(**10**, 100 mg, 0.35 mmol) and triethylsilane (0.28 mL, 1.75 mmol) in dry dichloromethane (2 mL) at 0 °C. The reaction mixture was warmed up to room temperature for 20 min and then neutralized with anhydrous potassium carbonate. The reaction mixture was diluted with dichloromethane and washed with water, and the aqueous layer was extracted twice with dichloromethane. The combined organic layer was washed with brine, dried ($MgSO_4$), filtered, and concentrated by rotary evaporation to give 90.7 mg (96%) of product. The spectral analyses were consistent with the structure of compound **11**.

Study of Stable Carbocations Derived from 1 and 10. Solutions were prepared by adding 40 mg of **1** or **10** into 1 mL of a rapidly stirred mixture of CF_3CO_2H:CH_3SO_3H (1:1) at −10 °C. The yellow solutions were examined by ^1H NMR spectroscopy. The spectra were the same, regardless of starting material. The chemical shifts were determined from Me_4Si mixed with acetone-d_6 (1:1 v/v) and sealed in a capillary tube inserted into the sample tube; ^1H NMR δ 8.20 (2 H, d, J = 8.78 Hz), 7.94 (2 H, t, J = 7.84 Hz), 7.73 (2 H, d, J = 9.00 Hz), 7.44 (2 H, t, J = 7.55 Hz), 6.42 (5 H, m), and 4.80 (2 H, s). These spectra were consistent with formation of the 9-benzyl-9-xanthyl cation (**12**). Due to the high instability of the initially formed 9-cycloheptatrienyl-9-xanthyl cation (**2**), efforts to obtain its NMR spectrum at −78 °C failed.

Acknowledgment. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work, the Ohio Supercomputer Center for time on the CRAY X-MP/24, the State of Ohio Academic Challenge Program for the funds for the high-field NMR spectrometer, and the U.S. Department of Education for a cost-sharing grant for the purchase of the GC/MS/DS instrument.

Supplementary Material Available: Geometries, heats of formation, and distributions of formal charge calculated by MNDO for the various species discussed in the text (4 pages). Ordering information is given on any current masthead page.

Formation of Acrylic Acid from Lactic Acid in Supercritical Water

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Supercritical (SC) water is an unusual medium in which fast and specific heterolytic reactions can be conducted at temperatures as high as 400 °C. In supercritical water, lactic acid decomposes into gaseous and liquid products via three primary reaction pathways. Products of the acid-catalyzed heterolytic decarbonylation pathway are carbon monoxide, water, and acetaldehyde. Products of the homolytic, decarboxylation pathway are carbon dioxide, hydrogen, and acetaldehyde. Products of the heterolytic, dehydration pathway are acrylic acid and water. The intramolecular nucleophilic displacement of the α-hydroxyl by the carbonyl group of lactic acid, producing α-propiolactone as an unstable intermediate which subsequently rearranges to become the unsaturated acid, is a likely mechanism for acrylic acid formation, although an intramolecular E2 elimination initiated by attack of the carbonyl oxygen on a methyl hydrogen cannot be ruled out. Support for the former mechanism comes in part from the observed 100% relative yield of acrylic acid from β-propiolactone in SC water.

Introduction

In the vicinity of its critical point (P_c = 22 MPa, T_c = 374 °C), water is a fascinating solvent with many unusual properties. For example, as the hydrostatic pressure P increases from P_c to 34.5 MPa, the dielectric constant of water[1] at 375 °C rises from 4 D to over 12 D, while its density increases from 0.2 to 0.6 g/mL and its ion product[2,3] k_w exceeds 10^{-12}. Thus the properties of supercritical (SC) water more closely resemble the familiar properties of low-temperature aqueous water than those of steam,[4,5] even at temperatures as high as 400 °C. Because of its high temperature, only trace concentrations (10^{-3} M) of acids or salts in SC water are required to effect changes in the pH and ion strength which can influence the rates and mechanisms of many aqueous phase heterolytic chemical reactions.[6,7] Similarly, the novel, gross variations in solvent dielectric constant and density near the critical point can also dramatically influence the reaction chemistry of dissolved species.[8] This paper illustrates the magnitude of these influences on a reaction of particular interest to the biotechnology community: the selective formation of acrylic acid from lactic acid in supercritical water.

Lactic (2-hydroxypropanoic) acid is a commerical fine chemical used primarily by the food, medical, and cosmetic industries. A wide array of biomass, including corn, whey, and sugarcane bagasse can be used as fermentation feedstocks in the manufacture of lactic acid. Lactic acid also appears as a byproduct of many industrial carbohy-

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drate refining processes, such as the alkaline degradation of sugar. In a recent review, Lipinsky and Sinclair[9] discussed the inherent advantages of lactic acid as a chemical feedstock. Bearing a carboxyl and a hydroxyl group, lactic acid exhibits reaction properties that are characteristic of both functionalities.[10,11] However, because of its proximity to the carboxyl group, the selective dehydration of the α-hydroxyl is difficult. A U.S. patent[12] describes an experimental procedure for the conversion of lactic acid to acrylic acid, which involved slowly dropping an aqueous solution of lacitc acid into a heated tube packed with a mixture of Na_2SO_4 and $CaSO_4$. Although a 68% yield of acrylic acid was claimed, no further development of the process has occurred since the patent publication in 1956. Subsequent reports of the conversion of lactic acid to acrylic acid were confined to the foreign patent literature, using processes similar to the one described in ref 12.

