

# Generalized Kinetic Model for Wet Oxidation of Organic Compounds

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*A generalized kinetic model for wet oxidation (WO) of organic compounds was developed based on a simplified reaction scheme considering acetic acid as the rate-limiting intermediate. The selectivity of product vs. intermediate formations was quantified by the ratio of the two reaction rate constants. This point selectivity  $\alpha$  may be used to characterize the "strength" of the feed stream to be treated. This global model was validated using WO kinetic data reported for temperatures ranging from 150°C to 550°C and pressures varying from 20 bar to 440 bar. Organic conversions predicted by this model, as compared to other models, more accurately reflect the actual performance of WO processes. The model has practical validity for a variety of organic compounds, wastewaters and sludges in both subcritical and supercritical water oxidation processes.*

## Introduction

As the amount of toxic wastewaters and sludges generated by industrial and domestic sources approaches 470 million metric tons per year (Gloyna, 1989), the development of effective and acceptable waste treatment processes is becoming increasingly important. Furthermore, in conjunction with future waste minimization and rigorous effluent quality control, EPA goals suggest destruction levels up to 99.9999% of some compounds and use of totally enclosed treatment facilities. To accomplish these objectives, novel waste treatment and process concepts are needed. Also, it must be noted that increased environmental constraints and unfavorable public opinion have challenged the continuing application of conventional waste management techniques which include incineration.

Practically, wet oxidation processes can be operated in a wide range of temperatures and pressures. For example, wet air oxidation (WAO), commonly associated with sludge conditioning and some organic destruction, is a low-temperature process. The Zimpro process (Zimmerman, 1958; Teletzke, 1964), is typically operated in a temperature range of 150°C to 350°C and pressure range of 20 to 200 bar. The operating pressure is maintained well above the saturation pressure corresponding to the operating temperature so that the reaction is carried out in the liquid phase. Residence times may range from 15 min to 120 min, and the chemical oxygen demand

(COD) removal may typically be about 75% to 90%. Volatile acids constitute a substantial portion of the remaining COD. The formation of volatile acids, particularly acetic acid, is a limitation for WAO (Foussard et al., 1989; Keen and Baillod, 1985; Baillod et al., 1982; 1980; Friedman et al., 1988; Wu et al., 1987; Ploos van Amstel and Rietema, 1973; Fisher, 1971; Teletzke et al., 1967). Furthermore, the effluent from incomplete (partial) wet oxidation of some wastewaters may be intensely colored and toxic (Sheppard, 1985; Larson et al., 1988).

Recent studies show that when the oxidation of organic compounds and wastewaters is carried out above the critical point of water, the organic conversion is relatively rapid and potentially complete (Price, 1981; Modell et al., 1982; Timberlake et al., 1982; Helling, 1986; Staszak et al., 1987; Gloyna et al., 1990; Lee et al., 1990). At these conditions, the properties of water such as dielectric constant, viscosity, and conductance differ greatly from those at lower temperatures and pressures. Supercritical water displays gas-like properties: high solubility of organics, complete miscibility in all proportions with oxygen, high diffusivities, low viscosity, and low solubility of inorganic salts. The complete miscibility of oxygen and organics in supercritical water creates a single-phase fluid, which greatly reduces interfacial diffusion. In supercritical water, high organic conversion levels (>99.99%) of many EPA priority pollutants can be achieved with a short residence time (<5 min) in a totally enclosed facility. Therefore, supercritical water oxidation (SCWO) provides a viable and environmentally at-

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tractive option to managing the growing organic sludge and toxic wastewater treatment problems.

However, kinetic information describing wet oxidation (WO), particularly SCWO, is limited. Clearly defined and validated mechanisms for WO are not available. Furthermore, these sources of kinetic data are scattered and the values of the reported kinetic parameters differ considerably. Therefore, for the design and development of WO processes, general, yet reliable, kinetic models are needed. The objectives of this article are: to analyze WO reaction mechanisms; to evaluate the existing WO kinetic models encompassing a range of temperatures and pressures from 150°C to 550°C and 20 bar to 440 bar; to propose a simplified WO reaction scheme; and to develop a generalized kinetic model.

## Wet Oxidation Reaction Mechanisms

Understanding the reaction mechanisms is essential for the development of kinetic models. For engineering purposes, however, it is sufficient to quantify the global reaction rate by identifying the major WO pathways. The type of oxidant, for a given organic compound, may influence both the reaction mechanism and pathway. The two commonly used oxidants have been oxygen (Yunis, 1967; Pruden and Le, 1976; Fousard, 1983; Thomason and Modell, 1984) and hydrogen peroxide (Welch and Siegwarth, 1989; Lee et al., 1990; Lee, 1990; Wilmanns, 1990).

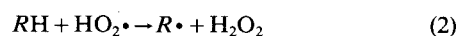
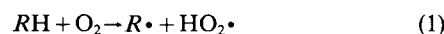
Many attempts have been made to study reaction mechanisms for subcritical WO of organics. Day et al. (1973) and Williams et al. (1973) concluded that the free-radical mechanism was involved in subcritical WO of propionic and butyric acids. It was concluded that the attack at the  $\alpha$ -carbon by oxygen was a key step in such a mechanism. Acetic acid (or acetate salt) was found to be a major intermediate and relatively difficult to remove at subcritical WO conditions. Shibaeva et al. (1969) in their report on a free-radical mechanism for subcritical WO of phenol using oxygen pointed out that the ionic strength did not affect the oxidation rate of phenol. Charest and Chornet's study (1976) on WO of active carbon also concluded that the reaction proceeded via a free-radical mechanism. Taylor and Weygandt (1974), however, stated that the radical-chain mechanism appeared to be more likely under nonaqueous conditions, and the nonchain mechanism was preferred in aqueous solutions.

The oxidation mechanisms were not addressed in early SCWO studies (Wightman, 1981; Price, 1981; Modell et al., 1982; Timberlake et al., 1982). Not until recently have Helling (1986), Webley and Tester (1988), and Rofer and Streit (1989), based on combustion theory, attempted to interpret SCWO mechanisms. Kinetic models for SCWO of methanol, methane, carbon monoxide, and ethanol have been obtained using this approach. Also, Bedenev et al. (1988) and Vedenev et al. (1988), using kinetic modeling of high-pressure methane oxidation, obtained similar results. Similarly, Yang and Eckert (1988) proposed two mechanisms for SCWO of *p*-chlorophenol. In this model, however, oxygen was not involved in the initiation steps. Oxygen was considered to participate only in the propagation steps to produce paraphenol peroxy radicals. Lee (1990) proposed a number of reaction pathways of oxidation of acetamide and acetic acid by hydrogen peroxide. The hydroxyl radical ( $\text{HO}\cdot$ ) was considered to be the dominant

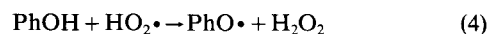
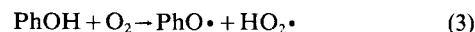
oxidizing species. Hydrogen abstraction was postulated to be involved in the initiation steps.

A free-radical reaction mechanism appears to be accountable for WO of organic compounds in both subcritical and supercritical water. Although supercritical water, as compared to liquid water, exhibits a drastic decrease in the ionic dissociation (Holzapfel, 1969; Quist, 1970), the changes in ionic concentration (the impact of solvent water) might not be a dominant factor affecting the radical formation and chain reactions. This suggestion is supported by a number of well-known free-radical reactions (summarized in Eqs. 1 through 8) generally considered to be associated with WO of organic compounds.

