Acetic Acid Oxidation and Hydrolysis in Supercritical Water

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Acetic acid (CH_3COOH) hydrolysis and oxidation in supercritical water were examined from 425–600°C and 246 bar at reactor residence times of 4.4 to 9.8 s. Over the range of conditions studied, acetic acid oxidation was globally 0.72 ± 0.15 order in acetic acid and 0.27 ± 0.15 order in oxygen to a 95% confidence level, with an activation energy of 168 ± 21 kJ/mol, a preexponential factor of $10^{9.9 \pm 1.7}$, and an induction time of about 1.5 s at 525°C. Isothermal kinetic measurements at 550°C over the range 160 to 263 bar indicated that pressure or density did not affect the rate of acetic acid oxidation as much as was previously observed in the oxidation of hydrogen or carbon monoxide in supercritical water. Major products of acetic acid oxidation in supercritical water are carbon dioxide, carbon monoxide, methane, and hydrogen. Trace amounts of propenoic acid were occasionally detected. Hydrolysis or hydrothermolysis in the absence of oxygen resulted in approximately 35% conversion of acetic acid at 600°C, 246 bar, and 8-s reactor residence time. Regression of the limited hydrolysis runs assuming a reaction rate first-order in organic gave a global rate expression with a preexponential factor of $10^{4.4 \pm 1.1}$ and an activation energy of 94 ± 17 kJ/mol.

Introduction

Supercritical water oxidation (SCWO) represents an innovative technology for complete and efficient destruction of hazardous wastes, without formation of harmful byproducts. Organic compounds and oxygen are completely soluble in water above its critical point of 374°C and 221 bar, which provides a single-phase medium for rapid oxidation of organic to CO_2, H_2O, and N_2. The scale-up and reliable operation of commercial-sized process equipment require a thorough understanding of oxidation kinetics (see Modell, 1989; and Tester et al., 1993, for reviews of SCWO technology).

Acetic acid has been identified as a refractory intermediate in the oxidation of more complex organics (Ploos van Amstel and Rietema, 1970; Skaates et al., 1981; Tongdhamachart, 1990; Shanableh and Gloyna, 1991; Holgate et al., 1995) above and below the critical point of water. Because of its relative stability, acetic acid oxidation may be a critical rate-limiting step in the overall oxidation to CO_2 and H_2O. The refractory nature of acetic acid has led many investigators to study its destruction via supercritical water oxidation (Wightman, 1981; Lee and Gloyna, 1990; Wilmanns and Gloyna, 1990; Frisch, 1992). These studies, as with most SCWO research, have focused on measurements of destruction efficiency rather than product identification and reaction kinetics.

Results from other investigations of acetic acid oxidation in supercritical water are listed in Table 1. One can see wide variations of activation energies, preexponential factors, and reaction orders in these results. Different experimental conditions used by each investigator could account for some of this disparity, and there is a possibility that the reactor material itself may have catalyzed reactions to some extent. Different reactor surface area to volume ratios may have also biased results. The agreement among first-order reactions ($a = 1$) seen in Table 1 is deceptive, because most researchers *assumed* first-order kinetics. Additionally, few studies reported product distributions or mass balance closures, which may have provided more mechanistic information. Although experimental conditions were not completely replicated among investigators, global rate law results should be in closer agreement. These incongruous results motivated additional study of acetic acid oxidation in our laboratory to provide kinetic parameters and product distributions under well-defined conditions of temperature, pressure, density, and residence time in supercritical water.

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Table 1. Global Kinetic Expressions for SCWO of Acetic Acid

$d[CH_3COOH]/dt = -A\exp(-E_a/RT)[CH_3COOH]^a[\text{Oxidant}]^b$

Units: kJ, mol, L, s

Source	log A	E_a	a	b	Conditions
Oxidant: O_2					
Lee et al. (1990)*	4.91	106	1	0	400–500°C Batch reactor
Frisch (1992)	9.73 ±???	165 ±37	1	0	$\rho = 0.3$ g/cm^3 380–470°C same batch reactor as Lee et al.
Wightman (1981)	18.0	231	1	1	400–445 bar 338–445°C
Boock and Klein† (1993)	—	88±21	1	0	350–500°C Batch reactor
Rice et al.† (1993)	13.4	205	1	0	441–532°C 269–276 bar Assumed complete conversion of H_2O_2 feed to O_2 and H_2O
This study	9.9 ±1.7	168 ±21	0.72 ±0.15	0.27 ±0.15	246 bar, 425–600°C isothermal, plug-flow reactor
Oxidant: H_2O_2					
Wilmanns and Gloyna (1990)	5.95 ±5.72	314 ±62	2.36 ±0.48	1.04 ±0.35	272 bar, 400–510°C
Lee and Gloyna (1990)	11.5 ±11.5	180 ±15	1.01 ±0.09	0.16 ±0.08	225–310 atm, 415–525°C flow reactor

*As reported by Frisch (1992).

†Values for pseudo-first-order rate expression.

Experimental and Analytical Methods

The experimental apparatus used in this research was the isobaric, isothermal plug-flow reactor used and described in similar supercritical water oxidation studies at MIT by previous investigators (Helling, 1986; Helling and Tester, 1987, 1988; Webley, 1989; Holgate, 1993; Holgate and Tester, 1993, 1994a; Holgate et al., 1995). Many improvements have been made to the apparatus throughout the years, but the current configuration is exactly as that described by Holgate and Tester (1993), and will not be further elaborated here.

Liquid effluent analysis was done by isocratic high-performance liquid chromatography (HPLC). A Rainin HPXL solvent delivery system with an Interaction ORH-801 analysis column and Interaction Ionguard guard column was used. A Rainin Dynamax UV-1 UV/visible detector was also used at a wavelength of 210 nm. A Timberline column heater maintained column temperature. This setup and method were developed by Holgate (1993), and are described in Holgate et al. (1995). Peaks were identified by injecting standard solutions of pure compounds and comparing retention times. Following peak identification, the HPLC was calibrated using varying concentrations of each pure compound that matched the experimental retention time. Peak height and area gave equally good results, but peak height was used for quantification, since occasional peak overlap occurred and distorted peak area. HPLC analysis was typically done within a few hours of sample effluent collection.

Two gas chromatographs (GCs) were used to analyze the gaseous effluent. All gases except hydrogen and helium were analyzed with a Hewlett-Packard 5890 Series II GC, equipped with thermal conductivity and flame ionization detectors. Thermal conductivity was used exclusively to detect O_2, N_2, CO_2, C_2H_4, C_2H_6, CH_4, C_2H_2, and CO (order of elution). The analytical method provided excellent peak separation and resolution. A second GC was employed to detect hydrogen. This Perkin-Elmer Sigma 1B GC used a thermal conductivity detector with nitrogen as the carrier gas, and thus was very sensitive to trace amounts of hydrogen.

Experimental Results

Fifty-three oxidation and ten hydrolysis experiments were conducted at a constant pressure of 246 bar to provide a comparable database to previous kinetic experiments in our laboratory (Helling and Tester, 1987, 1988; Webley and Tester, 1991; Webley et al., 1990, 1991; Holgate, 1993). The specified pressure is typical of proposed operating pressures in the SCWO process (Tester et al., 1993). In addition, eleven oxidation experiments were performed to examine pressure/density effects on the rate of reaction and product distribution. Temperatures ranged from 425 to 600°C, although 39 oxidation experiments were carried out at 525°C to study concentration and residence time effects. Reactor residence times spanned 4.4 to 9.8 s. Initial concentrations of acetic acid in the reactor were from 9.8×10^{-5} mol/L to 2.02×10^{-3} mol/L, while inlet oxygen concentrations varied between 1.91×10^{-5} (hydrolysis) and 3.95×10^{-3} mol/L. These concentrations resulted in inlet molar oxygen-to-acetic acid ratios from 0.020 to 11.02 (stoichiometric oxidation corresponds to 2.00); the experiments included both fuel-lean and

Table 2. Experimental Conditions and Results for Acetic Acid Oxidation and Hydrolysis in Supercritical Water at 246 bar

