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Quantifying Rate Enhancements for Acid Catalysis in CO_2-Enriched High-Temperature Water

Shawn E. Hunter and Phillip E. Savage
Chemical Engineering Dept., University of Michigan, Ann Arbor, MI 48109

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Thermodynamic calculations revealed that 10 to 100-fold increases in reaction rate are obtainable with added CO_2 (0.1–1 MPa) for an acid-catalyzed reaction in high-temperature liquid water (HTW) that is first order in H^+ concentration. These calculations suggest that CO_2 is most effective as a rate-enhancing additive in HTW at lower temperatures (150–200°C). When compared with increased temperature as a competitive option for accelerating acid-catalyzed reactions in HTW, CO_2 addition generally carries a lower pressure penalty (and no temperature penalty) for the model acid-catalyzed reaction with activation energies of up to 35 kcal/mol. An experimental survey revealed that CO_2 addition is effective for achieving increased reaction rates for dibenzyl ether hydrolysis in HTW, but that bisphenol A cleavage, methyl benzoate hydrolysis, and o-phthalic acid decarboxylation were not significantly impacted by added CO_2. This behavior is consistent with previous results for these reactions wherein mineral acid, rather than CO_2, was added to lower the pH. A summary of experimental results reported for reactions in CO_2-enriched HTW revealed that product yields of some reactions can be increased by a factor of 23 with added CO_2. Taken collectively, these results suggest that CO_2 addition may be a practical technique for making HTW more attractive as a reaction medium for acid-catalyzed organic synthesis. © 2007 American Institute of Chemical Engineers *AIChE J,* 54: 516–528, 2008

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Introduction

Many fundamental and commercially relevant chemical transformations are accessible through acid catalysis. As a result, acid catalysis abounds in the chemical industry, and is perhaps the most widespread catalytic technique applied commercially.[1] Although acid catalysis is the core technology behind a significant number of industrial chemical processes, environmental concerns associated with acid-catalyzed processes persist.[2,3] The classical acid-catalyzed reaction is achieved in the presence of a strong mineral acid such as HCl or H_2SO_4. One of the most significant environmental burdens associated with the use of these catalysts is the generation of waste salt. In processes that use mineral acids, it is more economical to neutralize the acid catalyst with caustic, and dispose of the resulting salt solution, than to recover the catalyst for reuse. Accordingly, these processes generate a tremendous amount of waste salt. The handling of corrosive mineral acids presents a materials-of-construction challenge, especially at elevated temperature, as corrosion can lead to equipment failure with potential for spill or release. Corrosion-resistant materials, such as expensive metals, delicate glass-linings, or temperature-limiting polymers, are therefore essential for safe operation using mineral acids. As environmental considerations become increasingly important for sustainable chemical processing, next generation process development must consider alternative technologies for acid-catalyzed reactions.

One technology that has been explored as an alternative and environmentally benign approach to acid catalysis is the

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Correspondence concerning this article should be addressed to P. E. Savage at psavage@umich.edu.

Current address of S. E. Hunter: Dow Chemical Co., Freeport, TX 77541.

use of high-temperature liquid water (HTW), or liquid water at 150°C $< T <$ 350°C, as a reaction medium. HTW is attractive as a medium for organic chemistry because it is nontoxic, nonflammable, inexpensive, and renewable, and its use is consistent with the principles of green chemistry.[4] Further, HTW is capable of dissolving significant amounts of small organic molecules when compared with room temperature water, with solubilities of up to 0.01 mole fraction (~0.6 mol/L) being achieved for nonpolar molecules such as benzene.[5] Acid catalysis is a particularly interesting application of HTW, as many acid-catalyzed transformations occur in HTW without added catalyst. Examples of these reactions are numerous in the literature, and include hydration, dehydration, hydrolysis, alkylation, condensation, and rearrangement.[6] The occurrence of these reactions in water without catalyst has been attributed to the high native ion product [$K_W = (H^+)(OH^-)$ up to 10^{-11} mol^2/kg^2], although recent evidence[7,8] suggests that H_2O may play a more important role for this phenomenon.