As shown in Eqs. 1 and 2, free radicals in the absence of initiators are formed by the reaction of oxygen with the weakest C-H bonds of the oxidized organic compound.



*R* denotes the organic functional group. However, in subcritical WO of phenol, the reaction of oxygen with the O-H bond may be involved in the initiation steps (Shibaeva et al., 1969), as expressed in Eqs. 3 and 4.

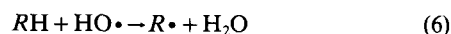


The common product of Eqs. 2 and 4 is hydrogen peroxide but it further decomposes to generate hydroxyl radicals, Eq. 5.



The term *M* can be either a homogeneous or heterogeneous species (Hoare et al., 1958). The effect of *M* on WO using hydrogen peroxide has been studied extensively (Bishop et al., 1968; Brett and Gurnham, 1973; Chowdhury and Ross, 1975; Chornet and Jaulin, 1988). The thermal decomposition of hydrogen peroxide at WO temperatures is significant, and the decomposition reaction proceeds as  $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + 1/2\text{O}_2$  (Schumb et al., 1955).

In the combustion reactions (oxidation at high temperatures and low pressures), the hydroxyl radical ( $\text{HO}\cdot$ ) plays an important role. Since the hydroxyl radical ( $\text{HO}\cdot$ ) has a large electron affinity (568 kJ), it oxidizes not only all organic compounds containing hydrogen but also reacts with most halide ions to produce halide radicals (Uri, 1961). The oxidation of organic compounds by hydroxyl radicals, as shown in Eq. 6, follows a hydrogen abstraction mechanism. The organic radical ( $\text{R}\cdot$ ) reacts with oxygen, Eq. 7, to form an organic peroxy radical ( $\text{ROO}\cdot$ ) (Emanuel et al., 1984). The organic peroxy radical further abstracts a hydrogen atom from the organic compound, producing an organic hydroperoxide ( $\text{ROOH}$ ) and another organic radical, Eq. 8.



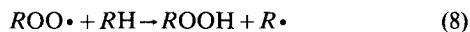
**Table 1. Initiation Mechanisms Associated with Hydroxyl Radicals\***

Reaction	$A^{**}$	$E^*$ (kJ/mol)	Reference
<i>Radical Formation</i>			
$H_2O_2 \rightarrow 2 HO\cdot$	$1.00 \times 10^{13}$	200.83	(Giguere and Liu, 1957)
	$3.00 \times 10^{14}$	207.94	(Bedeneev et al., 1988)
	$1.58 \times 10^{14}$	201.89	(Webley and Tester, 1991)
$H_2O + O_2 \rightarrow HO_2\cdot + HO\cdot$	$8.07 \times 10^{10}$	287.03	(Rofer and Streit, 1989)
$H_2O_2 + O_2 \rightarrow 2 HO_2\cdot$	$5.42 \times 10^{10}$	166.20	(Tsang and Hampson, 1986)
$CH_4 + O_2 \rightarrow CH_3\cdot + HO_2\cdot$	$4.04 \times 10^{10}$	238.00	(Tsang and Hampson, 1986)
$CH_4 + O_2 \rightarrow CH_3\cdot + HO_2\cdot$	$6.02 \times 10^{10}$	234.30	(Bedeneev et al., 1988)
$CH_4 + O_2 \rightarrow CH_3\cdot + HO_2\cdot$	$3.98 \times 10^{10}$	237.84	(Webley and Tester, 1991)
$RH + O_2 \rightarrow R\cdot + HO_2\cdot$	$7.94 \times 10^{12}$	167.0	(Khar'kova et al., 1989) <sup>†</sup>
<i>Hydrogen Abstraction</i>			
$CH_4 + HO\cdot \rightarrow CH_3\cdot + H_2O$	$7.95 \times 10^3$	11.25	(Bedeneev et al., 1988)
$CH_4 + HO\cdot \rightarrow CH_3\cdot + H_2O$	$1.58 \times 10^4$	11.70	(Webley and Tester, 1991)
$CH_4 + HO_2\cdot \rightarrow CH_3\cdot + H_2O_2$	$1.81 \times 10^8$	77.70	(Tsang and Hampson, 1986)
$CH_4 + HO_2\cdot \rightarrow CH_3\cdot + H_2O_2$	$1.81 \times 10^9$	89.96	(Bedeneev et al., 1988)
$CH_4 + HO_2\cdot \rightarrow CH_3\cdot + H_2O_2$	$2.00 \times 10^8$	77.75	(Webley and Tester, 1991)
$RH + HO\cdot \rightarrow R\cdot + H_2O$	$2.9 \times 10^{10}$	12.8	(Khar'kova et al., 1989)
<i>Radical Shift</i>			
$HO\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot$	$1.75 \times 10^9$	1.33	(Tsang and Hampson, 1986)
	$2.23 \times 10^9$	2.16	(Bedeneev et al., 1988)
	$1.58 \times 10^9$	1.25	(Webley and Tester, 1990)
$HO_2\cdot + H_2O \rightarrow H_2O_2 + HO\cdot$	$3.39 \times 10^9$	137.36	(Rofer and Streit, 1989)

\*The reaction rate constant ( $k$ ) =  $AT^n \exp(-E^*/RT)$ , where  $A$  is pre-exponential factor,  $n=0$  for the all reactions in this table,  $E^*$  is the activation energy (kJ/mol),  $R$  is the gas constant ( $= 8.314 \text{ J/mol}\cdot\text{K}$ ), and  $T$  is temperature (K).

\*\*The dimensions of the pre-exponential factors of the rate constants are:  $s^{-1}$  for monomolecular reactions,  $L/mol\cdot s$  for bimolecular reactions.

<sup>†</sup>RH = cyclohexane.



Since the organic hydroperoxides formed are relatively unstable, decomposition of such intermediates often leads to molecular breakdown and formation of subsequent intermediates with lower carbon numbers. These scission reactions continue rapidly until the formation of acetic or formic acid. Both acids will eventually be converted into carbon dioxide and water. Free radical mechanisms often involve the attack of peroxy radicals at the  $\alpha$ -carbon of high-molecular-weight alcohols, ketones, aldehydes, and carboxylic acids. However, other mechanisms of the rupture of a C-C bond (such as  $\beta$  or  $\gamma$  carbon position) are also considered to exist (Emanuel et al., 1967).