Oxidation

Run No.	Temp. °C	$[CH_3COOH]_0$ $\times 10^{-6}$ mol/cm^3	$[O_2]_0$ $\times 10^{-6}$ mol/cm^3	τ s	Conv. %	ln k^* s^{-1}	Carbon Balance Closure %
247A	550 ± 1	1.00 ± 0.03	2.03 ± 0.07	8.0 ± 0.4	98.0 ± 0.3	-0.71	99.1
248	475 ± 1	1.05 ± 0.03	2.14 ± 0.08	7.9 ± 0.4	13.2 ± 3.6	-4.02	70.6
250	575 ± 1	1.08 ± 0.03	2.04 ± 0.06	8.0 ± 0.4	99.9 ± 0.1	0.18	92.9
252	500 ± 1	1.04 ± 0.02	2.13 ± 0.06	7.9 ± 0.4	18.9 ± 2.0	-3.64	73.5
254A	525 ± 1	0.99 ± 0.02	2.07 ± 0.02	7.9 ± 0.4	52.7 ± 2.9	-2.35	99.8
256	450 ± 2	0.98 ± 0.02	2.13 ± 0.07	8.2 ± 0.4	8.7 ± 4.2	-4.50	34.5
258	600 ± 1	0.97 ± 0.03	2.07 ± 0.09	8.4 ± 0.4	99.9 ± 0.1	0.13	97.5
260	426 ± 2	0.99 ± 0.05	2.10 ± 0.02	8.3 ± 0.5	9.21 ± 8.9	-4.45	10.4
261	525 ± 2	0.96 ± 0.03	2.12 ± 0.09	5.1 ± 0.3	33.8 ± 3.3	-2.52	92.4
262	525 ± 1	0.97 ± 0.05	2.10 ± 0.02	7.3 ± 0.5	49.2 ± 5.2	-2.38	86.4
263A	525 ± 1	0.99 ± 0.02	2.06 ± 0.06	8.8 ± 0.4	60.9 ± 1.4	-2.24	98.9
264	525 ± 2	0.98 ± 0.04	2.12 ± 0.12	4.6 ± 0.3	31.0 ± 4.7	-2.51	85.6
265	525 ± 1	0.98 ± 0.03	2.12 ± 0.07	9.8 ± 0.5	62.2 ± 1.7	-2.31	97.6
266	525 ± 1	0.98 ± 0.03	2.08 ± 0.07	5.9 ± 0.3	38.5 ± 2.3	-2.50	99.3
267	525 ± 2	0.98 ± 0.03	1.08 ± 0.05	4.9 ± 0.3	29.6 ± 3.4	-2.63	93.9
268	525 ± 1	0.98 ± 0.03	1.08 ± 0.05	8.8 ± 0.5	52.7 ± 2.5	-2.46	98.3
269	525 ± 1	0.98 ± 0.03	1.10 ± 0.05	4.4 ± 0.2	27.7 ± 3.5	-2.61	93.1
270	525 ± 1	0.99 ± 0.03	1.09 ± 0.05	7.0 ± 0.4	40.4 ± 3.1	-2.60	97.1
271	525 ± 1	0.98 ± 0.03	1.10 ± 0.05	9.7 ± 0.5	55.1 ± 2.4	-2.49	100.3
272	525 ± 1	0.97 ± 0.02	1.10 ± 0.04	5.9 ± 0.3	37.0 ± 2.1	-2.56	94.8
273	525 ± 1	0.98 ± 0.03	1.09 ± 0.04	7.9 ± 0.4	47.9 ± 2.0	-2.49	97.9
274	525 ± 2	0.98 ± 0.03	3.86 ± 0.15	4.9 ± 0.3	46.9 ± 2.6	-2.04	101.4
275	525 ± 1	0.99 ± 0.02	3.85 ± 0.11	4.4 ± 0.2	41.6 ± 1.8	-2.09	96.2
276	525 ± 1	0.98 ± 0.02	3.87 ± 0.10	6.9 ± 0.3	59.7 ± 1.1	-2.03	100.5
277	525 ± 1	0.98 ± 0.02	3.86 ± 0.10	8.7 ± 0.4	70.0 ± 0.9	-1.97	103.8
278	525 ± 1	0.99 ± 0.02	3.86 ± 0.11	5.9 ± 0.3	52.8 ± 1.7	-2.06	98.9
279	525 ± 1	0.99 ± 0.02	3.85 ± 0.11	7.8 ± 0.4	66.4 ± 1.0	-1.96	100.8
280	525 ± 1	1.00 ± 0.02	3.88 ± 0.11	9.7 ± 0.5	76.5 ± 0.7	-1.91	101.1
281	525 ± 1	0.098 ± 0.002	1.08 ± 0.04	7.9 ± 0.4	72.4 ± 1.0	-1.82	108.3
282	525 ± 1	0.50 ± 0.01	1.06 ± 0.04	7.9 ± 0.4	51.8 ± 2.9	-2.39	93.6
283	525 ± 1	2.04 ± 0.04	1.06 ± 0.04	7.9 ± 0.4	41.5 ± 1.8	-2.69	89.7
284	525 ± 1	0.50 ± 0.01	1.09 ± 0.04	4.9 ± 0.2	34.2 ± 2.2	-2.46	96.1
285	525 ± 1	0.49 ± 0.01	1.10 ± 0.04	5.9 ± 0.3	41.6 ± 1.8	-2.40	98.4
286	525 ± 1	0.49 ± 0.01	1.09 ± 0.04	9.7 ± 0.5	63.5 ± 1.5	-2.26	99.3
287	525 ± 1	2.01 ± 0.05	3.92 ± 0.12	4.9 ± 0.2	45.5 ± 2.5	-2.08	99.0
288	525 ± 1	2.01 ± 0.05	3.92 ± 0.13	5.9 ± 0.3	55.8 ± 1.8	-1.97	95.7
289	525 ± 1	2.04 ± 0.05	3.89 ± 0.12	9.7 ± 0.5	76.7 ± 0.9	-1.90	97.5
290	525 ± 1	2.03 ± 0.04	3.91 ± 0.10	6.9 ± 0.3	61.8 ± 2.4	-1.97	95.0
291	525 ± 1	2.02 ± 0.04	3.92 ± 0.11	7.8 ± 0.4	67.5 ± 1.0	-1.93	96.4
292	525 ± 1	2.03 ± 0.05	3.85 ± 0.11	8.6 ± 0.4	71.9 ± 0.9	-1.92	96.0
293	487 ± 1	1.01 ± 0.02	2.03 ± 0.06	7.8 ± 0.4	24.7 ± 2.6	-3.32	76.7
294	462 ± 1	0.99 ± 0.02	2.06 ± 0.06	7.7 ± 0.4	14.6 ± 2.7	-3.89	69.4
295	437 ± 2	0.98 ± 0.03	2.12 ± 0.08	7.8 ± 0.4	7.9 ± 3.7	-4.55	58.0
296	513 ± 1	0.97 ± 0.02	2.08 ± 0.07	7.9 ± 0.4	42.6 ± 1.7	-2.65	94.0
297	575 ± 1	0.98 ± 0.03	2.10 ± 0.07	7.8 ± 0.4	99.9 ± 0.1	-0.08	94.7
298	550 ± 1	0.92 ± 0.02	2.11 ± 0.06	7.8 ± 0.4	96.1 ± 0.7	-0.88	96.2
299	536 ± 1	0.94 ± 0.02	2.09 ± 0.06	7.9 ± 0.4	77.6 ± 2.8	-1.66	98.8
300	525 ± 2	1.43 ± 0.04	3.15 ± 0.10	5.0 ± 0.2	42.2 ± 2.4	-2.20	94.3
301	525 ± 1	1.44 ± 0.04	3.14 ± 0.09	7.8 ± 0.4	61.3 ± 1.3	-2.10	95.3
302	525 ± 1	1.45 ± 0.04	3.13 ± 0.09	9.7 ± 0.5	69.6 ± 1.1	-2.10	97.5
303	525 ± 1	1.43 ± 0.05	3.16 ± 0.12	5.8 ± 0.3	49.9 ± 2.3	-2.13	99.4
304	525 ± 1	1.43 ± 0.05	3.15 ± 0.12	6.7 ± 0.4	55.7 ± 2.2	-2.11	99.9
305	525 ± 1	1.43 ± 0.05	3.16 ± 0.13	8.8 ± 0.5	66.9 ± 3.0	-2.08	103.0

Hydrolysis

Run No.	Temp. °C	$[CH_3COOH]_0$ $\times 10^{-6}$ mol/cm^3	$[O_2]_0$ $\times 10^{-8}$ mol/cm^3	τ s	Conv. %	ln k^* s^{-1}	Carbon Balance Closure %
246A	550 ± 1	0.97 ± 0.03	2.12 ± 0.06	8.1 ± 0.4	13.7 ± 3.4	-4.01	140.0
249	575 ± 1	1.06 ± 0.02	2.01 ± 0.05	8.1 ± 0.4	26.7 ± 2.4	-3.26	51.2
251	500 ± 3	1.04 ± 0.03	2.44 ± 0.07	8.0 ± 0.4	5.5 ± 3.8	-4.96	103.4
253	525 ± 1	1.06 ± 0.03	2.29 ± 0.06	8.0 ± 0.4	11.5 ± 3.5	-4.18	0.1
257	600 ± 1	0.96 ± 0.03	1.92 ± 0.06	8.6 ± 0.4	35.2 ± 2.7	-2.99	93.8
306	475 ± 1	0.98 ± 0.03	2.63 ± 0.07	7.7 ± 0.4	5.9 ± 3.5	-4.85	0.0
307	537 ± 1	0.97 ± 0.02	2.19 ± 0.05	7.7 ± 0.4	13.1 ± 2.2	-4.00	101.5
308	562 ± 1	0.98 ± 0.02	2.07 ± 0.04	7.7 ± 0.4	21.4 ± 2.2	-3.47	75.2
309	587 ± 1	0.99 ± 0.02	1.91 ± 0.04	7.6 ± 0.4	30.0 ± 1.5	-3.06	87.3
310	512 ± 1	0.99 ± 0.02	2.33 ± 0.06	7.7 ± 0.4	10.7 ± 2.5	-4.51	76.0

Note: $$\text{Carbon balance closure \%} = \frac{\Sigma_i[\text{product } i](\text{mol carbon/mol product } i)}{([CH_3COOH]_0 - [CH_3COOH])(2)} \times 100\%.$$

Table 3. Experimental Conditions and Results for Acetic Acid Oxidation in Supercritical Water at 550°C and 160–263 bar

Run No.	Pres. bar	$[CH_3COOH]_0$ $\times 10^{-6}$ mol/cm^3	$[O_2]_0$ $\times 10^{-6}$ mol/cm^3	τ s	Conv. %	ln k^* s^{-1}	Carbon Balance Closure %
311	242.3±2.8	0.93±0.02	2.05±0.05	5.9±0.3	89.9±0.6	−0.94	95.2
312	221.6±4.1	0.93±0.03	2.06±0.07	5.8±0.3	90.5±0.6	−0.90	95.8
313A	159.6±4.1	0.93±0.04	2.11±0.08	5.4±0.3	80.1±3.6	−1.21	111.2
314A	263.0±5.5	0.98±0.03	2.10±0.07	5.9±0.3	92.5±0.3	−0.83	96.5
315	200.9±3.4	0.94±0.02	2.09±0.06	5.8±0.3	90.5±0.6	−0.91	93.9
316	180.3±3.4	0.96±0.02	2.10±0.07	5.8±0.3	88.5±0.8	−0.99	99.2
318	263.0±6.2	0.96±0.03	2.11±0.08	4.0±0.2	85.6±1.3	−0.72	90.4
319	221.6±4.8	0.96±0.03	2.11±0.07	3.9±0.2	81.2±1.2	−0.85	94.6
321A	242.3±4.1	0.98±0.02	2.09±0.06	3.9±0.2	77.3±0.9	−0.98	97.8
322	200.9±6.9	0.95±0.04	2.11±0.10	3.8±0.2	74.9±1.5	−1.02	102.2
323	159.6±4.8	0.93±0.04	2.09±0.09	3.7±0.2	63.9±2.0	−1.29	116

fuel-rich conditions. Acetic acid conversions ranged from 7.89±3.71% to 100% (within analytical detection limits). Tables 2 and 3 list the raw data and key operating parameters from our studies. Complete experimental conditions and results are tabulated in Meyer (1993).