In addition to the problems associated with the competing activity of its two major functional groups, other difficulties must be overcome to maximize the conversion of lactic acid to acrylic acid. Lactic acid can undergo self-polymerization, forming a variety of esters. The free acid and the lactate anion react differently, leading to a shift of chemical pathways as a function of acid dissociation. Finally, undesirable secondary reactions must be restrained to prevent loss of acrylic acid. In view of these complexities, our approach to illuminating the reaction chemistry is (1) to identify all chemical pathways composing the reaction network of lactic acid in SC water, (2) to study the effects of various reaction parameters on the individual pathways, and (3) to understand their respective mechanisms.

Experimental Section

The operation of the supercritical flow reactor (SCFR) employed in this research has been described in detail in earlier publications.[6,7,13] In the present work, the liquid products were analyzed by reverse-phase HPLC (Alltech 25 cm × 4.6 mm 10 μ C-18 column with a mobile phase of pH 2 H_3PO_4 in water at 2 mL/min, employing a Waters 6000A solvent delivery system and a RI detector). Gaseous products were analyzed by GC (Hewlett-Packard Model 5840 GC equipped with FID and TCD, and a 6 ft × $^1/_8$ in. SS column packed with 100–120 mesh Supelco Carbosieve S-II, using a 20 mL/min flow of 8.5% H_2 in He, with a temperature program of 6 min at 50 °C followed by a 30 °C/min rise to 220 °C). The identification of species by GC and HPLC retention times was confirmed by GC–MS (Hewlett-Packard Model 5790 GC/5970 MSD, equipped with J & W FSOT DB1701 30 m × 0.25 mm × 0.25 μm capillary column).

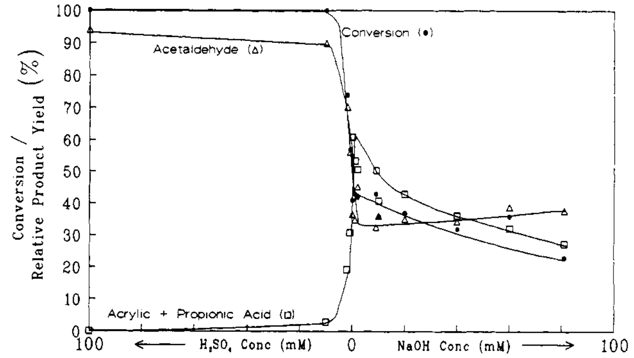

Figure 1. Effect of acid and base concentration on the conversion and liquid product yields from reactions of lactic acid in supercritical water. Experiments conducted at 385 °C, 5000 psi, ~30 s with an initial concentration of 0.1 M at NTP.

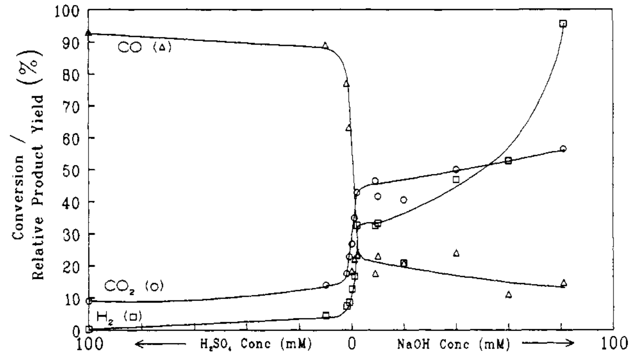

Figure 2. Effect of acid and base concentrations on the gaseous product yields. Experiments conducted at 385 °C, 5000 psi, ~30 s with an initial lactic acid concentration of 0.1 M at NTP.

DL-Lactic acid was obtained (from Sigma Chemical Company) in the form of an 85% syrup. Our initial inquiry into the vendor's literature led us to believe that the reagent contained 85% free acid, with the balance made up of lactic anhydride, lactic acid lactate, or other low molecular weight oligomers. Freshly prepared dilute solutions of this syrup of known concentrations (by weight of syrup) were found to give inconsistent responses when analyzed by HPLC. However, after heating the dilute aqueous solutions at 85 °C overnight, a process by which oligomers are hydrolyzed into free acid, a constant response factor (concentration of lactic acid/peak area) was obtained. Comparison of the ratio of response factors obtained from the untreated and treated standard solutions indicated an increase in lactic acid concentration of about 30%. In both cases, only one peak eluted from the HPLC column. Later, we were advised that the syrup contains an 85% mixture of free acid and oligomers with the balance (15%) water. This advice was proven correct by a quantitative analysis of the concentration of free acid in the heat-treated solutions of the syrup using a series of standards prepared from free-acid crystals (also obtained from Sigma).

For the experiments reported in this paper, the following standard preparation procedure was followed to prepare the reactant lactic acid solution. Typically, 10.58 g of the syrup was mixed with water in a 1-L volumetric flask and heated at 80–90 °C for about 15 h. When the solution returned to room temperature, catalyst (if any) was added and the flask was topped with water. Referenced against standards prepared from free-acid crystals, the concentration of free acid in the resultant solution was 0.1 M. No impurity was detected by HPLC. Sodium lactate, available as a 62% aqueous solution, and ^{13}C-labeled (99 atom%) sodium lactate were used as received.