To appreciate the rates of these elementary reactions, the kinetic parameters of the elementary reactions, radical formation/shift and hydrogen abstraction are summarized in Table 1. Notably, oxygen and hydrogen peroxide initiate free-radical chain reactions by two types of mechanisms. Oxygen reacts directly with an organic compound to produce organic radicals and hydroxyl radicals ( $HO_2\cdot$ ). Hydrogen peroxide thermally decomposes to generate hydroxyl radicals ( $HO\cdot$ ). The activation energies involved in both types of radical formation reactions are similar and are about 200 kJ/mol. Both  $HO_2\cdot$  and  $HO\cdot$  participate chain reactions primarily through hydrogen abstraction mechanisms. As an example, the activation energy of methane hydrogen abstraction by  $HO_2\cdot$  (80–90 kJ/mol) is seven to eight times larger than that of  $HO\cdot$  (11 kJ/mol). Although the radical formation rate constants appear to be larger than the propagation rate constants, hydrogen abstraction is considered as the rate-controlling step because

the concentrations of both  $HO_2\cdot$  and  $HO\cdot$  are much lower than those of molecular oxygen or hydrogen peroxide. What is more interesting is that a system initially containing only oxygen produces hydrogen peroxide through the propagation reactions, while a system initially containing only hydrogen peroxide produces oxygen through thermal decomposition reactions. This observation implies that the effectiveness of oxygen and hydrogen peroxide as oxidants for WO or organic compounds is kinetically comparable. The initial rates for subcritical water oxidation using oxygen are expected to be lower as compared to hydrogen peroxide due to the limited mass transfer rate between the gas and liquid phases. Accordingly, the difference in oxidation reactivity between oxygen and hydrogen peroxide is expected to become minimum in supercritical water.

## Wet Oxidation Kinetics

The practicality of understanding reaction mechanisms is to improve the development of kinetic models required to design for reactor systems. When an elementary reaction model is not available or when the feed stream (wastewater) is a complex mixture, it is necessary to resort to a global reaction model. The global models, however, may often be a poor predictor outside the stated experimental conditions.

The global rate equation for WO assumes a general form as shown in Eq. 9.

$$-\frac{dC}{dt} = k^o \exp(-E_a/RT) [C]^m [O]^n \quad (9)$$

where

$k^o$  = pre-exponential factor, (unit dependent on  $m$  and  $n$ )

$E_a$  = activation energy, kJ/mol

**Table 2. Global Kinetic Models for Subcritical Wet Oxidation of Organic Substances**

Compounds	Oxidant	Reactor Type	Kinetic Parameters*				Temp. (K)	Pres. (atm)	[C <sub>A</sub> ] <sub>0</sub> (g/L)	Reference
			<i>k</i> <sup>o</sup>	<i>E<sub>a</sub></i>	<i>m</i>	<i>n</i>				
Acetic Acid	O <sub>2</sub>	batch	5.60 × 10 <sup>10</sup>	167.7	1	0.37	543–593	20–200	~ 30	(Foussard et al., 1989)
Activated Sludge (COD)	O <sub>2</sub>	batch	—	96.3	1	1	453–563	43–150	~ 14	(Ploos van Amstel and Rietema, 1973)
Active Carbon	O <sub>2</sub>	batch	—	35.1	0	1	460–543	30–100	15	(Charest and Chornet, 1976)
Acetone	O <sub>2</sub>	batch	~ 3.70 × 10 <sup>3</sup>	67.4	1	1	473–513	68–136	~ 29	(Taylor and Weygandt, 1974)
Biological Sludge (TOD)	O <sub>2</sub>	batch	~ 3.04 × 10 <sup>3</sup>	~ 67	1	—	520–600	20–200	25	(Foussard et al., 1989)
Black Liquor (TOD)	O <sub>2</sub>	batch	9.08 × 10 <sup>8</sup>	135	1	0.38	550–590	20–200	125	(Foussard et al., 1989)
Brewery Waste (COD)	O <sub>2</sub>	batch	3.84 × 10 <sup>7</sup>	97.4	1	0	~ 477	20–60	3.5–10	(Chowdhury and Ross, 1975)
<i>n</i> -Butanol	O <sub>2</sub>	batch	~ 5.30 × 10 <sup>6</sup>	92.9	1	1	453–473	68–136	~ 37	(Taylor and Weygandt, 1974)
<i>sec</i> -Butanol	O <sub>2</sub>	batch	—	103.7	1	1	453–473	68–136	~ 37	(Taylor and Weygandt, 1974)
Butyric Acid	O <sub>2</sub>	batch	1.26 × 10 <sup>9</sup>	124	1.40	0.46	511–530	68–136	8.8–17.6	(Williams et al., 1973)
<i>o</i> -Chlorophenol (COD)	O <sub>2</sub>	batch	1.433 × 10 <sup>2</sup>	31.7	1	1	433–453	6–10	0.2	(Joglekar et al., 1991)
<i>p</i> -Chlorophenol (COD)	O <sub>2</sub>	batch	2.035 × 10 <sup>9</sup>	95.7	1	1	433–453	6–10	0.2	(Joglekar et al., 1991)
<i>m</i> -Chlorophenol (COD)	O <sub>2</sub>	batch	5.95 × 10 <sup>3</sup>	50.2	1	1	433–453	6–10	0.2	(Joglekar et al., 1991)
<i>m</i> -Cresol (COD)	O <sub>2</sub>	batch	0	12.4	1	1	433–453	6–10	0.2	(Joglekar et al., 1991)
<i>o</i> -Cresol (COD)	O <sub>2</sub>	batch	2.34 × 10 <sup>2</sup>	34.7	1	1	433–453	6–10	0.2	(Joglekar et al., 1991)
Cyanide**	O <sub>2</sub>	flow	2.43 × 10 <sup>-5</sup>	52.1	1	—	433–513	70–150	—	(Kalman et al., 1988)
<i>o</i> -Chlorophenol (TOC)	O <sub>2</sub>	batch	~ 1.84 × 10 <sup>4</sup>	~ 67.8	1	—	477–533	39–71	~ 5	(Baillod et al., 1982)
<i>p</i> -Chlorophenol	O <sub>2</sub>	flow	—	33	1	0	583–613	75	—	(Yang and Eckert, 1988)
2,6-Dimethylphenol	O <sub>2</sub>	batch	1.02 × 10 <sup>-2</sup>	24.9	1	1	433–453	6–10	0.2	(Joglekar et al., 1991)
<i>o</i> -Ethylphenol	O <sub>2</sub>	batch	0	0	1	1	433–453	6–10	0.2	(Joglekar et al., 1991)
Formic Acid	O <sub>2</sub>	batch	3.10 × 10 <sup>9</sup>	143.5	1.33	0.46	463–586	20–200	24–43	(Foussard, 1989)
Glucose (TOC)	O <sub>2</sub>	batch	—	130	0.5	1	450–533	109	~ 15	(Skaates et al., 1981)
<i>o</i> -Methoxyphenol	O <sub>2</sub>	batch	6.88 × 10 <sup>6</sup>	68.1	1	1	433–453	6–10	0.2	(Joglekar et al., 1991)
<i>p</i> -Methoxyphenol	O <sub>2</sub>	batch	3.43 × 10 <sup>7</sup>	20.1	1	1	433–453	6–10	0.2	(Joglekar et al., 1991)
Nitrilotriacetic Acid	O <sub>2</sub>	flow	8.41 × 10 <sup>4</sup>	54.3	1	1	473–523	55–152	1.4–3.0	(Pruden and Le, 1976)
Oxalic Acid	O <sub>2</sub>	batch	6.83 × 10 <sup>8</sup>	133.8	1	0.31	500–583	20–200	0.1–0.2	(Foussard et al., 1983)
Phenol	O <sub>2</sub>	flow	4.71 × 10 <sup>4</sup>	45.1	1	1	473–523	55–152	1.4–3.0	(Pruden & Le, 1976)
Phenol	O <sub>2</sub>	batch	1.96 × 10 <sup>9</sup>	107	1	1	453–483	35	1.9–3.8	(Shibaeva et al., 1969)
Phenol (TOC)	O <sub>2</sub>	batch	~ 7.4 × 10 <sup>3</sup>	~ 62.9	1	—	477–533	39–71	~ 6	(Baillod et al., 1982)
Propionic Acid	O <sub>2</sub>	batch	9.32 × 10 <sup>12</sup>	135	1.43	0.39	505–561	68–136	7.4–14.8	(Days et al., 1971)
Spent Earth	O <sub>2</sub>	batch	3.10 × 10 <sup>3</sup>	41.5	1	1	413–473	4–16	50	(Kalam and Joshi, 1988)

\*Kinetic parameters are defined in Eq. 9, where *E<sub>a</sub>* is in kJ/mol, *T* in K, *R* = 8.314 kJ/mol·K, and *k*<sup>o</sup> = L/s(first-order), L/mol/s (second-order).