No spurious peaks were seen in the gas analysis chromatograms, so it was assumed that the gas phase was well-characterized by the identified products. Typically, twelve gas samples were analyzed during each experiment—six using a nitrogen carrier gas and six using a helium carrier.

Identifiable liquid effluent analyzed via liquid chromatography (Holgate, 1993) with UV detection at 210 nm (2,100 Å) consisted mainly of acetic acid and propenoic acid appearing occasionally (in concentrations of order 10^{-7} molar). Other reproducible oxidation peaks eluted at retention times of approximately 5.0 and 17.7 min. Since these species could not be identified among 39 previously tested compounds (Holgate, 1993; and Holgate et al., 1995), 14 additional suspected compounds were tested. Unfortunately, none of these eluted at retention times of 5.0 or 17.7 min. Even without identification of unresolved peaks, carbon balance closures for oxidation were reasonably good, particularly at the higher temperatures (90+% carbon accounted for in all but three runs above 500°C) where greater gasification, a disappearance in the 5.0-min peak, and a reduction in the 17.7-min peak occurred. In addition, more recent evidence of spurious peak detection by HPLC in the liquid effluent of methylene chloride oxidation further suggests that it is unlikely that the unidentified peaks at 5.0 and 17.7 min correspond to any additional compounds present in a significant amount in the product stream.

A limited number of hydrolysis experiments were conducted at 246 bar and a reactor residence time of 8 s, with reactor inlet concentrations of approximately 1×10^{-3} mol/L acetic acid over a temperature range of 475–600°C. Conversions ranged from 5.46±3.85% to 35.15±2.69% with 95% confidence intervals as shown. UV absorbance of the liquid effluent at 210 nm gave propenoic acid as a consistent product and another unidentified peak with a retention time of about 18.4 min (less consistently).

Conversion of acetic acid in the preheater was considered negligible and not included in our calculations. Since a hydrolysis run at 525°C and 8-s residence time yielded only 11.5% conversion, it was assumed that the considerably shorter residence times in the preheater and lower temperatures produced little conversion.

Experimental errors are estimates based on uncertainties in measured values. Normally all measured quantities are given with 95% confidence intervals. Measurement uncertainties are propagated to uncertainties in calculated parameters using standard propagation-of-error formulas (Aikens et al., 1984).

Derivation of Oxidation Global Rate Expression

Justification in assuming this apparatus acts as an isothermal plug-flow reactor has been provided by Webley (1989) and Holgate (1993). Based on their analysis, we estimate that plug-flow-like conditions existed over our entire operating regime. Thus, the kinetics should obey the isothermal plug-flow design equation:

$$\frac{\tau}{C_{i0}} = \int_0^{X_i} \frac{dX_i}{-R_i} \tag{1}$$

where

X_i = conversion of reactant
R_i = rate of reaction for reactant i
C_{i0} = initial concentration of reactant
τ = reactor residence time

Because water is in vast excess (mole fraction > 0.999), any change in volume due to reaction stoichiometry should have little effect on overall density for the isobaric runs. Because a negligible pressure drop was measured through the reactor (typically (±6 bar) with a system pressure of 246 bar) as well as a negligible temperature variation, the constant water density assumption appears valid; thus the volumetric flow rate through the reactor was assumed constant. Consequently, the reactor residence time only depends on reactor volume, supercritical water density, and the water mass-flow rate.

The reaction rate in Eq. 1 is assumed to be in the form of a global rate expression,

$$R_{CH_3COOH} = k[CH_3COOH]^a[O_2]^b[H_2O]^c \tag{2}$$

where k is the rate constant, which can be expressed in the Arrhenius form as

$$k = A\exp(-E_a/RT). \qquad (3)$$

Because water is present in such excess, its concentration was assumed to be virtually constant. Although the density (or concentration) of water is temperature dependent, we operate sufficiently far from the critical point that variations in temperature result in only modest density changes compared with changes in k caused by its exponential Arrhenius temperature dependence. Thus the water concentration effect is absorbed into the rate constant term.

Substituting Eqs. 2 and 3 into Eq. 1, and applying stoichiometry for total oxidation of acetic acid

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O,$$

the following isothermal, plug-flow equation is derived:

$$[CH_3COOH]_0^{a+b-1}(k\tau) = \int_0^X \frac{dX}{(1-X)^a(F-SX)^b} \qquad (4)$$

where

$[CH_3COOH]_0$ = initial concentration at reactor inlet
$F = [O_2]_0/[CH_3COOH]_0$
X = acetic acid conversion
$S = O_2/CH_3COOH$ stoichiometric ratio

A nonlinear multivariable regression program employing a modified Marquardt method (Press et al., 1986) was used to obtain best-fit values of the rate parameters A, E_a, a, and b. Fifty of the fifty-three constant pressure oxidation results were used in the nonlinear regression (a few results gave final acetic acid concentrations below our detectable limits and were therefore not used). In choosing the predicted variable for the regression program, neither X nor F can be chosen since the integral in Eq. 4 cannot be evaluated without knowledge of these values. Of the remaining variables (T, $[CH_3COOH]_0$, and τ), the one chosen as the predicted variable must have all values known to good accuracy and of all the same order of magnitude to avoid skewed results that arise when considering the percentage difference between predicted and observed values for values of different orders of magnitude. As elaborated on further by Holgate (1993), T is the best choice since it is known not only to high accuracy (unlike τ), but also varies over a relatively narrow range from 425°C to 600°C (a factor of 1.4) (unlike $[CH_3COOH]_0$, which varies more than fourfold). With temperature as the predicted variable, the best-fit expression is

$$R_{CH_3COOH} = 10^{9.9 \pm 1.7}\exp\left(\frac{-168 \pm 21}{RT}\right) \times [CH_3COOH]^{0.72 \pm 0.15}[O_2]^{0.27 \pm 0.15}. \qquad (5)$$

Units for the rate are mole/cm^3 s^{-1}, concentration is in mol/cm^3, and activation energy is in kJ/mol. All parameter uncertainties are at the 95% confidence interval and were determined by an inverted curvature matrix (Press et al., 1986). This nonlinear regression gives a significance level of 100%, with an F-statistic of 110 and a 0.85 R-squared value (adjusted for degrees of freedom). These statistical parameters, as defined in Press et al. (1986), compare the actual data to those data as predicted from the regression.

In the nonlinear regression of Eq. 4, a value for S of 2 was used, representing the stoichiometric relation between acetic acid and O_2 for the complete oxidation reaction to CO_2 and H_2O. This stoichiometry would be completely correct if CO_2 were the only carbon-containing product formed. Figures 4 and 5 show that CO_2 is the major product, but also show that some acetic acid is converted to products that require fewer than 2 moles of O_2. Thornton and Savage (1990) have pointed out that it is not possible to choose a value for S *a priori*, and experiments must be conducted under excess oxygen conditions (where the oxygen concentration remains essentially constant during the experiments and the kinetic results are independent of S) in order to ascertain a more appropriate value for S. In view of the incomplete conversion of all carbon to CO_2, we regressed the data with $S = 1.5$. The value of the rate parameters obtained in this case were as follows: $A = 10^{9.6 \pm 1.6}$, $E_a = 160 \pm 18$ kJ/mol, $a = 0.70 \pm 0.14$, $b = 0.38 \pm 0.16$. The parameters of this rate expression are not statistically different from those in Eq. 5. The only difference of note is the seemingly increased fractional dependence on oxygen concentration.