Results and Discussion

The results of experiments conducted in the SCFR are presented in Table I, which summarizes the reaction conditions, the conversion, and carbon and product yields. A distinction should be noted here between the absolute (mole of product/mole of reactant fed) and relative (mole of product/mole of reactant consumed) product yields, both of which are used in this paper. While the former provides an insight into the influence of reaction conditions on the rates of formation of various products, the latter illustrates more clearly the competition between the various reaction pathways. Major products include acetaldehyde, acrylic acid, propionic acid, acetic acid, CO_2, CO, and H_2. Small amounts of CH_4, C_2H_4, and acetone are also present. Products of esterification and polymerization are not detected by our analytic methods. However, the complete recovery of carbon indicates that these reactions do not occur under our experimental conditions.

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Table I. Selected Results of Lactic Acid Experiments in Supercritical Water

	reaction conditions						absolute product yields, mol %										C bal, %
	init conc, M	temp, °C	pres, psi	time, s	cat.[a]	conv, %	CH_3-CHO	C_2H_3-COOH	C_2H_5-COOH	CH_3-COOH	CH_3-$COCH_3$	CO_2	CO	H_2	CH_4	C_2H_4	
							Effect of pH										
1	0.1	385	5000	33	0.1 M A	100	94	0.0	0.0	7.7		8.7	93	0.3	0.0	0.0	102
2	0.1	385	5000	32	10 mM A	100	90	2.9	0.0			14	89	4.5	1.6	0.0	98
3	0.1	385	5000	33	2 mM A	74	52	8.6	5.6			13	57	5.5	0.9	0.3	99
4	0.1	385	5000	28	1 mM A	57	32	8.8	8.8			13	36	4.9	0.7	0.7	99
5	0.1	385	5000	28	nil	41	15	11	14			11	7.5	5.2	0.4	0.3	100
6	0.1	385	5000	28	1 mM B	43	15	10	13			15	9.5	7.2	0.5	0.6	99
7	0.1	385	5000	31	2 mM B	42	19	13	8.3	5.9	0.6	18	9.8	13	0.4	0.7	106
8	0.1	385	5000	28	9 mM B	43	14	8.7	13			20	7.6	14	0.6	2.2	98
9	0.1	385	5000	32	10 mM B	36	13	9.3	5.4			15	8.3	12	0.3	1.0	96
10	0.1	385	5000	32	20 mM B	37	13	8.0	7.9			15	7.7	7.7	0.3	0.6	96
11	0.1	385	5000	32	40 mM B	32	11	6.4	5.2	3.6	0.3	16	7.7	15	0.3	0.6	99
12	0.1	385	5000	30	60 mM B	36	14	5.3	6.3	5.5	0.5	19	4.0	19	0.2	0.3	97
13	0.1	385	5000	32	81 mM B	23	8.7	2.8	3.5	3.9	0.3	13	3.4	22	0.2	0.2	97
							Effect of Residence Time										
5	0.1	385	5000	28	nil	41	15	11	14			11	7.5	5.2	0.4	0.3	100
14	0.1	385	5000	60	nil	72	30	18	13			25	22	14	0.6	2.8	96
							Effect of Temperature										
15	0.1	350	5000	31	nil	12	2.7	3.6	1.9								96
16	0.1	365	5000	31	nil	21	8.4	7.7	3.7			6.9	8.9	4.0	0.2	0.3	102
17	0.1	375	5000	30	nil	27	9.8	8.5	4.9			9.9	8.2	3.3	0.2	0.3	99
5	0.1	385	5000	28	nil	41	15	11	14			11	7.5	5.2	0.4	0.3	100
18	0.1	400	5000	31	nil	59	21	12	15			20	18	10	0.5	0.8	95
							Effect of Concentration										
19	0.1	385	5000	32	2 mM B	61	26	14	9.2			31	7.3	44	0.8	0.4	
20	0.05	385	5000	32	2 mM B	49	18	11	7.2	4.9		21	11	19	0.5	0.9	95
21	0.1	385	5000	31	2 mM B	39	15	14	5.9	3.7		13	12	10	0.5	0.7	102
22	0.2	385	5000	31	2 mM B	38	17	14	5.4	1.6		10	13	6.6	0.3	0.7	102
							Effect of Solvent Density										
23	0.1	500	5000	26	2 mM B	91	31	0.0	27	24	1.4	68	15	95	10	0.5	108
24	0.1	385	3675	32	2 mM B	84	23	1.7	26	18	1.4	40	10	42	0.8	0.0	89
25	0.1	385	4226	32	2 mM B	57	24	10	13	5.8	0.7	26	12	22	0.7	0.5	99
7	0.1	385	5000	31	2 mM B	42	19	13	8.3	5.9	0.6	18	9.8	13	0.4	0.7	106
26	0.1	350	3000	61	2 mM B	20	7.3	6.7	3.8			8.1	3.9	4.9	0.3	0.5	100
27	0.1	350	4000	60	2 mM B	18	5.8	7.0	2.6	1.0	0.1	7.8	3.8	3.8	0.2	0.2	100
28	0.1	350	5000	56	2 mM B	20	6.1	8.6	3.3	1.3	0.1	6.3	4.6	3.5	0.3	0.2	101
29	0.1	325	5000	195	2 mM B	15	6.7	6.7	4.2	1.1	0.8	6.0	2.8	4.7	0.1	0.3	102

[a] Catalyst: A = H_2SO_4, B = NaOH.