\*\*Hydrolysis.

~ Estimated values from reported data.

The abbreviations used after some compounds indicate the analytical techniques used (COD = chemical oxygen demand; TOC = total organic carbon; TOD = total oxygen demand), and all other compounds were analyzed by chromatographic techniques. The excess oxidants are used in all tests. Kinetic parameters reported are for the overall reaction in water.

*R* = gas constant, 8.314 J/mol·K

*T* = temperature, K

*C* = concentration of the organic reactant, mol/L

*O* = concentration of the oxidant, mol/L

*m* = order of the reaction with respect to the organic reactant

*n* = order of the reaction with respect to the oxidant

*t* = time, s

Kinetic data for the subcritical WO of organic compounds and mixtures are summarized in Table 2. In most cases, a first-order reaction with respect to the organic reactants was obtained through either statistical treatment or assumed data.

An oxygen mass transfer factor was considered in some global rate equations (Charest and Chornet, 1976; Pruden and Le, 1976; Ploos van Amstel and Rietema, 1973). Notably, the activation energies for volatile acids were higher than those for organic compounds possessing a lower oxygen content. Acetic acid exhibited the highest activation energy, 167.7 kJ/mol.

Table 3 summarizes the kinetic data on the supercritical WO of organic compounds, organic mixtures, ammonia and carbon monoxide. It should be noted that both best-fit and pseudo-

**Table 3. Global Kinetic Models for Supercritical Water Oxidation of Organic Substances\***

Compounds	Oxidant	Reactor Type	Kinetic Parameters**				Temp. (K)	Pres. (atm)	[C <sub>A</sub> ] <sub>0</sub> (g/L)	Reference
			<i>k</i> <sup>o</sup>	<i>E<sub>a</sub></i>	<i>m</i>	<i>n</i>				
Acetamide	H <sub>2</sub> O <sub>2</sub>	flow	$2.75 \times 10^5$	88.3	1.15	0.05	673–803	240–350	1.5–4.0	(Lee, 1990)
Acetamide*	H <sub>2</sub> O <sub>2</sub>	flow	$5.01 \times 10^4$	94.7	1	0.17	673–803	240–350	1.5–4.0	(Lee, 1990)
Acetic Acid	H <sub>2</sub> O <sub>2</sub>	flow	$3.47 \times 10^{11}$	179.5	1.01	0.16	673–803	240–350	1.3–3.3	(Lee, 1990)
Acetic Acid	H <sub>2</sub> O <sub>2</sub>	flow	$2.63 \times 10^{10}$	167.1	1	0	673–803	240–350	1.3–3.3	(Lee, 1990)
Acetic Acid	H <sub>2</sub> O <sub>2</sub>	flow	$8.94 \times 10^5$	314	2.36	1.04	673–773	240–350	1.0–5.0	(Wilmanns, 1990)
Acetic Acid	H <sub>2</sub> O <sub>2</sub>	flow	$9.23 \times 10^7$	131	1	0	673–773	240–350	1.0–5.0	(Wilmanns, 1990)
Acetic Acid	O <sub>2</sub>	flow	$9.82 \times 10^{17}$	231	1	1	611–718	394–438	0.525	(Wightman, 1981)
Acetic Acid	O <sub>2</sub>	flow	$2.55 \times 10^{11}$	172.7	1	0	611–718	394–438	0.525	(Wightman, 1981)
Activated Sludge (COD)	O <sub>2</sub>	batch	$\sim 1.5 \times 10^2$	$\sim 54$	1	0	573–723	240–350	46.5	(Shanableh, 1990)
Ammonia	O <sub>2</sub>	flow	$3.16 \times 10^6$	157	1	0	913–973	246	0.03–0.11	(Webley et al., 1990)
Carbon Monoxide	O <sub>2</sub>	flow	$3.16 \times 10^6$	112	1	0	673–814	246	0.02–0.11	(Helling and Tester, 1987)
Digested Sludge (COD)	O <sub>2</sub>	batch	$4.36 \times 10^3$	20.4	1.86	0	573–723	240–350	46.5	(Tongdhamachart, 1990)
Ethanol	O <sub>2</sub>	flow	$6.46 \times 10^{21}$	340	1	0	755–814	241	0.03–0.036	(Helling, 1986)
Formic Acid	O <sub>2</sub>	flow	—	$\sim 96$	1	1	683–691	408–432	1.0	(Wightman, 1981)
Glucose (TOC)	—	batch	—	130	0.5	1	653–683	$\sim 400$	$\sim 10$	(Whitlock, 1978)
Methane	O <sub>2</sub>	flow	$1.26 \times 10^7$	156.8	1	0	913–973	245	—	(Rofer and Streit, 1989)
Methanol	O <sub>2</sub>	flow	$2.51 \times 10^{24}$	395.0	1	0	723–823	243	—	(Rofer and Streit, 1989)
Methanol	O <sub>2</sub>	flow	$2.51 \times 10^{29}$	478.6	1	0	723–823	243	—	(Webley and Tester, 1989)
Methanol	O <sub>2</sub>	flow	$3.16 \times 10^{26}$	408.4	1.1	–0.02	723–823	243	0.038–0.17	(Webley et al., 1990)
Phenol	O <sub>2</sub>	flow	$2.61 \times 10^5$	63.8	1	1	557–702	292–340	0.1–0.4	(Wightman, 1981)
Phenol	O <sub>2</sub>	flow	—	—	0.5	0	653	188–278	0.25–1.0	(Thornton and Savage, 1990)

\*See notes in Table 2.

\*\*For oxidation only (overall reaction-hydrolysis).

first-order reaction models proposed by Wightman (1981), Lee (1990), and Wilmanns (1990) were included. The activation energy from the best-fit model for SCWO of acetic acid by oxygen was 231 kJ/mol based on a first-order reaction for both acetic acid and oxygen, (Wightman, 1981). An initial comparison of kinetic results obtained from SCWO of acetic acid by hydrogen peroxide using two different flow reactor systems showed considerable differences in reaction orders and activation energies (Lee, 1990; Wilmanns, 1990). However, when Wightman's, Lee's and Wilmanns' data were treated using a pseudo-first-order reaction model, the activation energies became 172.7 kJ/mol, 167.1 kJ/mol, and 131 kJ/mol, respectively. The changes in the mean deviation derived from using the pseudo-first-order model were less than 5% as compared to their best-fit models. In addition, recent studies found that the oxidation rate of acetic acid increased sharply near a temperature range of 410°C to 450°C (Wilmanns et al., 1989; Lee, 1990; Wilmanns, 1990). This rate increase translated into a change in the activation energy from 179.5 kJ/mol to 292.5 kJ/mol (Lee, 1990). Further study on the reaction mechanisms in this temperature range may explain the rate change.