Previous investigators have assumed reaction orders of 1.0 with respect to acetic acid and zero with respect to oxygen. With such an overall first-order assumption, Eq. 4 reduces to

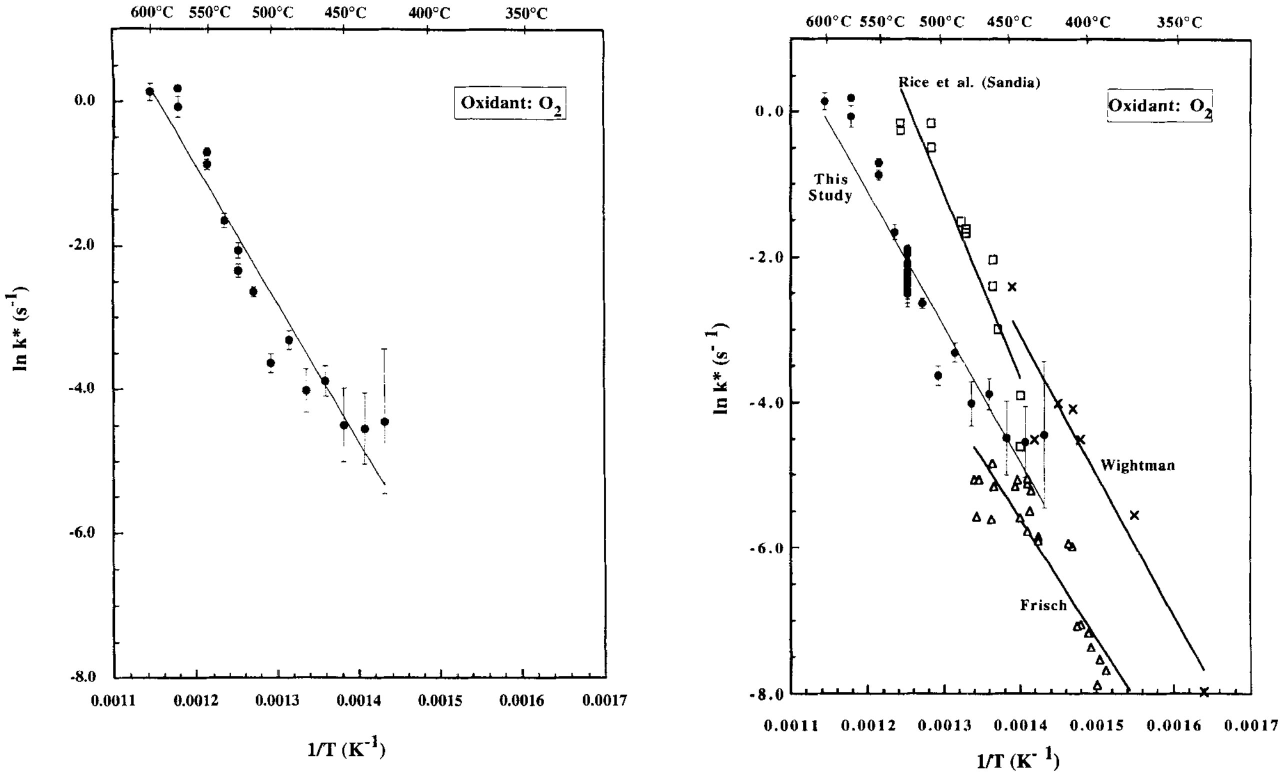
$$k = -\ln(1-X)/\tau, \qquad (6)$$

and the *first-order* rate expression regressed from our data is

$$R_{CH_3COOH} = 10^{11.1 \pm 1.6}\exp\left(\frac{-183 \pm 24}{RT}\right)[CH_3COOH], \qquad (7)$$

with parameter 95% confidence intervals shown. Although there is significant error associated with the exact value of the order with respect to oxygen, notice it is still *nonzero* at a statistically significant confidence level exceeding 99%. This fractional order dependence on O_2 is similar to the fractional order H_2O_2 dependence reported by Lee and Gloyna (1990) for acetic acid oxidation in supercritical water.

Figure 1a shows the Arrhenius plot generated from the data obtained in this study. Again, error bars on each data point represent a 95% confidence interval. A graphical comparison of previous investigator results with this study (all using O_2 as the oxidant) taken from data in Table 1 is shown in Figure 1b. Data of each investigator were plotted *assuming a reaction rate first-order in acetic acid and zero-order with respect to oxygen and water* over the respective ranges of temperatures investigated. The fact that previous investigators have assumed a first-order reaction with respect to acetic acid and attained relatively good fits is not entirely surprising. The data closely approximate first-order behavior consistent with previous studies in our own laboratory of other model compounds such as CH_4, CH_3OH, and H_2 (Helling and Tester, 1987; Webley and Tester, 1989; Holgate and Tester, 1993), where we have observed global kinetics independent of oxygen and first-order in the organic. Still, the experimental data



(a) (b)

Figure 1. Assumed first-order Arrhenius plot for acetic acid oxidation in supercritical water at 246 bar.

(a) This study's results. (b) Comparison with data from other investigators (see Table 1). *Linear* least-squares fit is shown, corresponding to Eq. 7.

presented deviate from first-order behavior (0.72 in acetic acid, 0.27 in oxygen), in accordance with the rate expression obtained from the *nonlinear* regression (Eq. 5).

The two data points in Figure 1a at both 550°C and 575°C give some indication of our ability to reproduce experimental conditions and results. Data points at each temperature were obtained about 2½ months apart, with the lower ln k^* values attained in the most recent experimental runs.

Two other characteristics of our Arrhenius plot are particularly noteworthy. The three data points at reactor temperatures of 450°C and below show a leveling off, as well as a general increase in the size of the error bars. This is a result of the relatively low conversion ($<10\%$) of acetic acid under the stated experimental conditions. A small absolute error in conversion at low conversions ($<20\%$) can lead to much larger propagated error than a comparable experimental error at higher conversions ($>70\%$). For example, an error of $\pm 2\%$ at a conversion of 80% gives an error of about 6% in the observed rate constant k. However, a $\pm 2\%$ error in conversion at 5% conversion propagates into an error of over 40% in k!

The other noteworthy observation is the "stacking" of our data points at 525°C. Since approximately 50% conversion was attained at stoichiometric feed reactor conditions of 525°C, 246 bar and residence time of 8 s, we decided to study concentration, residence time, and pressure effects as variations from this base set of conditions to allow for maximum changes in conversion. Twenty-three experimental runs were conducted with a stoichiometric ratio of organic feed to oxygen, but with varying concentrations. Six experiments were conducted at an initial feed ratio of 4 mM of oxygen to 2 mM acetic acid (4:2); six experiments at 3:1.5; seven runs at 2:1; and four runs at 1:0.5. If the data followed a first-order rate expression exactly, all data at one temperature would be represented by a single point. The scatter of these points is clearly not due to experimental error alone, but is likely due to an identified induction time and other possible non-first-order concentration effects (described in more detail later).

As shown in Table 1 and Figure 1b, our results are comparable with other investigators who performed similar experiments over somewhat different experimental conditions. Perhaps somewhat fortuitously, results from this study are in closest agreement to results achieved by Lee and Gloyna (1990) in a flow reactor using hydrogen peroxide rather than oxygen as the oxidant.

Apparent Induction Times and Acetic Acid Oxidation Decay Profiles

Four sets of experiments were conducted with a stoichiometric feed ratio at constant temperature and pressure. Two other sets of experiments were conducted to help verify global reaction order with respect to oxygen. These sets of runs were conducted at oxygen-to-acetic-acid-feed ratios of 4:1 (oxygen-rich) and 1:1 (oxygen-lean). All six sets of experiments were conducted at a fixed pressure of 246 ± 7 bar and a fixed temperature of 525 ± 2°C. These conditions were chosen to give as wide a range of both residence time and con-

Table 4. Apparent Induction Times and Decay Constants for Acetic Acid Oxidation at 246 bar and 525 ± 2°C*

Initial Conditions (10^{-3} mol/L)	k' s^{-1}	τ_{ind} s	Avg. Feed Ratio $[O_2]$:$[CH_3COOH]$
$[O_2]_0 = 1.09 \pm 0.02$ $[CH_3COOH]_0 = 0.50 \pm 0.01$	0.12 ± 0.01	1.5 ± 0.6	2.19 ± 0.04
$[O_2]_0 = 1.09 \pm 0.02$ $[CH_3COOH]_0 = 0.98 \pm 0.01$	0.09 ± 0.01	1.1 ± 0.6	1.11 ± 0.02
$[O_2]_0 = 2.08 \pm 0.04$ $[CH_3COOH]_0 = 0.98 \pm 0.01$	0.12 ± 0.01	1.7 ± 0.5	2.13 ± 0.05
$[O_2]_0 = 3.15 \pm 0.04$ $[CH_3COOH]_0 = 1.44 \pm 0.02$	0.14 ± 0.02	0.8 ± 0.7	2.19 ± 0.04
$[O_2]_0 = 3.86 \pm 0.04$ $[CH_3COOH]_0 = 0.99 \pm 0.01$	0.17 ± 0.01	1.2 ± 0.4	3.91 ± 0.06
$[O_2]_0 = 3.90 \pm 0.05$ $[CH_3COOH]_0 = 2.02 \pm 0.02$	0.17 ± 0.02	1.3 ± 0.6	1.93 ± 0.02

*Ninety-five % confidence intervals are shown.

version as possible with our apparatus and analytical methods.

The Reynolds numbers corresponding to the residence times spanned for each set of different feed ratios ranged from 4,852 for $\tau = 4.4$ s to 2,150 for $\tau = 9.8$ s. Although the Reynolds number at 9.8 s is close to the traditional lower limit for turbulent flow, having turbulent flow is not necessarily a requirement for achieving plug flow with respect to concentration. The primary requirements for a nonradial dependence of concentration in plug flow as detailed by Cutler et al. (1988) are (1) that radial diffusion occur rapidly enough to ensure that the reactor fluid is well mixed radially, and (2) that axial diffusion is slow relative to convection. Cutler et al. (1988) provides a set of "plug-flow criteria" summarized from many literature sources that, when satisfied, ensure plug-flow concentration profiles even under laminar fluid flow conditions. Webley (1989) and Holgate (1993) have shown that for typical run conditions with our reactor system, these criteria are satisfied, and thus any radial dependencies of species concentration are probably negligible.

Figure 2 displays acetic acid decay profiles as a function of residence time for the four stoichiometric feed mixtures. Acetic acid concentration has been normalized by the initial acetic acid concentration ($[CH_3COOH]_0$). The curves shown are exponential fits to each data set with the initial concentration ($[CH_3COOH]/[CH_3COOH]_0 = 1$) omitted. For all four oxidation runs at stoichiometric feed conditions, acetic acid follows an exponential decay characteristic of a *first-order* reaction. This observed exponential decay suggests that the reaction is indeed first-order with respect to acetic acid and that the linear regressed global rate expression (Eq. 7) may be preferred over the nonlinearly regressed rate expression (Eq. 5).