Table II. Results of Acrylic Acid Experiments in Supercritical Water

reactant	pres, psi	temp, °C	time, s	conv, %	absolute product yield, mol %
0.05 M acrylic acid	5000	385	157	51	29% CO_2, 11% H_2, 26% C_2H_4
0.05 M acrylic acid + 0.1 M formic acid	5000	385	124	96	72% C_2H_5COOH, 3% C_2H_4, 8% CH_4

Identification of the Reaction Network. To identify the various pathways in the reaction network, a series of experiments designed to study the effects of pH will first be described. These experiments were conducted at 385 °C, 34.5 MPa, with an initial lactic acid concentration of 0.1 M and a residence time of approximately 30 s. The conversions and relative product yields are plotted as a function of catalyst concentration in Figures 1 and 2. Values of [H^+] and [OH^-] are measured at NTP and will be different at the reaction conditions. As will be discussed in a later paragraph, propionic acid is the product of a secondary reaction of acrylic acid. Its yield is therefore combined with acrylic acid for the present discussion of the primary reaction pathways.

In the presence of the strong acid catalyst H_2SO_4, lactic acid exists primarily in its free acid form, and the lactate anion concentration is very low. The reaction is fast and specific, producing only acetaldehyde and CO (see Figures 1 and 2; exp 1, Table I) in equal proportions. These products indicate the first reaction pathway (pathway I) for the free acid.

As the pH of the reactant solution increases, the overall rate of conversion decreases (see Figure 1). This is accompanied by a major shift in the product distribution. Figure 2 shows the rise in the relative yields of CO_2 and H_2 at the expense of CO, indicating the increased importance of decarboxylation in a basic medium. Decarboxylation represents the second reaction pathway (II).

Referring again to Figure 1, a rapid rise in the formation of acrylic and propionic acid is observed when the acid catalyst is removed. The formation of these acids reaches a maximum with a small amount of base catalyst but declines with further increases in base concentration. These results constitute the first observation of the direct dehydration of lactic acid to acrylic acid in a homogeneous aqueous environment. This is the third and final primary reaction pathway (III) which consumes lactic acid.

To verify that propionic acid is produced by the hydrogenation of acrylic acid, two experiments (see Table II) were conducted. In the absence of free hydrogen, acrylic acid reacts solely via decarboxylation, producing CO_2 and C_2H_4. In the presence of formic acid, which we have found to decompose immediately at this temperature to hydrogen and carbon dioxide, acrylic acid reacts rapidly to give a high yield of propionic acid. These two reactions account for the destruction of acrylic acid formed by pathway III.

Finally, acetaldehyde was introduced into the reactor under similar conditions, and the primary products were

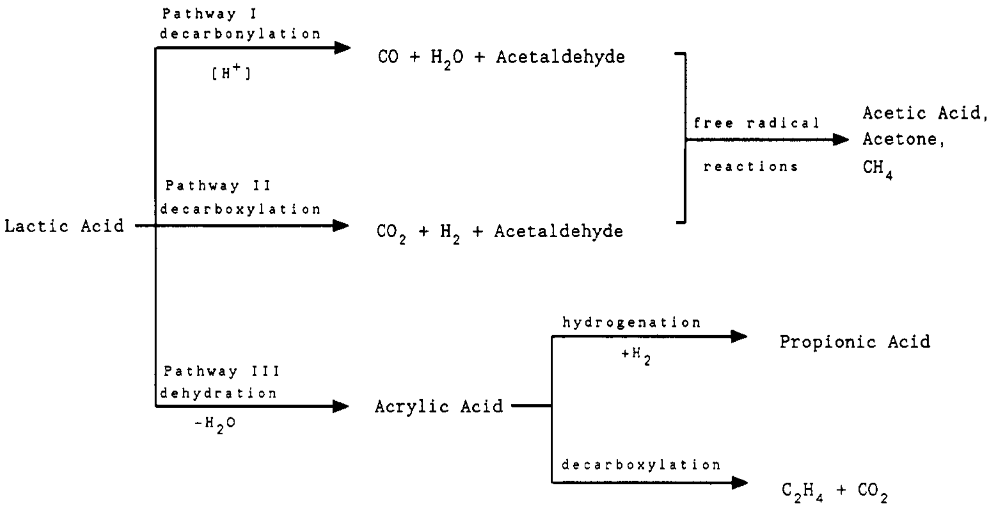

Figure 3. Reaction network governing lactic acid decomposition in near- and supercritical water.

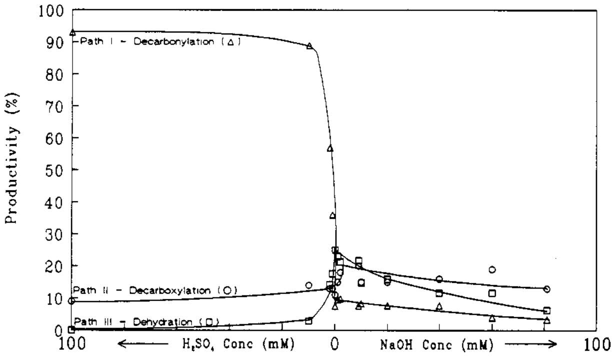

Figure 4. Effect of acid and base concentrations on the productivity of various chemical pathways. Experiments conducted at 385 °C, 5000 psi, ~30 s with an initial lactic acid concentration of 0.1 M at NTP.

acetic acid and H_2 in roughly equal molar proportions. Crotonaldehyde, a well-known aldol condensation product from acetaldehyde,[14] was also observed, together with a small amount of CH_4. This experiment led to the conclusion that acetic acid and CH_4, as well as a portion of the H_2, are all products of secondary reactions involving acetaldehyde.