Beside acetic acid, methanol (395.0 kJ/mol) and ethanol (340.0 kJ/mol) exhibited higher activation energies. Therefore, it may be assumed that methanol, ethanol, and acetic acid were intermediates in the WO reactions. However, the amount of ethanol and methanol formed in WO was usually negligible as compared to acetic acid (Taylor and Weygandt, 1974; Conditt and Sievers, 1984; Keen and Baillod, 1985; Baillod et al., 1982; McGinnis et al., 1983; Hurwitz et al., 1965; Teletzke et al., 1967; Fisher 1971; Shanableh, 1990; Tongdhamachart, 1990). Furthermore, the pre-exponential factors for methanol and

ethanol were much higher than that for acetic acid, indicating a much faster rate of reaction for the alcohols. Thus, acetic acid is assumed to be the key rate-limiting intermediate for WO of organic compounds.

The reaction orders for oxygen, Tables 2 and 3, support the kinetic similarity between oxygen and hydrogen peroxide. Most subcritical WO kinetic studies have reported a half to first-order dependence on the oxygen concentration. One interpretation is that the apparent difference in oxidation efficiency between oxygen and hydrogen peroxide for subcritical WO may be due primarily to the limitation of oxygen mass transfer between the gas and liquid phases. In supercritical water, where the oxygen mass transfer is not a rate-limiting factor for chemical reactions, the oxidation rates are independent of the oxygen concentration.

While the kinetic data presented in Tables 2 and 3 are for overall oxidation reaction, hydrolysis, pyrolysis, and dehydration reactions may also exist and compete. The role and extent of the side reactions depend largely on water concentration and reaction temperature, but the characteristics of the organic compounds may become involved. Hydrolysis of acetamide in supercritical water is essentially a first-order reaction with respect to acetamide (Lee, 1990). The pre-exponential factor and activation energy are  $5.01 \times 10^2$  and 94.7 kJ/mol, respectively. Lee's results indicate that at 400°C, hydrolysis dominates the overall reaction, while at 530°C the overall reaction is one order of magnitude faster than that predicted by hydrolysis.

Little information exists about the competing reactions in water other than oxidation. Antal et al. conducted a series of studies on the dehydration of ethanol in supercritical water.

The dehydration rate constant involving an acid-catalyzed *E2* mechanism was reported to be 7.48 L/mol/s (Xu et al., 1990). Recent studies on hydrolysis and pyrolysis in supercritical water by Huppert et al. (1989) and Wu et al. (1991) reported a first-order rate constant for the disappearance of guaiacol of  $8.03 \times 10^{-4} \text{ s}^{-1}$  at 383°C. Tiffany et al. (1984) reported that the conversions via hydrolysis of quinoline and isoquinoline in supercritical water were about 30% at 400°C and about 70% at 500°C for a reaction time of 48 hours. At these conditions, benzonitrile and tetralin were converted to benzene and naphthalene, respectively. Lee (1990) has showed that more than 50% acetamide conversion occurred as a result of hydrolysis during SCWO.

The effects of water concentration and pressure should be considered in a global kinetic model. Since water is likely to be involved in the intermediate oxidation steps as well as the hydrolysis reaction, the overall rate equation should include a concentration term for water. However, the relative amount of water available is large. Therefore, the water concentration term generally is not explicitly expressed in the rate equation. Also, since the application of pressure in subcritical WO processes is maintained primarily to sustain reactions in the liquid phase, the destruction rate as a function of pressure has not been systematically studied.

In SCWO, pressure may play a more important role because the density of supercritical water may vary greatly with pressure at a given temperature. The pressure effect on the rate constant can be expressed by Eq. 10.

$$(\partial \ln k / \partial P)_T = -\Delta V^\circ / RT \quad (10)$$

where

- $k$  = rate constant, unit dependent on the overall reaction order
- $\Delta V^\circ$  = volume of activation,  $\text{cm}^3/\text{mol}$
- $R$  = gas constant,  $82.05 \text{ atm} \cdot \text{cm}^3/\text{mol} \cdot \text{K}$
- $T$  = temperature, K
- $P$  = pressure, atm

The volume of activation is a measure of the pressure dependence of the rate constant in a way similar to the activation energy being a measure of the temperature dependence of the rate constant. For example, Thornton and Savage (1990) reported a volume of activation of  $-1,400 \text{ cm}^3/\text{mol}$  for SCWO of phenol at 380°C. Yang and Eckert (1988) reported a volume of activation of  $-2,300 \text{ cm}^3/\text{mol}$  for WO of *p*-chlorophenol at 340°C. Other studies indicate that pressure (density) has less effects on destruction rates than temperature does (Lee et al., 1990).

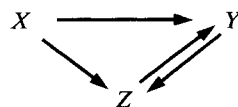
In summary, most kinetic studies assume that the overall reaction rate is dominated by oxidation. Generally, experiments are not designed to deduct the effect of side reactions. The kinetic models reviewed in this section, unless otherwise specified, describe the overall reaction which may include oxidation, hydrolysis, pyrolysis and dehydration.

## Wet Oxidation Reaction Schemes

Based on the global reaction rates in WO experiments, some generalized mathematical models describing simplified reaction pathways have been proposed. Takamatsu et al. (1970) suggested a model for thermal decomposition of activated sludges derived from wastewater treatment processes. They considered sludge to consist of four basic elements:

1. Solid matter (denoted by  $X$ )
2. Soluble nonevaporative matter at 120°C (denoted by  $Y$ )
3. Soluble evaporative matter at 120°C (denoted by  $Z$ )
4. Water.

The weight and chemical oxygen demand of  $X$ ,  $Y$ , and  $Z$ . These are the state variables in the Takamatsu et al. model. Their model may be illustrated as follows:



In another kinetic study of subcritical WO of sludges (Ploos van Amstel and Rietema, 1973), the organic load was divided into three components: 1. rather high reactivity, 2. intermediate reactivity, and 3. no reactivity. Other assumptions included negligible hydrolysis effect and first-order reaction for sludge components as well as oxygen.

Foussard et al. (1989) further simplified Ploos van Amstel and Rietema's model. Foussard's model included only easily oxidized components ( $a$ ) and not easily oxidized components ( $b$ ). Foussard et al. evaluated the total oxidation rate by adding the rates of ( $a$ ) and ( $b$ ), assuming that ( $a$ ) and ( $b$ ) were two parallel, first-order reactions.

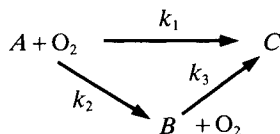
## A Generalized Kinetic Model

The generalized kinetic model for WO as proposed is based on a simplified reaction scheme involving the formation and destruction of rate-controlling intermediates. As WO proceeds, some of the organic compounds are destroyed to form the final oxidation products, while others are transformed to relatively stable intermediates. The global rate of WO depends on the final product formation rate as well as the formation and destruction rates of stable intermediates. Typical stable intermediates are acetic acid, methanol, and ethanol. The activation energies (170–350 kJ/mol) of these intermediates are greater than those of higher-molecular-weight organic compounds (20–100 kJ/mol). Therefore, the rate of formation and destruction of stable intermediates must be included in a global rate expression.