The exponentially regressed decay curves should extrapolate back to the initial acetic acid concentration (or $[CH_3COOH]/[CH_3COOH]_0 = 1$) at time $t = 0$. This does not occur in the curve fits depicted. Rather, the extrapolated exponential decay curves predict that the initial concentration still exists at times of 1 to 2 s. This behavior is characteristic of an apparent induction time, or "ignition" delay that is frequently observed in combustion reactions. All data sets exhibit these induction times. Derived decay constants and induction times are shown in Table 4. The 95% confidence intervals given were determined using a modified Monte Carlo technique (Press et al., 1986).

Note in Table 4 that the three lower stoichiometric concentration data sets appear to have the same decay constant and have slopes within regression error (the 1:0.5 and 2:1 feeds are almost indistinguishable), but the highest feed concentration (4:2) has a decay constant (k') that is statistically different, where

$$k' = -\frac{1}{C_i}\frac{dC}{dt} = -\frac{d\ln C_i}{dt}. \tag{8}$$

Though not conclusive, the induction time seems to decrease slightly with increasing feed concentrations, but increases for the most concentrated feed. However, there is a large error associated with estimating the induction time and a quantitative analysis cannot be made at this time.

A definitive trend observed is that as acetic acid and oxygen concentrations are stoichiometrically increased, overall conversion is increased. This can be seen by comparing data in Figure 2 at a specific residence time. In general, the more concentrated mixtures have the lower $[CH_3COOH]/[CH_3COOH]_0$ ratios, which translates into higher conversions ($X = 1 - \{[CH_3COOH]/[CH_3COOH]_0\}$). This trend runs counter to results found by Holgate and Tester (1993) in similar studies of hydrogen oxidation in supercritical water, where conversions decreased with increasing stoichiometric concentrations.

The presence of an induction time is indicative of a complex reaction mechanism and severely interferes with modeling of global reactions. The rate form of Eq. 2 assumes the reaction is initiated at $\tau = 0$. Experimental evidence suggests that the reaction does not begin until $\tau \approx 1$ to 2 s for acetic acid oxidation in supercritical water, and that induction time (τ_{ind}) itself may be a function of other experimentally controlled variables. Ignition delay results in differing k (rate constant) values. The regressed rate form cannot replicate this behavior, as the induction time effect is subsumed in the rate equation. The scatter in ln k^* seen at 525°C in Figure 1b can be partly attributed to the variation in k^* due to the

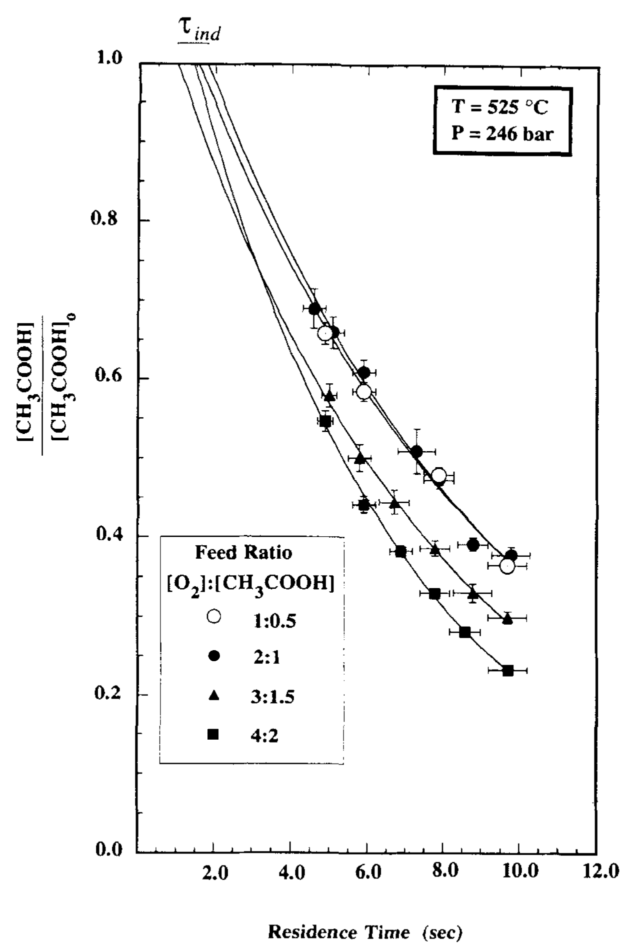


Figure 2. Normalized decay profiles for stoichiometric oxidation of acetic acid in supercritical water, showing induction times.

Curves are exponential fits to data points. Error bars represent 95% confidence intervals.

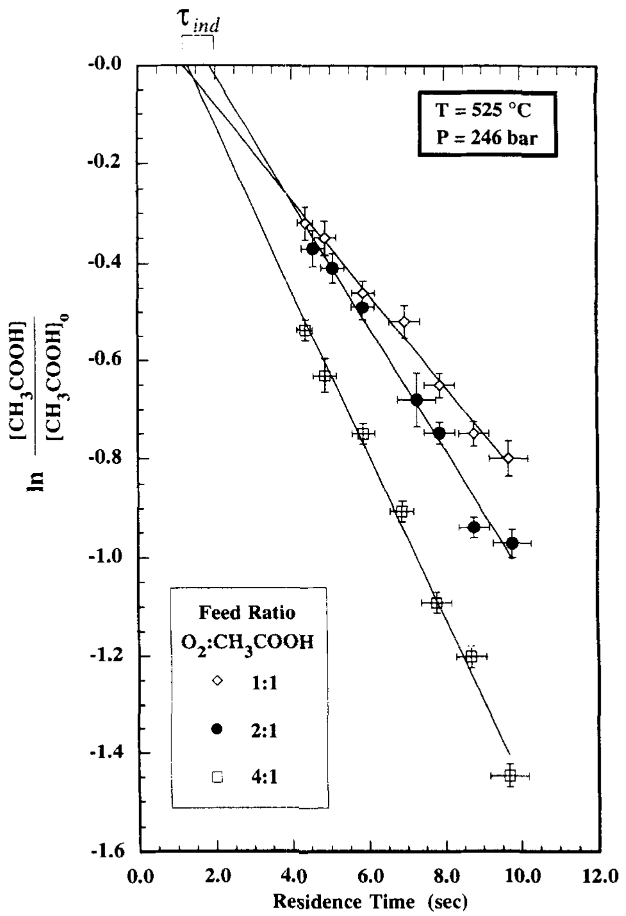


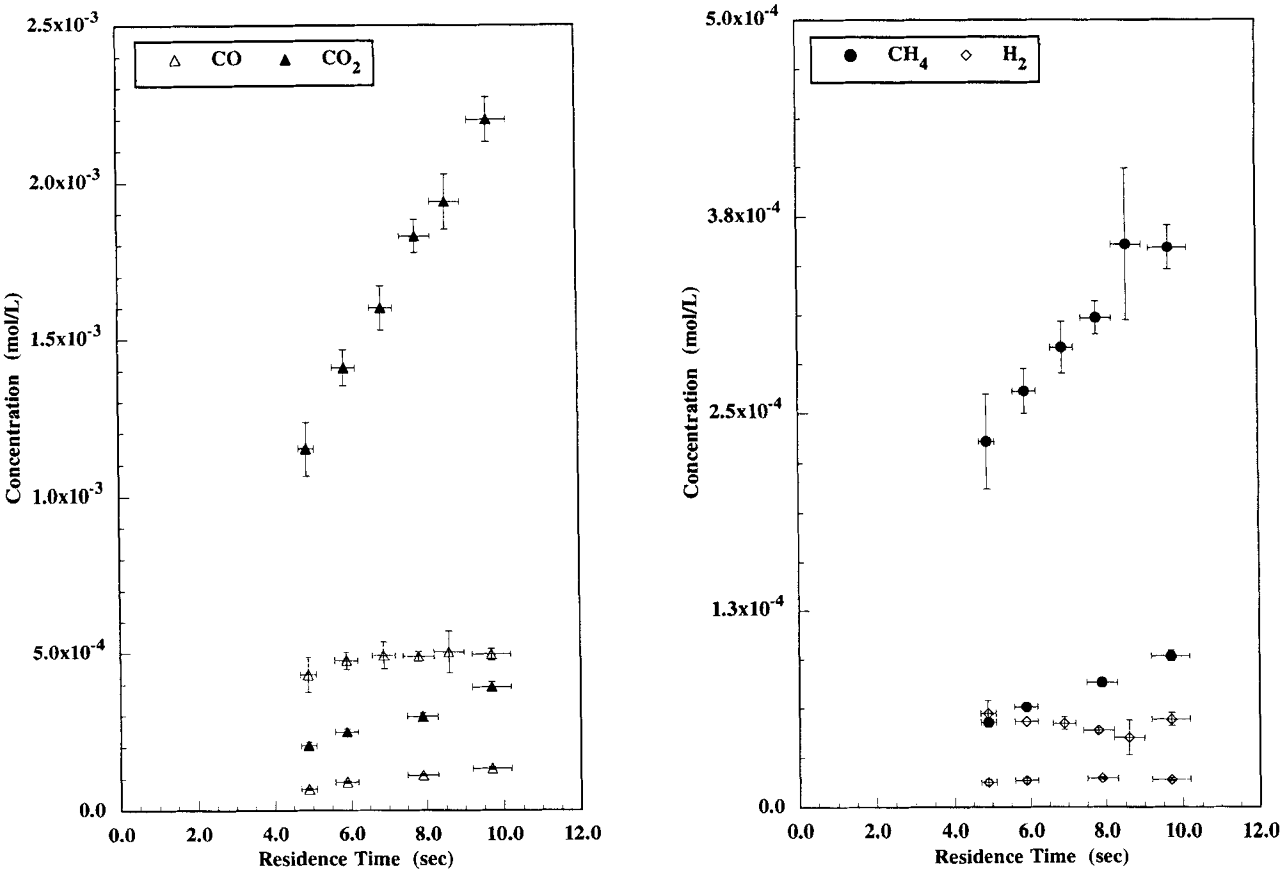
Figure 3. Normalized decay profiles for oxidation of acetic acid in supercritical water at 525°C and 246 bar, showing induction times.

