain these parameters but rather to

TABLE 1. Global Rate-Law Parameters and 95% Confidence Intervals for Disappearance of TOC during the SCWO of Substituted Phenols[a]

substituent	k'	a	b
o-CH$_3$	−1.90	0.36 ± 0.29	0.71 ± 0.36
m-CH$_3$	−2.21 ± 0.96	0.51 ± 0.18	0.59 ± 0.45
p-CH$_3$	−3.15 ± 2.03	0.34 ± 0.36	0.41 ± 0.72
o-CH$_2$CH$_3$	−0.29 ± 0.36	0.74 ± 0.05	0.71 ± 0.16
m-CH$_2$CH$_3$	−1.28 ± 1.36	0.83 ± 0.20	0.23 ± 0.57
p-CH$_2$CH$_3$	−1.10 ± 1.00	0.56 ± 0.19	0.67 ± 0.43
o-COCH$_3$	−0.18 ± 1.25	0.30 ± 0.19	1.26 ± 0.48
m-COCH$_3$	−0.38 ± 0.93	0.49 ± 0.15	0.83 ± 0.42
p-COCH$_3$	0.06 ± 1.16	0.50 ± 0.17	1.01 ± 0.44
o-CHO	−0.17 ± 3.18	0.52 ± 0.37	0.94 ± 1.13
m-CHO	−2.00 ± 2.35	0.44 ± 0.20	0.62 ± 0.92
p-CHO	−1.44 ± 1.50	0.49 ± 0.27	0.66 ± 0.51
m-OH	−1.82 ± 1.03	0.38 ± 0.14	0.23 ± 0.43
m-OCH$_3$	−0.29 ± 0.25	0.75 ± 0.03	0.52 ± 0.10
p-OCH$_3$	−0.59 ± 1.40	0.74 ± 0.15	0.28 ± 0.57
m-NO$_2$	−1.01 ± 0.39	0.52 ± 0.09	0.60 ± 0.12
p-NO$_2$	0.11 ± 6.88	1.14 ± 1.07	0.26 ± 2.39

[a] Rate has units of mol/L·s.

compare the TOC disappearance rates for the different compounds. Obtaining the parameters in the rate law was simply the means we employed to this end. As we will see shortly, the uncertainties in the reaction rates are not as large.

Table 2 displays the variances and covariances associated with each parameter for each of the different phenolic reactants. The variances ($\sigma_{x_i}^2$) and covariances (σ_{x_i,x_j}^2) for the parameters in the rate law are required when one wants to determine the uncertainty in the value of the oxidation rate calculated at any set of reaction conditions. In general, the variance in a quantity y (σ_y^2), where $y = f(x_1, x_2, x_3, ...)$ is calculated from the propagation of errors formula below.

$$\sigma_y^2 = \sum_{i=1}^{l}\left(\frac{\partial y}{\partial x_i}\right)^2 \sigma_{x_i}^2 + 2\sum_{i=1}^{l-1}\sum_{j=i+1}^{l}\left(\frac{\partial y}{\partial x_i}\right)\left(\frac{\partial y}{\partial x_j}\right)\sigma_{x_i,x_j}^2 \quad (15)$$

The index l in eq 15 is the number of variables in $f(x_1, x_2, x_3, ...)$. In the present case this equation can be applied to compute the variance (uncertainty) in the TOC disappearance rate (eq 1) given the variances and covariances associated with the parameters k', a, and b.

Table 1 shows that the parameter a, the reaction order for TOC, ranges from 0.30 to 1.14. These values are similar to but almost always lower than the values previously determined (*10, 12, 13*) for the global reaction orders for reactant disappearance for these same compounds. The parameter b, the reaction order for oxygen, ranges from 0.23 to 1.26. These values are similar to but almost always higher than the oxygen reaction orders in the rate laws for reactant disappearance (*10, 12, 13*). This observation indicates that the rate of TOC disappearance is usually a stronger function of the oxygen concentration than is the rate of reactant disappearance during SCWO. The same trend was observed previously for SCWO of phenol and *o*-chlorophenol (*6*).