Previous studies on reaction mechanisms and product analysis of WO have indicated that short-chain carboxylic acids, ketones, aldehydes and alcohols are the major oxidation intermediates. For example, acetone, 2-butanone, and acetaldehyde are precursors of acetic acid, as analyzed by Taylor and Weygandt (1974), Fisher (1971), Baillod et al. (1982), and Day et al. (1973). Peroxy radicals attack at the  $\alpha$ -carbon of high-molecular-weight alcohols, ketones, aldehydes, and carboxylic acids. Similarly, other mechanisms involving the rupture of a C-C bond ( $\beta$ ,  $\gamma$ ) may also produce low-molecular-weight compounds. Although methanol and ethanol have higher activation energies than acetic acid, the pre-exponential factors for methanol and ethanol are considerably higher than that for acetic acid (see Table 3). Therefore, acetic acid is assumed to represent the group of rate-controlling intermediates in the generalized model.

Three groups of organic substances are defined to exist in the liquid and gaseous effluents. Group  $A$  includes all initial and relatively unstable intermediate organic compounds except

acetic acid, group *B* contains the refractory intermediates represented by acetic acid, and group *C* is designated as the oxidation end products. Group *A* compounds are converted to group *C* compounds through three simplified reaction pathways. A schematic of these simplified pathways is illustrated below:



If groups *A*, *B*, and *C* are expressed in concentration terms, then

$[A]$  = [all initial and intermediate organic compounds] – [acetic acid]

$[B]$  = [acetic acid]

$[C]$  = [oxidation end products]

The concentrations of group *A* or *B* may be expressed in forms of total organic carbon (TOC), chemical oxygen demand (COD), or total oxygen demand (TOD).

Based on Tables 2 and 3, the reaction rate may be assumed to be first order to group *A* or *B*, i.e.,  $m = 1$ , and  $n$ th order to oxygen. Thus, the rate equations for the oxidation of groups *A* and *B* in an isothermal, ideal, stirred batch reactor or plug-flow reactor with a constant volumetric flow rate can be expressed by Eq. 11 and 12.

$$-\frac{d[A]}{dt} = k_1^\circ e^{-E_1/RT} [A][O_2]^{n_1} + k_2^\circ e^{-E_2/RT} [A][O_2]^{n_2} \quad (11)$$

$$-\frac{d[B]}{dt} = k_3^\circ e^{-E_3/RT} [B][O_2]^{n_3} - k_2^\circ e^{-E_2/RT} [A][O_2]^{n_2} \quad (12)$$

Equations 11 and 12 can be rewritten as Eqs. 13 and 14.

$$-\frac{d[A]}{dt} = (k_1 + k_2) [A] \quad (13)$$

$$-\frac{d[B]}{dt} = k_3 [B] - k_2 [A] \quad (14)$$

where

$$k_1 = k_1^\circ e^{-E_1/RT} [O_2]^{n_1} \quad (15)$$

$$k_2 = k_2^\circ e^{-E_2/RT} [O_2]^{n_2} \quad (16)$$

$$k_3 = k_3^\circ e^{-E_3/RT} [O_2]^{n_3} \quad (17)$$

In many cases,  $n_1$ ,  $n_2$ , and  $n_3$  are either near zero (Tables 2 and 3), or excess oxygen is used. Therefore, the oxygen terms in Eqs. 15–17 may be assumed as a constant.

At time  $t = 0$ ,  $[A] = [A]_0$  and  $[B] = [B]_0$ . Equations 13 and 14 can be solved analytically, as shown in Eqs. 18 and 19.

$$[A] = [A]_0 e^{-(k_1 + k_2)t} \quad (18)$$

$$[B] = [B]_0 e^{-k_3 t} + \frac{k_2 [A]_0}{k_1 + k_2 - k_3} [e^{-k_3 t} - e^{-(k_1 + k_2)t}] \quad (19)$$

Combining Eqs. 18 and 19 produces Eq. 20:

$$\begin{aligned}
 \frac{[A + B]}{[A]_0 + [B]_0} &= \frac{[A]_0}{[A]_0 + [B]_0} \left[ \frac{k_2}{k_1 + k_2 - k_3} e^{-k_3 t} + \frac{(k_1 - k_3)}{k_1 + k_2 - k_3} e^{-(k_1 + k_2)t} \right] \\
 &\quad + \frac{[B]_0}{[A]_0 + [B]_0} e^{-k_3 t} \quad (20)
 \end{aligned}$$

If  $[B]_0 = 0$ , Eq. 20 can be further simplified to Eq. 21.

$$\frac{[A + B]}{[A + B]_0} = \frac{k_2}{k_1 + k_2 - k_3} e^{-k_3 t} + \frac{(k_1 - k_3)}{k_1 + k_2 - k_3} e^{-(k_1 + k_2)t} \quad (21)$$

The three rate constants,  $k_1$ ,  $k_2$ , and  $k_3$ , may require further description. Values of  $k_1$  are usually determined from the initial reaction rate, and most of the rate equations in the literature are actually expressions for  $k_1$ . To determine  $k_3$ , Foussard's rate equation for acetic acid may be used for subcritical temperatures. For SCWO,  $k_3$  should be determined by Wightman's rate equation when oxygen is used as the oxidant. If  $H_2O_2$  is used as the oxidant, the rate constant reported by Lee (1990) for SCWO of acetic acid is recommended. If  $k_2$  is much smaller than  $k_1$ , the organic compounds in the waste stream may be oxidized more easily to the final oxidation products. If  $k_2$  is larger, more acetic acid is formed.

For most organic wastes,  $E_2$  Eq. 16, is approximately equal to  $E_1$ , Eq. 15, since groups *B* and *C* represent series degradation products from similar reactions.  $E_3$  in Eq. 17 is greater than either  $E_1$  or  $E_2$ , which means that the energy barrier for the oxidation of acetic acid is higher and acetic acid is a relatively stable intermediate.

Since the WO of group *A* can be considered as a parallel reaction system, the point selectivity,  $\alpha$ , is defined as the formation rate of acetic acid to that of carbon dioxide (the oxidation end product) from group *A*. If both reactions are assumed to be a first order,  $\alpha = k_2/k_1$ . The values of  $k_2$  or  $\alpha$  can be experimentally determined.