Lines are linear fits to data, suggesting exponential decay. Error bars represent 95% confidence intervals.

induction time. Similarly, the regressed expression found in Eq. 5 (or any other regression of similar form) is less accurate due to this anomaly.

Unfortunately, the induction time cannot be measured directly in our plug-flow reactor. Mixing times were estimated at 1 s or less based on correlations in Uhl and Gray (1986). Conservatively, the mixing length is about 50 tube diameters. Since the tubular reactor is over 2,700 diameters long, this mixing length corresponds to less than 2% of the reactor length, or 2% (conservatively) of the reactor residence time (Holgate, 1993). Although mixing times are extremely short relative to reactor residence times (which vary from 4.4 to 9.8 s), they are still finite and may affect the magnitude of the extrapolated 1 to 2 s induction times. Ignition can also be significantly affected by minor concentration variations during mixing (Yetter et al., 1985).

Two additional series of experiments were conducted to better characterize the reaction order with respect to oxygen. Seven experiments were conducted in which the initial oxygen concentration was twice that required for complete oxidation of acetic acid to CO_2 (oxygen to acetic acid ratio of 4:1). Similarly, seven runs were conducted in which the initial oxygen concentration was one-half the stoichiometric requirement (1:1). Although oxygen-lean, these experiments were never oxygen-limited in that conversion of acetic acid at the longest residence time was only 55% (and not all acetic acid converted was totally oxidized). Results of these investigations are plotted in Figure 3, which linearizes normalized acetic acid profiles logarithmically and shows straight-line fits to the data. In addition to the excellent straight-line behavior, the figure shows the presence of an apparent induction time. Also note that each profile exhibits a somewhat different decay rate. Kinetic decay constants and induction times from the acetic acid profiles for the data sets are summarized in Table 4. The decay constant under fuel-rich (1:1) conditions decreases relative to that under stoichiometric conditions. The fuel-rich induction time may be somewhat shorter, but still subject to considerable error, and approximately 1 to 2 s. The oxygen-rich profile depicts a correspondingly higher decay constant relative to stoichiometric feed. If the global reaction rate is independent of oxygen concentration, the decay constant should be the same since the inlet organic concentrations, temperature, pressure, and residence times were essentially the same for comparable experiments in the same reactor system. The difference in profiles can only be explained by some level of oxygen dependence. These profiles



(a) (b)

Figure 4. Combined major products profiles for stoichiometric (1:0.5 and 4:2) acetic acid oxidation in supercritical water at 525°C and 246 bar.

(a) Species CO and CO_2. (b) Species CH_4 and H_2. Actual average $[O_2]_0$:$[CH_3COOH]_0$ feed concentrations are $([1.09\pm0.2]:[0.50\pm0.01])\times10^{-3}$ mol/L for the lower profile of each species, and $([3.90\pm0.5]:[2.02\pm0.2])\times10^{-3}$ mol/L for the higher profile of each species. Error bars represent 95% confidence intervals.

substantiate the oxygen dependence of acetic acid destruction in accordance with Eq. 5. Oxygen-rich (fuel-lean) induction time is still around 2 s, suggesting that ignition time may be independent of the oxygen-to-acetic-acid feed ratio. This is in agreement with similar work reported by Holgate and Tester (1994a,b) involving oxidation of carbon monoxide in supercritical water.

Effects of Initial Conditions on Oxidation Products

In addition to CO_2 and H_2O, gaseous effluents from incomplete oxidation were CO, CH_4, H_2, and O_2. Again, the acetic acid and oxygen profiles are well fit by exponential decay. Extrapolation to the initial concentration verified that induction periods were present. In a typical series of experiments (525°C, 246 bar, $[O_2] = 2.08\times10^{-3}$ mol/L, $[CH_3COOH] = 0.98\times10^{-3}$ mol/L), induction times τ_{ind} ranged from 1 to 2 s at reactor residence times τ of 4.6 to 9.8 s. CO and CH_4 exhibit a small net increase in concentration (from about 1×10^{-4} to 2×10^{-4} mol/L), while CO_2 concentration shows a sharper rise from 45% of the total carbon reacted at $\tau = 4.6$ s to nearly 62% of total carbon reacted at $\tau = 9.8$ s. Overall H_2 concentrations are relatively low (1×10^{-6} to 6×10^{-6} mol/L). This implies that H_2 oxidation offsets the rate at which H_2 is formed from the water–gas shift and/or any acetic acid oxidation. Other stoichiometric feeds show similar trends.

More information can be extracted by comparing the most concentrated and least concentrated stoichiometric feeds. As would be expected, respective product profiles for the 3:1.5 and 2:1 stoichiometric feeds lie in between the limits defined by the nominally 4:2 and 1:0.5 feeds. Comparison of acetic acid and oxygen decay profiles for the 4:2 and 1:0.5 runs reveals distinctly different behavior, reflecting complex kinetics and a change in induction time.

The effect of initial concentration on gaseous product distribution can be seen in comparison of the results of the 4:2 and 1:0.5 feeds in Figure 4a and 4b. The CO production expectedly increases, but has little net gain beyond 6-s reactor residence time, while CO_2 production increases rapidly (to 2.2×10^{-3} mol/L at $\tau = 9.8$ s). Similarly, the fourfold increase in initial CH_3COOH and O_2 concentrations gives an approximately fourfold increase in CH_4 production. While produced in greater quantities, H_2 still appears to reach a steady-state concentration level within the first 4 s in the reactor and undergoes little net change through 10 s.

The effects of varying initial O_2 concentration while keeping acetic acid feed concentration constant can be seen by

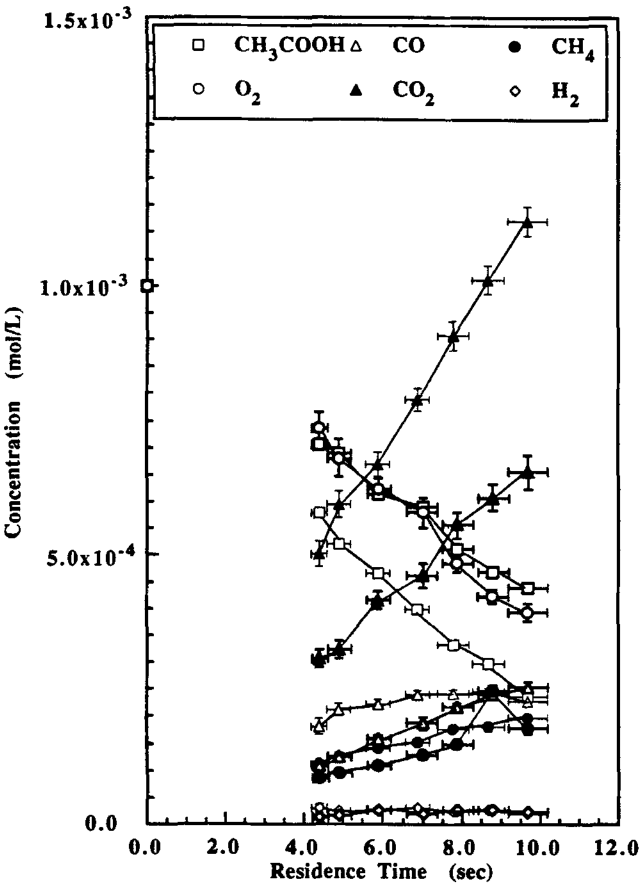


Figure 5. Combined major species profiles for oxygen-lean and oxygen-rich acetic acid oxidation in supercritical water at 525°C and 246 bar.

$[O_2]_0 = (1.09 \pm 0.2) \times 10^{-3}$ mol/L, $[CH_3COOH]_0 = (0.98 \pm 0.01) \times 10^{-3}$ mol/L (lower profile for each species except acetic acid); $[O_2]_0 = (3.86 \pm 0.4) \times 10^{-3}$ mol/L, $[CH_3COOH]_0 = (0.99 \pm 0.01) \times 10^{-3}$ mol/L (higher profile for each species except acetic acid). Error bars represent 95% confidence intervals.

comparing sets of runs in which O_2 feed was increased fourfold, while CH_3COOH feed concentration remained essentially constant. By plotting both series of runs ($[O_2]_0$:$[CH_3COOH]_0$ = 4:1, 1:1) on the same scaling in Figure 5, the oxygen dependence of acetic acid oxidation in supercritical water is profoundly evident in the shift of the acetic acid decay profile. Note that we omitted the O_2 decay profile of the 4:1 run to enhance detail of lower concentration compounds. Product concentrations of CH_4 and CO seem to be significantly less affected by increased O_2 feed concentration. Overall, H_2 concentrations show little variation with the change in O_2 feed under these experimental conditions.