To compare the TOC disappearance rates for the different phenols, we used the global rate laws to calculate a pseudo-first-order rate constant (k'') for TOC disappearance for each compound (rate = k''[TOC]). These pseudo-first-order rate constants were calculated as

$$k'' = k[TOC]^{a-1}[O_2]^b \quad (16)$$

Table 3 displays these TOC disappearance rate constants, which correspond to SCWO at 460 °C, 25.3 MPa, a phenolic

TABLE 2. Variances and Covariances for Global Rate Law Parameters

substituent	$\sigma^2_{k'}$	σ^2_a	σ^2_b	$\sigma^2_{k',a}$	$\sigma^2_{k',b}$	$\sigma^2_{a,b}$
o-CH$_3$		2.039×10^{-2}	3.177×10^{-2}			-1.985×10^{-2}
m-CH$_3$	1.796×10^{-1}	6.191×10^{-3}	3.919×10^{-2}	9.340×10^{-3}	6.934×10^{-2}	-4.760×10^{-3}
p-CH$_3$	6.233×10^{-1}	1.975×10^{-2}	7.888×10^{-2}	7.088×10^{-2}	1.764×10^{-1}	1.767×10^{-3}
o-CH$_2$CH$_3$	2.539×10^{-2}	5.218×10^{-4}	5.182×10^{-3}	6.301×10^{-4}	1.026×10^{-2}	-4.634×10^{-4}
m-CH$_2$CH$_3$	3.471×10^{-1}	7.737×10^{-3}	6.006×10^{-2}	1.784×10^{-2}	1.276×10^{-1}	-2.847×10^{-3}
p-CH$_2$CH$_3$	1.868×10^{-1}	6.540×10^{-3}	3.427×10^{-2}	1.189×10^{-2}	6.533×10^{-2}	-3.937×10^{-3}
o-COCH$_3$	3.041×10^{-1}	7.355×10^{-3}	4.467×10^{-2}	2.430×10^{-2}	9.614×10^{-2}	-1.058×10^{-3}
m-COCH$_3$	1.678×10^{-1}	4.572×10^{-3}	3.390×10^{-2}	6.440×10^{-3}	6.301×10^{-2}	-4.195×10^{-3}
p-COCH$_3$	2.649×10^{-1}	5.323×10^{-3}	3.779×10^{-2}	1.969×10^{-2}	8.766×10^{-2}	7.455×10^{-4}
o-CHO	1.898	2.632×10^{-2}	2.420×10^{-1}	1.364×10^{-1}	6.160×10^{-1}	1.810×10^{-2}
m-CHO	1.217	8.727×10^{-3}	1.857×10^{-1}	6.176×10^{-2}	4.490×10^{-1}	1.238×10^{-2}
p-CHO	4.666×10^{-1}	1.471×10^{-2}	5.319×10^{-2}	5.116×10^{-2}	1.238×10^{-1}	7.061×10^{-5}
m-OH	2.291×10^{-1}	4.069×10^{-3}	3.991×10^{-2}	1.100×10^{-2}	8.732×10^{-2}	-5.818×10^{-4}
m-OCH$_3$	9.628×10^{-3}	1.513×10^{-4}	1.652×10^{-3}	4.404×10^{-4}	3.644×10^{-3}	-2.056×10^{-5}
p-OCH$_3$	2.962×10^{-1}	3.524×10^{-3}	4.983×10^{-2}	1.146×10^{-2}	1.132×10^{-1}	-6.130×10^{-5}
m-NO$_2$	2.882×10^{-2}	1.562×10^{-3}	2.649×10^{-3}	5.109×10^{-3}	4.927×10^{-3}	-2.098×10^{-4}
p-NO$_2$	7.911	1.921×10^{-1}	9.526×10^{-1}	8.531×10^{-1}	2.399	1.089×10^{-1}

TABLE 3. Pseudo-First-Order Rate Constants (k') for TOC Disappearance during SCWO of Substituted Phenols at 460 °C and 25.3 MPa with [Organic] = 100 μmol/L and [O$_2$] = 7 mmol/L

substituent	k'' (10^3/s)	$k_{TOC}/k_{reactant}$
-H[a] (phenol)	6.33	0.21
o-CH$_3$	39.6 ± 9.1	0.22
m-CH$_3$	11.9 ± 1.6	0.28
p-CH$_3$	10.8 ± 3.3	0.14
o-CH$_2$CH$_3$	102 ± 7	0.10
m-CH$_2$CH$_3$	56.2 ± 12.6	0.29
p-CH$_2$CH$_3$	67.9 ± 10.9	0.20
o-COCH$_3$	186 ± 54	0.26
m-COCH$_3$	264 ± 55	0.55
p-COCH$_3$	272 ± 57	0.50
o-CHO	208 ± 132	0.17
m-CHO	27.2 ± 13.2	0.24
p-CHO	57.6 ± 19.8	0.39
m-OH	467 ± 86	0.59
m-OCH$_3$	241 ± 9	0.65
p-OCH$_3$	423 ± 102	0.32
m-NO$_2$	172 ± 15	0.53
p-NO$_2$	126 ± 47	0.32

[a] Calculated from rate law in ref 6.