The reaction network governing lactic acid decomposition in supercritical water, consisting of three primary pathways and multiple secondary reactions, is summarized in Figure 3.

Effects of Reaction Parameters. An examination of the network displayed in Figure 3 reveals that the extent of reaction along each individual pathway can be tracked by the absolute yield of one or a combination of products. The yield of CO is uniquely identified with pathway I, and the sum of acrylic acid, propionic acid, and C_2H_4 indicates the extent of reaction along pathway III. Although CO_2 is a product of both pathway II and the secondary reaction of acrylic acid, the contribution from the latter should be equal to the yield of C_2H_4, which is always insignificant compared to the total yield of CO_2. Hence, the yield of CO_2 is a good indication of the extent of pathway II. Finally, the yields of propionic acid, acetic acid, and ethylene track the extent of the various secondary reactions.

Effects of $[H^+]$ and $[OH^-]$. The data from Figures 1 and 2 is replotted in Figure 4 in terms of productivity, which we define to be the sum of the absolute yields of products associated with a pathway. Increasing $[H^+]$ rapidly increases the rate of pathway I, but decreases the yield of reaction III. Increasing $[OH^-]$ also lowers the yield of reaction III. The effects of $[H^+]$ and $[OH^+]$ on the productivity of reaction II are small.

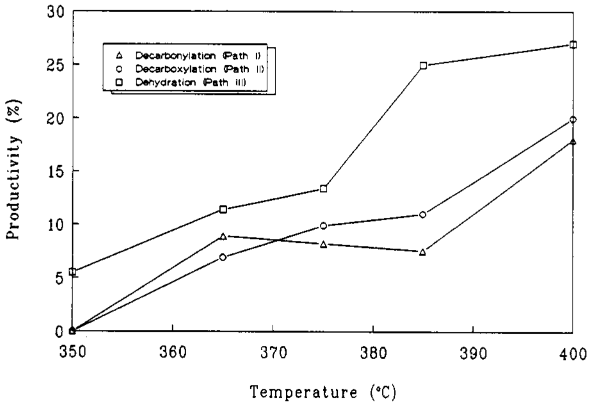

Figure 5. Effect of temperature on the productivity of various reaction pathways. Experiments conducted at 5000 psi, ~30 s with an initial lactic acid concentration of 0.1 M (at NTP) and no catalyst.

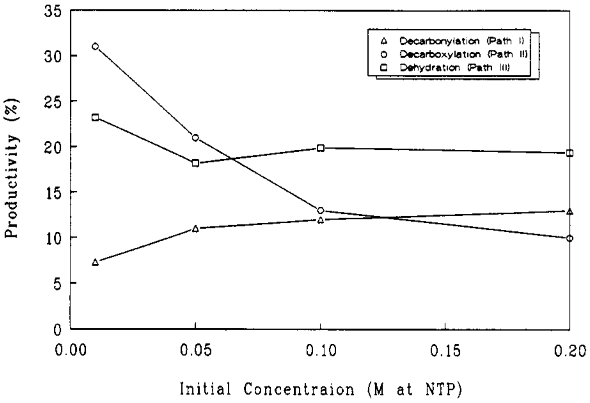

Figure 6. Effect of initial lactic acid concentration on the productivity of various chemical pathways. Experiments conducted at 385 °C, 5000 psi, ~30 s with 2 mM NaOH in the original reactant solution.

Effects of Temperature and Initial Concentration. Figure 5 shows that increasing temperature increases the rate of all reactions, but does not significantly favor any particular pathway. Increasing the initial concentration

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Table III. Effect of Salt Addition on Lactic Acid Reactions in Water

reaction conditions						productivity,[a] mol %		
lactic acid conc, M	NaCl conc, M	pres, psi	temp, °C	time, s	conv, %	decarbonylation (path I)	decarboxylation (path II)	dehydration (path III)
0.1	0[b]	5000	350	58	20	6	5	12
0.1	1	5000	350	60	47	22	10	23

[a] Producitivity = sum of absolute yields of products associated with a pathway. [b] 2 mM NaOH catalyst added.

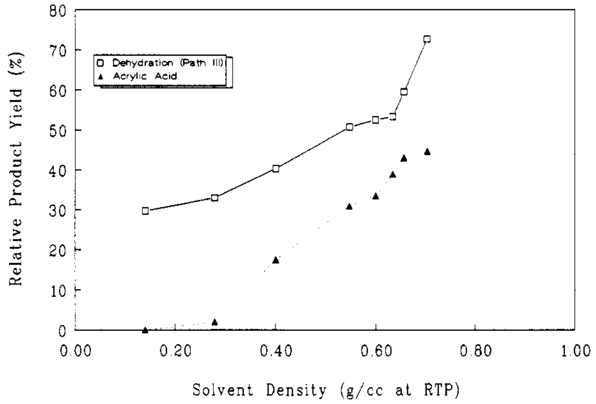

Figure 7. Effect of solvent density on the relative product yields associated with the dehydration pathway.

(see Figure 6) inhibits the decarboxylation pathway, slightly increases the rate of decarbonylation, but does not significantly affect the dehydration pathway. Thus pathway III follows an apparent first-order rate law.