The physical meaning of  $\alpha$  can be further explained by presenting an example describing the WO of organic compounds. First,  $A_n$  is defined as representing a given compound or a

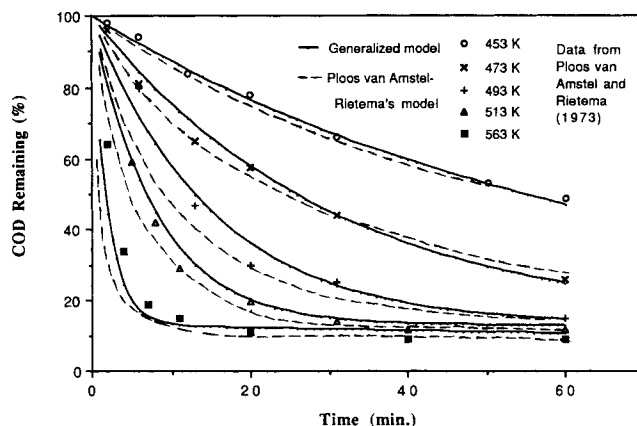
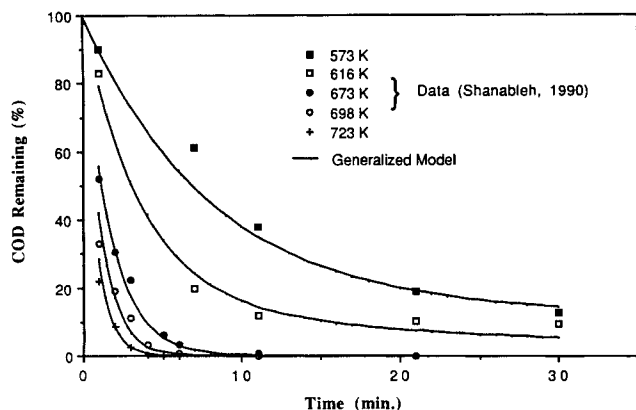
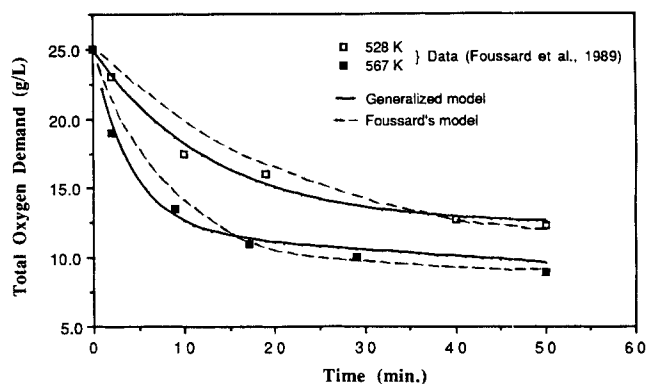


Figure 1. Wet oxidation of activated sludge: model predictions vs. experimental data.



**Figure 2. Supercritical water oxidation of industrial activated sludge: model prediction vs. experimental data.**

Initial conditions: total solids = 5%; COD = 46,500 mg/L water density = 0.25 g/cm<sup>3</sup>, and oxygen pressure = 82 bar



**Figure 4. Wet oxidation of biological sludge: model predictions vs. experimental data.**

( $n-2$ ) moles of carbon dioxide, the following relationship holds for the average point selectivity  $\bar{\alpha}$ ,

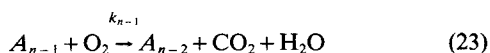
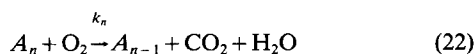
$$\bar{\alpha} = \frac{\text{avg. formation rate of acetic acid}}{\text{avg. formation rate of carbon dioxide}} = \frac{1}{(n-2)}$$

According to this equation, the value of  $\alpha$  for a feed stream matching the above assumptions, should be between 0 and 1. If the concentration of short-chain organic compounds, including those with two carbon atoms (other than acetic acid) such as ethanol, is high in a wastewater, the value of  $\alpha$  will be large. Therefore,  $\alpha$  can be used to characterize the "strength" of the waste stream for a WO process.

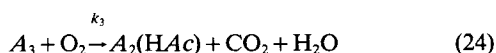
## Results and Discussion

A kinetic model is useful only if it truly reflects experimental results for a range of given conditions. The generalized kinetic model described above is adaptable to a variety of experimental data. In the following, six examples for obtaining values of  $k$ 's, a first-order reaction for organic compounds, and zero-order reaction for oxygen are assumed. Figure 1 is a comparative plot showing the experimental data derived from the WO of excess activated sludge (Ploos van Amstel and Rietema, 1973) and the predictions using both the generalized kinetic model and the model derived by Ploos van Amstel and Rietema (1973). The  $k_1$  value is based on calculated activation energy data provided by Ploos van Amstel and Rietema (1973). The

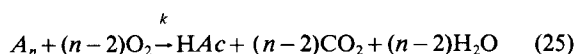
mixture. For a pure compound, the subscript  $n$  signifies the number of carbon atoms in each molecule. For a mixture the subscript  $n$  is the averaged number of carbon atoms per molecule. Thus, the oxidation of  $A_n$  can be expressed as a series of scission reactions involving hydroperoxides:



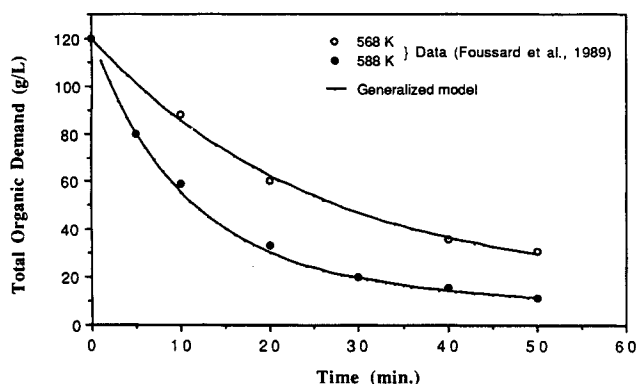
⋮



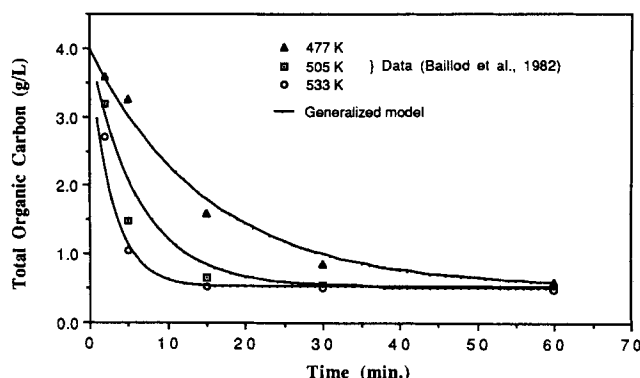
If it is assumed that the rate constants for each step reaction are approximately equal and represented by  $k$ , the global reaction equation for Eq. 22–24 inclusive becomes Eq. 25.



Since the formation of one mole of acetic acid produces



**Figure 3. Wet oxidation of black liquor: model prediction vs. experimental data.**



**Figure 5. Wet oxidation of phenol: model prediction vs. experimental data.**



**Table 4.  $\alpha$  Values Determined by the Reported Experimental Data**

Organic Wastes	$k_1$	$\alpha$
Activated Sludge (COD)		
(Ploos van Amstel and Rietema, 1973)	$1.2 \times 10^4 \exp(-8,056/T)$	0.15
Black Liquor (TOD) (Foussard et al., 1989)	$7.17 \times 10^7 \exp(-14,500/T)$	0.20
Brewery Waste (COD) (Chowdhury and Ross, 1975)	$3.85 \times 10^7 \exp(-11,716/T)$	0.33
Biological Sludge (TOD) (Foussard et al., 1989)	$3.84 \times 10^3 \exp(-8,179/T)$	1.0
Activated Sludge (COD) (Shanableh, 1990)	$1.5 \times 10^2 \exp(-6,495/T)$	0.15
Phenol (TOC) (Baillod et al., 1982)	$7.4 \times 10^3 \exp(-7,569/T)$	0.15
2-Chlorophenol (TOC) (Baillod et al., 1982)	$5.7 \times 10^4 \exp(-8,660/T)$	0.37–0.96

$k_3$  value for oxidation of acetic acid derived from Foussard's results (1989). The results provided by the generalized model and the Ploos van Amstel and Rietema's model appear to be comparable.