TABLE 4. Relative Rates of TOC Disappearance in SCW at 460 °C and 25.3 MPa for Substituted Phenols at [Organic] = 100 μmol/L and [O$_2$] = 7 mmol/L[a]

ortho		meta		para	
—H[b]	1.0	—H[b]	1.0	—H[b]	1.0
—Cl[b]	2.9	—CH$_3$	1.9	—CH$_3$	1.7
—CH$_3$	6.3	—CHO	4.3	—CHO	9.1
—CH$_2$CH$_3$	16	—CH$_2$CH$_3$	8.9	—CH$_2$CH$_3$	11
—COCH$_3$	29	—NO$_2$	27	—NO$_2$	20
—CHO	33	—OCH$_3$	38	—COCH$_3$	43
		—COCH$_3$	42	—OCH$_3$	67
		—OH	74		

[a] There are no entries for o-NO$_2$ and o-OCH$_3$ because no SCWO experiments were done with these compounds. They disappeared very quickly in SCW even in the absence of added oxygen. [b] From ref 6.

Table 3 also provides the ratio of the rates of TOC disappearance and reactant disappearance (*10*, *12*, *13*) at the stated reaction conditions for each compound. These ratios range from 0.10 to 0.65. All of the ratios are less than unity, indicating that the rate of TOC disappearance is always less than the rate of reactant disappearance. For five of the six different substituted phenols where multiple isomers were investigated, the meta isomer has the highest ratio. Hydroxybenzaldehydes are the only exception to this trend. Interestingly, the meta isomer also always had the slowest reactant disappearance rate (*13*). Thus, the high ratios for the meta isomers in Table 3 are largely due to a low reactant disappearance rate.

The substituent effects for TOC disappearance are more clearly delineated in Table 4. For the four substituted phenols for which rate laws exist for all three isomers, the ortho isomer is the most reactive in three instances. The only exception is the hydroxyacetophenones. The high reactivity of the ortho isomer was also observed for the kinetics of reactant disappearance (*10*–*13*).

The pronounced substituent effects for TOC disappearance kinetics have implications for the reaction networks for SCWO of phenolic compounds. It has been postulated that SCWO produces refractory intermediates that can control or at least limit the rate of TOC disappearance. Acetic acid (*19*) and CO (*20*) have been presented as potential refractory intermediates. If such a rate-controlling refractory intermediate existed, then the rate of CO$_2$ formation should be roughly the same for all phenolics for it would always be the rate of oxidation of this refractory intermediate. The results in Tables 3 and 4, however, which show nearly a 70-fold variation in TOC disappearance rates for different substituted phenols,

concentration of 10^{-4} M, and an O$_2$ concentration of 7×10^{-3} M. The uncertainties given are the 95% confidence intervals. The 95% confidence interval is related to the variance in the calculated rate constant, which can be obtained by using the variances ($\sigma^2_{x_i}$) and covariances ($\sigma^2_{x_i,x_j}$) of the parameters in the rate law (given in Table 2) in eq 15.

By comparing the values of k'' in Table 3, we can in effect compare the reaction rates for these phenolic compounds at this particular set of conditions. One conclusion that can immediately be drawn from Table 3 is that the TOC disappearance rates for all of the substituted phenols exceed that of phenol itself. Additionally, the substituent identity and its location have a profound influence on the TOC disappearance rate. For example, the reactivity (k') of the para-substituted phenols varies by a factor of nearly 70 for the different substituents investigated. Similarly, the reactivity of a given substituted phenol varies by up to a factor of 7 depending on whether the substituent is at the ortho, meta, or para position. These ranges in relative reactivities exceed those reported (*10*, *12*, *13*) for the kinetics of reactant disappearance for the same set of compounds, which shows that substituent effects are more significant for TOC disappearance kinetics than for reactant disappearance kinetics.

argue against the existence of any common rate-controlling organic, refractory intermediate at these reaction conditions.

Our previous experimental work showed that the identity and location of substituents influence the kinetics of reactant disappearance, and the present results show that the same is true for the kinetics of TOC disappearance. Thus, substituted phenols, which disappear more quickly during SCWO than phenol itself, do not attain this enhanced reactivity simply by being converted into other organic compounds. Rather, the presence of substituents causes a real increase in the complete oxidation rate and the production of CO_2.

Acknowledgments

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