The only liquid product conclusively detected in all oxidation experiments was unreacted acetic acid. An HPLC peak with a retention time corresponding to propenoic acid was also detected in some experiments. As observed in Figure 5, this concentration of acetic acid in the liquid effluent decreased with increasing O_2 concentrations in the feed. This trend is indicated by the following values of acetic acid conversion and the associated O_2:CH_3COOH feed ratios (all under the same conditions of 525°C, 246 bar, 9.8-s residence time, and $[CH_3COOH]_0 = 1 \times 10^{-3}$ mol/L): 76% for a 4:1 ratio (oxygen-rich), 63% for a 2:1 ratio (stoichiometric), and 55% for a 1:1 ratio (oxygen-lean). As mentioned earlier, two smaller peaks were seen on HPLC chromatograms for liquid effluent samples at 5.0 and 17.7 min. Comparison with 53 other known compounds that we tested ranging over 1 to 6 carbon alcohols, aldehydes, ketones, esters, and acids (including compounds like maleic acid that could possibly result from additive combinations of acetic acid monomers) yielded no conclusive match. Since the time of these experiments, however, we have since found proof by comparison with other analytical methods that similar types of unidentifiable peaks observed on HPLC chromatograms of methylene chloride oxidation effluents did not correspond to anything in the injected sample. These results lead us to believe that unreacted acetic acid was probably the only compound in the liquid effluent in significant quantity (at least above 500°C) for the oxidation runs.

As indicated in Table 2, carbon balances for the majority of runs performed were generally good (>86%). However, there were some oxidation runs (#248, #252, #256, #260, #293–#295) and some hydrolysis runs (#249, #253, #306, #308, #310) where carbon balances were < 86%. All but one of these runs were conducted at the lower end of our investigated temperature range (≤ 525°C) and all had low conversions (≤ 27%). Less gaseous products were formed during these runs and the low carbon balances indicate that more products may have been in the liquid effluent that went undetected by the analytical method used (HPLC).

Pressure (Density) Effects on Oxidation

A series of experiments was conducted to determine the effects of operating pressure on the rate of acetic acid oxidation. These experiments were similar to an earlier study of pressure effects on H_2 and CO oxidation (see Holgate and Tester, 1994a,b). Two series of experiments were carried out, at 4 and 6 s residence time, respectively. All reactions were conducted at 550°C and nominal stoichiometric reactant concentrations of 1×10^{-3} mol/L acetic acid and 2×10^{-3} mol/L of oxygen. Operating pressures ranged from 159.6 ± 4.8 to 263.0 ± 6.2 bar. These conditions were chosen to give the widest range of conversions over the domain of experiments. The pressure range investigated incorporated both supercritical and subcritical pressures, and corresponds to water densities of 0.047 to 0.084 g/cm^3, or almost a twofold variation. The complicating effect of residence time observed in previous work (Holgate, 1993) resulted in a concerted effort to keep residence time relatively constant at 4 and 6 s throughout these experiments.

For runs at 4-s residence time, conversion varied from 64 to 86%. At a residence time of 6 s, acetic acid conversion ranged from 80 to 93%. Figure 6 shows that the apparent first-order rate constant, k^*, increases with increasing operating pressure at 550°C for both 4- and 6-s residence times. However, the observed increase in k^* is not quite as pronounced as Figure 6 suggests. As discussed earlier, the presence of an induction time complicates the calculation of k^*. Without an induction time effect, and with all other experimental conditions the same, k^* should be constant, regard-

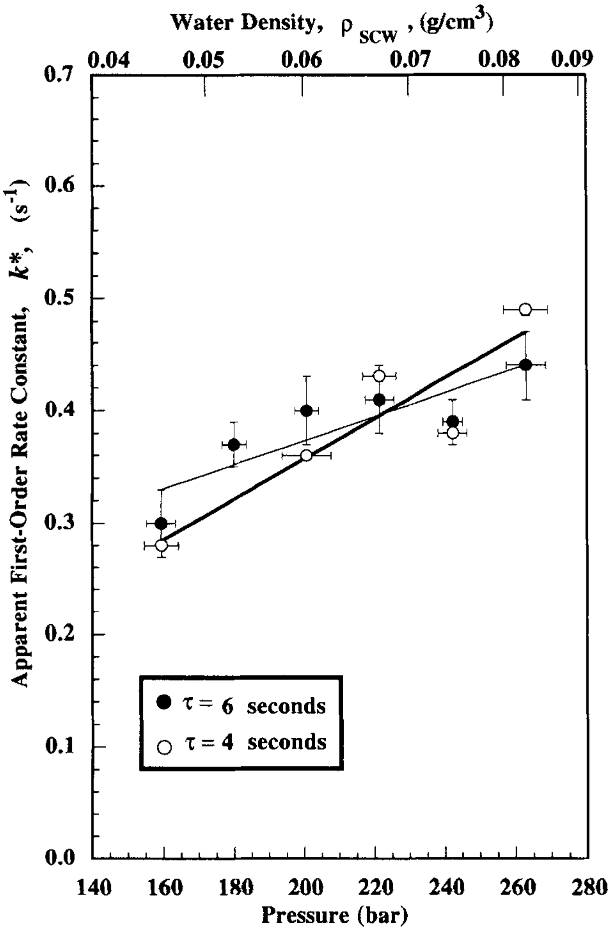


Figure 6. Effects of operating pressure (fluid density) on the apparent first-order rate constant, k^*, for acetic acid oxidation at 550°C.

Experimental conditions: $[CH_3COOH]_0 = (0.95 \pm 0.01) \times 10^{-3}$ mol/L; $[O_2]_0 = (2.09 \pm 0.02) \times 10^{-3}$ mol/L; 95% confidence intervals are shown.

less of residence time. But with residence times on the order of the induction time, k^* increases with increasing residence time. Specifically, in six experiments, acetic acid's k^* value changed from 0.12 to 0.14 s^{-1} over residence times of 4.9 to 9.7 s at 246 bar and a 4:2 oxygen-to-organic feed ratio. Admittedly, the increase is slight and is much smaller than the increase reported by Holgate and Tester (1994a) with H_2 where k^* increased from 0.13 to 0.28 s^{-1} over residence times of about 3.4 to 5.5 s at 246 bar.

In our apparatus, variation in fluid density combined with flow restrictions imposed by the feed pump and the desire to maintain a Reynolds number (*Re*) above the critical value of 2100 to ensure turbulent flow caused unavoidable variation in residence time with operating pressure. At low pressures or densities, the maximum residence time is governed by the need to maintain turbulent conditions, while at high pressures, the minimum residence time is set by the maximum pump flow rate. Therefore, longer residence times generally correspond to higher pressures as well as increased values of k^*. The pressure dependence of k^* is therefore somewhat exaggerated. Since residence times are coupled with pressure, true pressure or density effects are probably less pronounced than shown in Figure 6. The fact that not all values of k^* at 6-s residence time are greater than the corresponding experiment at 4 s may indicate that induction time itself is a function of pressure.

Concentrations of the major gaseous product species in the reactor effluent were examined as a function of pressure for a constant residence time of 4 s. Pressure variation over the conditions studied indicate virtually no effect on CH_4 concentration, while at the higher pressures, CO_2 production is slightly enhanced at the expense of CO (in the range 160 to 260 bar). As partial oxidation products form, the oxidation of acetic acid occurs simultaneously with the oxidation of product intermediates (CH_4, CO, and so on). The possibility that the oxidation profile of carbon monoxide differs in the presence of other compounds when all other conditions remain the same cannot be tested since CO is no doubt being created and destroyed simultaneously.

Liquid product distributions may change slightly with pressure, as indicated by the trace of propenoic acid detected under conditions of 550°C, 160 bar, and residence time of 5.4 s. This experiment gave about 80% conversion of acetic acid. A comparable experiment at 263 bar, 550°C, and a residence time of 5.9 s gave nearly the same liquid chromatogram, but slightly increased acetic acid conversion (to 93%), and increased CH_4 yield from 12% of the gaseous effluent to 16%.

Although these few variable-pressure experiments are by no means conclusive, they indicate that acetic acid oxidation kinetics are less influenced by pressure than that observed for CO and H_2 oxidation (Holgate and Tester, 1994a,b).

Acetic Acid Hydrolysis in Supercritical Water

Ten experimental runs were conducted without oxygen under pyrolysis or thermohydrolysis conditions. Initially, five hydrolysis runs were performed from 500 to 600°C at 25°C intervals. The remaining five hydrolysis runs were conducted two months later to augment the original data set and to verify reproducibility (see Table 2). One run was conducted at 475°C, while the four others were conducted at 25°C intervals beginning at 512°C and continuing through 587°C. All ten experiments had residence times of about 8.0 s. Although we are unable to introduce water totally free of oxygen, inlet O_2 concentrations in the reactor were approximately 2×10^{-5} mol/L during these hydrolysis experiments, about two orders of magnitude less than for a typical oxidation experiment. It is possible, however, that the small amount of oxygen present may have had some effect. The inlet acetic acid concentration was nominally 1×10^{-3} mol/L. Although none of the experimental conditions in the first set were exactly duplicated, profiles from the second series of experiments followed the same decay profiles obtained in the first set.