Figure 2 shows that the generalized model prediction results agree very well with SCWO experimental data obtained by using an industrial excess activated sludge (Shanableh, 1990). The  $k_3$  value for SCWO of acetic acid was determined by Wightman's rate equation (1981).

Figures 3 and 4 show excellent agreement between the generalized model results and the experimental data produced from WO of black liquor wastes from a paper mill and a biological sludge (Foussard et al., 1989). In Figure 4, the generalized model shows a slight improvement over the Foussard's model. The  $k_1$  values were based on the activation energy values given by Foussard et al. The  $k_3$  value for acetic acid were obtained from Foussard's results (1989). Figures 5 and 6 compare the generalized model results with experimental data describing WO of phenol and 2-chlorophenol (Baillod et al., 1982).

The  $\alpha$  values associated with the WO systems discussed in Figures 1 to 6 are given in Table 4. The  $\alpha$  values for most compounds remained relatively constant. The  $\alpha$  value associated with the oxidation of 2-chlorophenol exhibited some variations with temperatures,  $\alpha = 1.1 \times 10^{-4} \exp(4,330/T)$ . This variation in reaction kinetics was most likely due to different pathways for the destruction of 2-chlorophenol. The reaction intermediates might be converted both by oxidation and other reactions involving chlorine radicals. The effect of these side reactions may depend on a temperature since different activation energies are involved. Similarly, a temperature dependence of  $\alpha$  may be observed in the WO of chlorine-containing organic compounds.

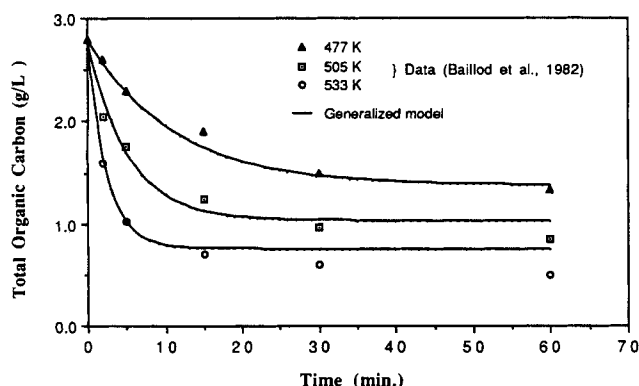
The generalized model prediction results shown in all the figures were obtained using Eq. 21. This equation is a simplified form of Eq. 20. It was assumed that the feed stream did not contain acetic acid. However, it was possible that the wastewaters used for the above examples contained some acetic acid. In such case, using Eq. 20 would further improve the prediction results. The predictive and experimental results have indicated that the proposed kinetic model has practical validity for a variety of organic compounds, wastewaters and sludges in both subcritical and supercritical WO.

The generalized model requires three kinetic parameters:  $k_1$ ,  $k_2$ , and  $k_3$ . The values of  $k_1$  and  $k_2$  can be determined from experimental data (initial rate data). If experimental results are not available, an approximation may be used for  $k_1$  and  $k_2$  on the basis of similarities of the waste stream to a known feed listed in Table 2 or 3. In most cases, the activation energies for  $k_1$ 's are in the range of 54 kJ/mol to 78 kJ/mol, and  $\alpha$  is in the range of 0.15 to 1. Wastewaters containing high levels of short-chain alcohols and saturated carboxylic acids, such as biological sludges and brewery wastewaters, tend to have higher activation energies and  $\alpha$  values. The third parameter,  $k_3$ , can be derived from Foussard's rate equation (1989) for subcritical WO using oxygen. For SCWO of acetic acid by oxygen and hydrogen peroxide, respectively, the pseudo-first-order reaction rate constants obtained by Wightman (1981) and Lee (1990) are recommended.

## Conclusions

Through reaction mechanism analyses, it is concluded that the global effectiveness of oxygen and hydrogen peroxide for WO of organic compounds is kinetically comparable. In a homogeneous environment (supercritical water), the oxidation rate is independent of the molecular oxygen concentration and the oxidation is statistically first-order with respect to organic compounds. It is also suggested that free-radical reaction mechanisms be accountable for WO of organic compounds in both subcritical and supercritical water.

A simplified reaction scheme has been proposed based on the reaction pathways of WO of organic compounds and wastewaters. The potential for parallel pathways requires that attention to be given to the formation rate of acetic acid as compared to carbon dioxide. This pathway relationship can be quantified by the ratio of  $k_2/k_1$  or the point selectivity  $\alpha$ . The value of  $\alpha$  can be used to characterize the "strength" of the feed stream in WO processes. The higher the  $\alpha$  value, the larger fraction of the feed that is converted to acetic acid. The values of  $\alpha$  obtained using reported experimental data are between 0.15 and 1.0, which fall within the predicted range of 0 to 1.



**Figure 6. Wet oxidation of 2-chlorophenol: model prediction vs. experimental data.**

A generalized kinetic model has been developed and validated. Compared to other models, the generalized kinetic model provides a simpler, yet more appropriate, description of the WO process. The kinetic model has practical validity for both subcritical and supercritical WO of organic compounds, wastewaters and sludges.

## Acknowledgment

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## Notation

- $a$  = easily oxidized components  
 $A$  = all initial and relatively unstable intermediate organic compounds except acetic acid  
 $[A]$  = concentration of species  $A$ , mol/L  
 $b$  = components not easily oxidized  
 $B$  = refractory intermediates represented by acetic acid  
 $[B]$  = concentration of species  $B$ , mol/L  
 $C$  = oxidation end products  
 $[C]$  = concentration of species  $C$ , mol/L  
 $[C]$  = concentration of the organic reactant (Eq. 9), mol/L  
 $[C_A]$  = concentration of organic reactant (Tables 2 and 3), mol/L  
 $E_a$  = activation energy, kJ/mol  
 $k$  = reaction rate constant (unit dependent on  $m$  and  $n$ )  
 $k^*$  = pre-exponential factor (unit dependent on  $m$  and  $n$ )  
 $m$  = order of the reaction with respect to the organic reactant  
 $n$  = order of the reaction with respect to the oxidant (Eq. 9)  
 $n$  = number of carbon atoms in each molecule (Eq. 25)  
 $[O]$  = concentration of the oxidant, mol/L  
 $[O_2]$  = concentration of oxygen, mol/L  
 $P$  = pressure, atm  
 $R$  = gas constant (8.314 J/mol·K in Eq. 9; 82.05 atm·cm<sup>3</sup>/mol·K in Eq. 10)  
 $t$  = time, s  
 $T$  = temperature, K  
 $\Delta V^\circ$  = volume of activation, cm<sup>3</sup>/mol  
 $X$  = solid matter  
 $Y$  = soluble nonevaporative matter at 120°C  
 $Z$  = soluble evaporative matter at 120°C

## Greek letters

- $\alpha$  = point selectivity  
 $\bar{\alpha}$  = average point selectivity

## Subscript

- $A$  = reactant A  
 $0$  = initial condition  
 $1,2,3$  = reactions indicated in the simplified pathways  
 $3, \dots, n-1, n$  = reactions of the initial hydrocarbons consisting of 3, ...,  $n-1$ , and  $n$  carbon atoms, respectively (Eqs. 22-24)

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