Effects of Pressure/Solvent Density. Le Chatelier's Principle suggests that increasing pressure should preferentially favor the formation of acrylic acid via pathway III (which produces two product molecules from one molecule of lactic acid) over pathways I and II (which generate three molecules each). But if the yields are controlled by kinetic effects, the influence of pressure may be more subtle. For example, increasing pressure dramatically increases solvent density near the solvent's critical point. Associated with a change in solvent density are changes in other physical properties, such as solvent polarity and dielectric constant, both of which play an important role in ionic chemistry. The sum of the relative yields of acrylic and propionic acid is plotted against solvent density in Figure 7. This graph is composed of four sets of data from experiments of varying pressures at four different constant temperatures. Together, they reveal a coherent trend as a function of solvent density. Clearly, increasing solvent density favors pathway III.

A comparison of the absolute product yields at different pressures (but constant temperature and residence time) provides further insights into the effect of pressure. Figure 8 shows that increasing pressure (solvent density) inhibits pathway II and has no effect on pathway I. While the rate of reaction III does not change appreciably, pressure is also effective in inhibiting the secondary hydrogenation of acrylic acid to propionic acid.

Effects of Ionic Strength. Table III shows the effect of conducting the reaction in a 1 M NaCl solution. Increasing ionic strength increases the rates of all reaction pathways.

Reaction Mechanisms

Pathway I. The acid-catalyzed mechanism of pathway I was investigated using ^{13}C-labeled lactate ($CH_3CHOH^{13}COO^-$). Unlabeled and labeled sodium lactate were mixed in 1.25:1 M ratio to provide 100 mL of 0.05 M lactate solution. Subsequently, 0.04 M of H_2SO_4 was added to the solution to convert at least a portion of the lactate to lactic acid. The experiment was conducted at 385 °C, 5000 psi, and 32-s residence time. Analysis of products by GC–MS revealed the formation of ^{13}CO, whereas no labeled carbon was found on acetaldehyde. These results point to the elimination of the carboxylic OH and subsequent loss of the carbonyl group as CO. Figure 9 suggests the probable mechanism for this pathway. α-Hydroxy acids are known[15] to lose carbon monoxide in the presence of strong acids like H_2SO_4, and the acyl cation is the likely intermediate. This decarbonylation mechanism is further supported by the increase in the rate of the reaction by the addition of salt, which helps to stabilize the charged transition state.

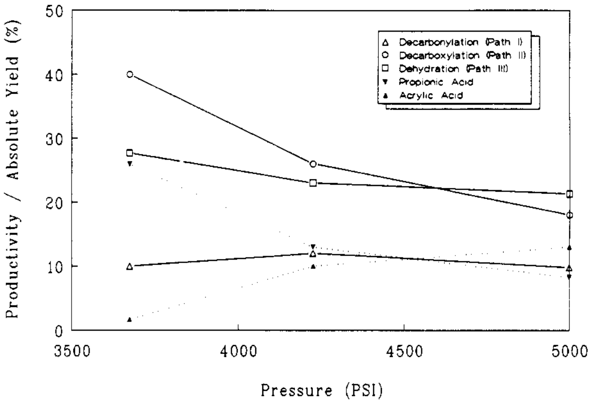

Figure 8. Effect of pressure on the productivity of various chemical pathways and yields of dehydration products. Experiments conducted at 385 °C, ~30 s with an initial lactic acid concentration of 2 mM NaOH at NTP.

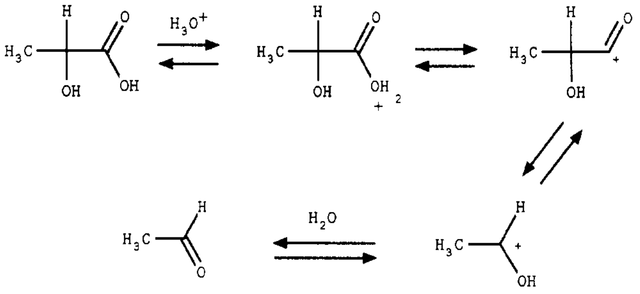

Figure 9. The probable mechanism for acid-catalyzed decarbonylation.

Pathway II. In addition to the ^{13}CO, $^{13}CO_2$ was also found in the product mixture of the labeling experiment described above, thus confirming the formation of CO_2 via decarboxylation of the carboxyl group of lactic acid. However, a "simple" decarboxylation mechanism is unable to account for the formation of hydrogen in this pathway. Instead, simple decarboxylation predicts the formation of ethanol, which (though reported as a decarboxylation product in the literature[11]) was never detected under our operating conditions. Decarboxylation of β-hydroxy acids is well known. It is a common side reaction in the Perkin

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Table IV. Effect of Reactant Ionization on Acrylic Acid Formation

reactant	pres, psi	temp, °C	time, s	conv, %	productivity[a] of pathway III, %
0.1 M lactic acid	5000	385	28	41	25
0.12 M lactate + 50 mM H_2SO_4	5000	385	30	24	8.4
0.12 M lactate + 20 mM H_2SO_4	5000	385	30	16	4.8
0.12 M lactate + 10 mM H_2SO_4	5000	385	31	11	3.6
0.12 M lactate	5000	385	30	7.6	1.4

[a] Productivity = sum of absolute yields of products associated with a pathway.