Figure 7 shows that despite its reputation as one of the more refractory intermediate compounds in supercritical water reactions below 500°C (Ploos van Amstel and Rietema, 1970; Skaates et al., 1981; Tongdhamachart, 1990; Shanableh and Gloyna, 1991; Holgate 1993), acetic acid can be appreciably destroyed even in the absence of oxidant above 550°C. In fact, its 35% conversion at 600°C and 8-s residence time is quite good compared to some other previously studied compounds. For example, negligible conversion was observed for methane hydrolysis at 652°C and residence times up to 14.8 s

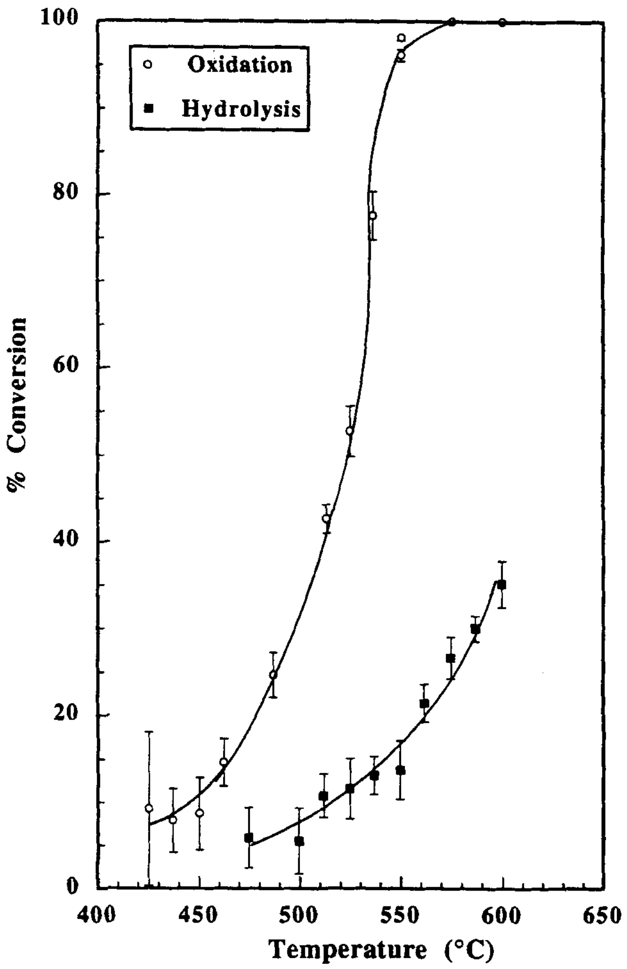


Figure 7. Comparison of acetic acid hydrolysis and oxidation conversion at 246 bar and 8-s residence time.

For hydrolysis, $[CH_3COOH]_0 = (1.00 \pm 0.01) \times 10^{-3}$ mol/L; $[O_2]_0 = (2.19 \pm 0.02) \times 10^{-5}$ mol/L. For oxidation, $[CH_3COOH]_0 = (0.99 \pm 0.01) \times 10^{-3}$ mol/L; $[O_2]_0 = (2.09 \pm 0.02) \times 10^{-3}$ mol/L; 95% confidence intervals are shown.

(Webley and Tester, 1991); hydrolysis of methanol was negligible (2.1%) at 544°C and 6.6-s residence time (Tester et al., 1992); and only 11% of ammonia was converted at 700°C and 10.8-s residence time (Webley et al., 1990, 1991) under oxidative conditions. Thus whether acetic acid is considered refractory or not depends on the thermal intensity of the reactor conditions. Certainly acetic acid hydrolysis and oxidation are occurring simultaneously in the presence of oxygen. This is similar to the concurrent water–gas shift and oxidative pathways present in CO oxidation in supercritical water. Ultimately, some credit (though perhaps small) must be given to hydrolysis when reporting the destruction efficiencies of acetic acid oxidation in supercritical water. Not only is hydrolysis aiding in the breakdown, but its products may also be undergoing further hydrolysis or oxidation. Another comparison of acetic acid hydrolysis with oxidation is given in the form of a first-order Arrhenius plot in Figure 8.

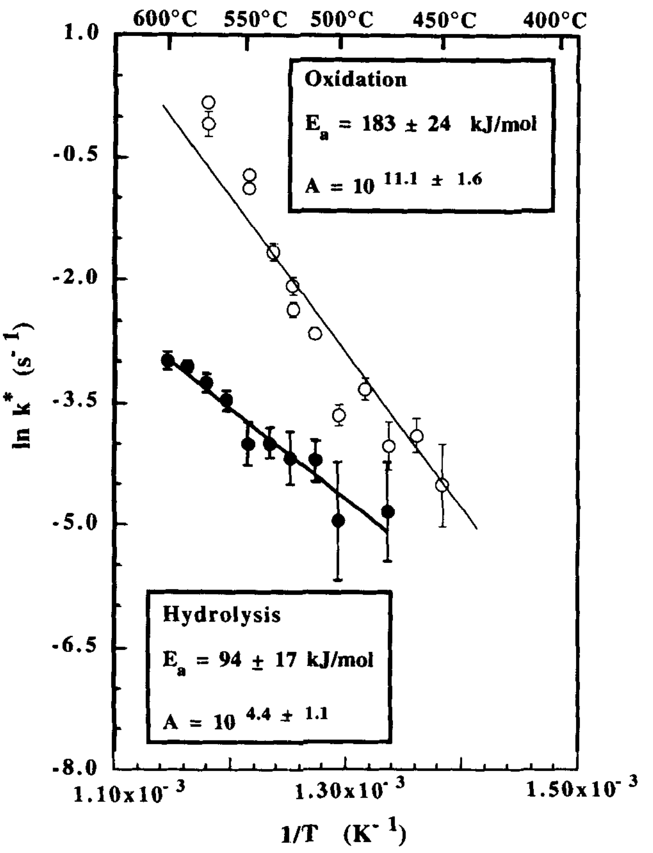


Figure 8. Comparison of acetic acid hydrolysis and oxidation first-order Arrhenius plots at 246 bar and 8-s residence time.

For hydrolysis, $[CH_3COOH]_0 = (1.00 \pm 0.01) \times 10^{-3}$ mol/L; $[O_2]_0 = (2.19 \pm 0.02) \times 10^{-5}$ mol/L. For oxidation, $[CH_3COOH]_0 = (0.99 \pm 0.01) \times 10^{-3}$ mol/L; $[O_2]_0 = (2.09 \pm 0.02) \times 10^{-3}$ mol/L; 95% confidence intervals are shown.

Analysis of the hydrolysis liquid effluent via HPLC at 210 nm gave only unreacted acetic acid and trace amounts ($\sim 10^{-7}$ mol/L) of propenoic acid, identified by retention-time matches with pure compounds. The propenoic acid peak was no doubt at the limit of detection of our HPLC method, as it was not always detected in every liquid sample taken from a specific experiment. For the experimental conditions of $[CH_3COOH]_0 = 1 \times 10^{-3}$ mol/L, 550°C, 246 bar, $\tau = 8$ s, hydrolysis conversion of acetic acid was approximately 14%. Similar oxidation conditions ($[O_2]_0 = 2 \times 10^{-3}$ mol/L) gave about 98% conversion of acetic acid.

The major products of acetic acid hydrolysis were gaseous. Gases accounted for $76.0 \pm 16.6\%$ of the carbon reacted at 512°C and generally increased to $93.8 \pm 7.5\%$ of carbon reacted at 600°C. However, at lower temperatures (conversions), the effluent gas flow rate was below the lower limit (~ 0.3 mL/min) of measurability for our apparatus. At low ($< 15\%$) conversion, although CO_2 and CH_4 were the major products, their proportional compositions were not reproducible, hence we obtained somewhat erratic carbon balance closures. At higher gas flow rates (≥ 0.5 mL/min), gaseous compositions were reproducible, but based on only three to four dual gas samples as opposed to the normal six samples taken. At temperatures above 550°C, CH_4 and CO_2 were produced in nearly equal amounts, accounting for $>95\%$ of gas-phase products. CO accounted for 1–2% of the carbon balances, and less than 1% of the total gas. Trace amounts of hydrogen, on order of 10^{-5} mol/L were also detected, accounting for less than 1% of the gaseous products. Other gases specifically tested for but not detected were ethane, ethylene, and acetylene. Minute amounts of nitrogen (from air dissolved in the aqueous feeds and possibly introduced in transferring the gas sample from the sampling port to the GC) and helium (used to pressurize the feeds) were also detected.

An assumed first-order regression of the hydrolysis data gave surprisingly good results, with a rate expression of

$$R_{CH_3COOH} = 10^{4.4 \pm 1.1} \exp\left(\frac{-94 \pm 17}{RT}\right)[CH_3COOH] \quad (9)$$

with 95% confidence intervals shown. Although the assumed first-order linear regression seems plausible (Figure 8), this regression must be considered somewhat suspect because of the relatively few data on which it is based. A catalytic mechanism model may be more appropriate, but was not attempted in this work. Any model verification will require more experiments over a wider variability of temperature, concentrations, and residence times.

Conclusions

The oxidation kinetics of acetic acid were examined at 246 bar and 425–600°C and over an extended range of fuel equivalence ratios. For the conditions studied, the reaction is nearly first-order (0.72 ± 0.15) in acetic acid and fractionally (0.27 ± 0.15) dependent on oxygen, with a preexponential factor of $10^{9.9 \pm 1.7}$ and an activation energy of 168 ± 21 kJ/mol. Major products of acetic acid oxidation in supercritical water were carbon dioxide, carbon monoxide, methane, and hydrogen. A secondary product detected in lesser amounts was propenoic acid.

Under hydrolysis conditions in the virtual absence of oxygen, approximately 35% conversion of acetic acid was obtained at 600°C and 246 bar, with an 8-s reactor residence time. Regression of the limited hydrolysis data assuming a reaction rate first order in organic gave a global rate expression with a preexponential factor of $10^{4.4 \pm 1.1}$ and an activation energy of 94 ± 17 kJ/mole.

As found in previous studies of hydrogen and carbon monoxide oxidation in supercritical water (Holgate and Tester, 1993, 1994a,b), acetic acid exhibited a delayed reaction ignition, or induction time. This is indicative of free-radical mechanisms and complicates global reaction modeling. Acetic acid oxidation in supercritical water is less pressure (water density) dependent than carbon monoxide or hydrogen (Holgate and Tester, 1994a,b). The presence of an induction time distorts the pressure effect, making reaction rates seem more pressure dependent than they truly are.

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Notation

A = Arrhenius pre-exponential factor
$[A]_0$ = initial concentration of A
E_a = Arrhenius activation energy
k = reaction rate constant
k' = kinetic decay constant
k^* = apparent first-order reaction rate constant
R = universal gas constant
R_i = reaction rate for species i
ρ = density

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