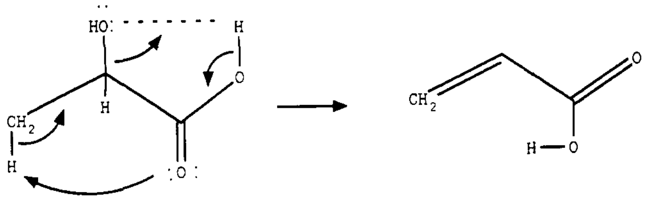

Figure 10. Elimination mechanism for dehydration of lactic acid in supercritical water.

reaction,[15] for instance. However, this loss of CO_2 from an α-hydroxy acid poses a more difficult mechanistic question. Lead tetraacetate induced decarboxylations are known,[15] and the products are the corresponding aldehydes or ketones. Our results point to a free-radical mechanism in the decarboxylation pathway. For instance, parameters which change the ionic characteristics of the reaction environment, such as $[H^+]$, $[OH^-]$, and salt addition, have only a slight effect (relative to the effects on pathways I and III) on the rate of decarboxylation. However, increasing pressure effectively inhibits this pathway, in accord with the expectation that increasing solvent density inhibits free-radical reactions via the cage effect. The appearance of acetic acid, acetone, and CH_4 as free-radical byproducts further supports this conclusion (see the following discussion on secondary pathways).

Pathway III. Acrylic acid appears at first to be the product of a simple acid-catalyzed dehydration. However, the experimental data indicate that this pathway is catalyzed by neither acid nor base, as might have been expected. Instead, acids and bases inhibit the reaction. The highest acrylic acid yield is achieved in a close to neutral condition. This result, combined with the observed first-order rate law, suggests a purely intramolecular reaction.

The first intramolecular reaction mechanism we considered involved an internal attack on a β-hydrogen by a basic group, together with the loss of the α-OH group via an E2 elimination mechanism. The carbonyl group is the obvious candidate for the attacking base (see Figure 10). However, if the basicity of the carbonyl group is the key in this intramolecular elimination, one would expect the rate of dehydration to increase when the reactant is lactate anion, which is much more basic. But our data indicate the contrary. As shown in Table IV, the absolute yield from pathway III was substantially reduced when the starting material was lactate ion and increased somewhat with the addition of an acid catalyst, which partially converted the lactate to free acid. This behavior is the same as observed when base is added to the free-acid reactant. The most probable mechanistic explanation for this behavior involves hydrogen bonding between the carboxyl hydrogen and the oxygen of the α-hydroxyl group. The carboxyl proton may be transferred to the departing hydroxyl during the elimination, thereby making it a better leaving group. It is worthwhile to note that this hydrogen-bonding aspect of the mechanism can include a solvent water molecule (or several) as a bridge which is hydrogen bonded to both the departing hydroxyl group and the carboxyl hydrogen. The rapid structural diffusion of $H_9O_4^+$ complexes by the fast formation and dissociation of hydrogen bonds has been used to explain the unusually high mobility of protons in water at high temperatures and pressures.[16] Thus the low yield of acrylic acid from lactate ion probably reflects the inability of the anion to donate a proton to the leaving hydroxyl group during elimination.

The arguments for the critical role played by the acidic proton in the dehydratio mechanism are in accord with the results of another experiment which showed that elimination of the α-hydroxyl does not occur in the absence of the carboxylic hydroxyl. This experiment was conducted in water at 34.5 MPa, 385 °C, with 3-hydroxy-2-butanone as substrate (no catalyst). If the carboxylic hydroxyl group plays no role in the dehydration reaction, then methyl vinyl ketone should appear as the dehydration product. On the other hand, if the carboxyl hydroxyl is needed for dehydration, no methyl vinyl ketone should appear. The major product detected in this experiment was 2,3-butanedione; no methyl vinyl ketone was found.

A related experiment involving 0.1 M lactic acid in D_2O at 34.5 MPa and 385 °C for 32 s suggests the relative ease by which the proton is transferred to the leaving hydroxyl group. In this experiment, the acrylic acid yield did not change relative to the reference experiment in H_2O. Moreover, only minor reductions in the yields of all other major products were observed. If the transfer of the proton were not facile, the substitution of D for H in the carboxyl group would have reduced the yield of acrylic acid as an artifact of the kinetic isotope effect. The absence of a detectable kinetic isotope effect is consistent with findings (mentioned earlier in this paper) concerning the high mobility of protons in supercritical water.[16] Note that the facile transfer of protons during a concerted reaction differs from dissociation of lactic acid into lactate anion and H_3O^+. As already described, specific acid catalysis by H_3O^+ leads to enhanced yields of CO and acetaldehyde. Apparently, in supercritical water protons can be transferred without the formation of an H_3O^+ intermediate species.

An alternative intramolecular reaction mechanism involves nucleophilic displacement of the hydrogen-bonded α-hydroxyl by the carbonyl group, resulting in the formation of an intermediate α-lactone and the loss of a water molecule (see Figure 11). Although α-lactones are very unstable and have never been isolated, they have been postulated as reaction intermediates.[17] On the other hand, β- and γ-lactones are stable. Their formations from corresponding hydroxy acids[15] as well as their reactions to yield unsaturated acids[18] have been reported.

If the displacement mechanism outlined in Figure 11 is in fact responsible for the formation of acrylic acid, high yields of unsaturated acids from lactones are to be expected. Since α-propiolactone cannot be obtained, we

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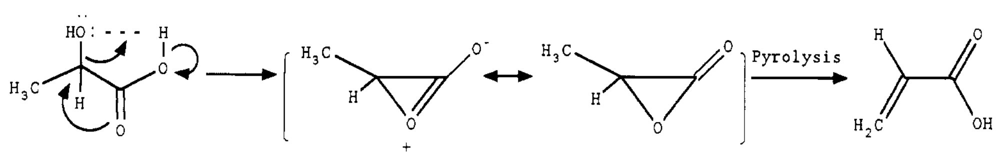

Figure 11. The likely mechanism for formation of acrylic acid from lactic acid in supercritical water.

Table V. Results of Model Compound Studies

reactant	pres, psi	temp, °C	time, s	absolute product yields, mol %
0.125 M β-butyrolactone	5000	385	32	4% β-hydroxybutyric acid 5% 2-butenoic acid 81% CO_2, propene
0.125 M β-hydroxybutyric acid	5000	385	32	4.5% β-hydroxybutyric acid 7% 2-butenoic acid 70% CO_2, propene

conducted a series of experiments using as reactants γ-, β-, and α-hydroxybutyric acids (obtained by adding H_2SO_4 to the commercially available hydroxybutyric acid sodium salt in a acid/salt molar ratio of 4:5) and their associated lactones. γ-Butyrolactone forms rapidly at room conditions from the γ-acid, giving a stable mixture of lactone and hydroxybutyric acid in a 2:1 ratio. Both components were found to be stable after 30 s at 385 °C and 34.5 MPa. In a companion experiment employing identical reaction conditions with γ-butyrolactone as the starting material, 100% of the lactone was recovered. Next, two experiments employing β-hydroxybutric acid and β-butyrolactone as reactants were conducted. The results are shown in Table V. Since 2-butenoic acid is very unstable and reacts rapidly to form propene and CO_2 (this was verified by yet another experiment involving 2-butenoic acid as reactant, showing rapid conversion to propene and CO_2), the propene yield should be added to that of the 2-butenoic acid to measure the total formation of the unsaturated acid. The following conclusions can be drawn from these two experiments. First, the β-lactone is not very stable: it either opens to form the hydroxy acid or collapses to form the unsaturated acid. In fact, an analysis of the original reactant solution (of β-lactone in water) indicated a 50:50 mixture of β-lactone and β-hydroxybutyric acid. Second, under the same experimental conditions, a higher yield of dehydration products (2-butenoic acid and propene) is obtained from the lactone than from the acid. These findings are consistent with the assertion that the lactone is an unstable intermediate in the dehydration of the hydroxy acid to the unsaturated acid. The product yields from an experiment involving α-hydroxybutyric were similar to those obtained from the β isomer.

Finally, an experiment using β-propiolactone was conducted under similar conditions. A 88% conversion of the lactone was observed, with a 74% absolute yield of acrylic acid and a 14% yield of C_2H_4 (which is a secondary product of acrylic acid decarboxylation). This extremely (nominal 100%) selective formation of acrylic acid from the lactone provides further support for the notion that strained lactones may be intermediates along the dehydration pathway.

Secondary Pathways. The most simple and satisfactory explanation for the formation of acetic acid is the hydrolysis of ketene formed from acetaldehyde through the acetyl radical. Other products of this chain reaction include H_2, CH_4, and acetone as observed. Propionic acid is also a likely product of the free-radical hydrogenation of acrylic acid. The inhibition of its formation by increased solvent density (via the cage effect) supports this conclusion.

Conclusions

1. Three major reaction pathways compete to consume lactic acid in supercritical water.
2. Carbon monoxide, water, and acetaldehyde are products of the acid catalyzed, heterolytic, decarbonylation pathway.
3. Carbon dioxide, hydrogen, and acetaldehyde are products of the homolytic, decarboxylation pathway.
4. Acrylic acid and water are products of the dehydration pathway.
5. The mechanism for acrylic acid formation from lactic acid probably involves the intramolecular, nucleophilic displacement of the α-hydroxyl by the carbonyl group, producing α-propiolactone as an unstable intermediate. In SC water this lactone quickly collapses to form the unsaturated acid.
6. In SC water, β-propiolactone very quickly and selectively decomposes to acrylic acid, thereby supporting the posited nucleophilic displacement mechanism for acrylic acid formation from lactic acid.
7. In SC water, the β-lactone of hydroxybutyric acid also offer higher yields of 2-butenoic acid than the corresponding β-hydroxybutyric acid. Again, this finding supports the nucleophilic displacement mechanism.
8. Despite the lactone results, we cannot rule out a mechanism involving an E2 elimination initiated by attack of the carbonyl oxygen on a methyl hydrogen.
9. Any method for effecting the isomerization of α-hydroxypropanoic acid to β-hydroxypropanoic acid will enable lactic acid to become a major potential feedstock for the production of acrylic acid.

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Registry No. H_2O, 7732-18-5; CH_3CHO, 75-07-0; $C_2H_3CO_2H$, 79-10-7; $C_2H_5CO_2H$, 79-09-4; CH_3CO_2H, 64-19-7; CH_3COCH_3, 67-64-1; CO_2, 124-38-9; CO, 630-08-0; H_2, 1333-74-0; CH_4, 74-82-8; C_2H_4, 74-85-1; DL-lactic acid, 598-82-3; β-butyrolactone, 3068-88-0; β-hydroxybutyric acid, 300-85-6; propene, 115-07-1; 2-butenoic acid, 3724-65-0.