Although acid catalysis occurs in HTW without added catalyst, and despite the environmental benefits that result from its implementation, industrial application of HTW as a reaction medium has been slow to occur. The development of a technique to accelerate acid-catalyzed reactions in HTW should make HTW more appealing for large-scale processes. One such technique, which we explore here, is the use of CO_2 as an additive. In an aqueous medium, CO_2 dissolves to form carbonic acid, which dissociates to lower the pH of the mixture. The resulting acidic medium is expected to provide acid-catalyzed reaction rates that are greater than those that occur in HTW alone. Rate enhancements achieved with added CO_2 could make HTW a more industrially attractive technology.

Application of CO_2 to HTW for accelerated acid catalysis holds some environmental advantages over the use of mineral acids. As a catalyst (or catalyst-forming additive), CO_2 is more environmentally benign than mineral acid and does not require neutralization. In fact, nearly complete catalyst recovery should be possible in a CO_2-enriched HTW process, because of the volatile nature of CO_2. Figure 1 presents a flow diagram for an idealized acid-catalyzed process using CO_2-enriched HTW as the medium. In this process, the homogeneous reactor effluent is depressurized to form a CO_2-rich vapor, an H_2O-rich liquid, and an organic-rich liquid. The CO_2-rich vapor and H_2O-rich liquid are recycled back to the reactor, whereas the organic-rich liquid is decanted off as the product. Clearly, this process presents fewer environmental challenges than one that employs mineral acid as the catalyst.

CO_2-enriched HTW has been demonstrated as a more effective medium than HTW for some acid-catalyzed reactions.[7,9–12] In these cases, the observed increases in conversion or product yield are consistent with increased rates resulting from a more acidic reaction medium. In this article, we seek to further explore the application of CO_2-enriched HTW as an environmentally benign medium for acid catalysis. Our previous work[10] provided proof-of-concept results for two reactions in CO_2-enriched HTW and determined the pH attainable in a batch reactor with added CO_2. In this article, we provide an overview of the relevant thermodynamic constants for CO_2-enriched HTW and then extend our earlier work on several fronts. We first examine the increase in operating pressure that will occur as the result of CO_2 addition. We then use this information to estimate potential rate increases for acid-catalyzed reactions in HTW with added CO_2, and compare these rate increases with those expected in HTW at higher temperatures. We then present new experimental results for four different reactions in HTW with added CO_2. We conclude this study by summarizing this work in light of previous data reported for acid-catalyzed reactions in CO_2-enriched HTW.

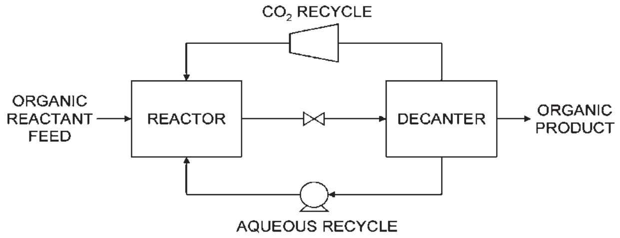


Figure 1. Idealized process flow diagram for an acid-catalyzed process using CO_2-enriched HTW as the reaction medium.

Experimental

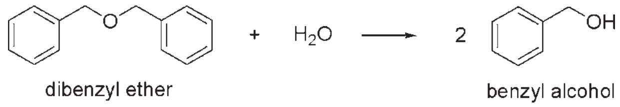
Materials

Deionized water was obtained from tap water using an in-house water purification system composed of ion exchange, reverse osmosis, high-capacity ion exchange, UV sterilization, and submicron filtration units. Dibenzyl ether (DBE), benzyl alcohol, bisphenol A (BPA), phenol, methyl benzoate, benzoic acid, *o*-phthalic acid, sulfuric acid, methanol, acetone, and dimethyl sulfoxide (DMSO) were purchased from Aldrich and used as received. Carbon dioxide was obtained from a commercial source as either dry ice or as "bone dry" grade cylinder gas.

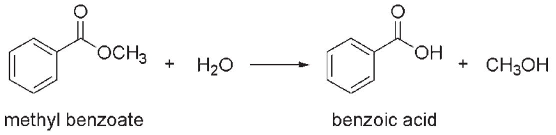
Methods

We conducted experiments in HTW with and without added CO_2 using tubing bomb mini batch reactors assembled from 316 SS Swagelok fittings. Two different reactor assemblies were used, depending on the nature of CO_2 addition. In the first assembly, reactors were constructed from a ¼″ port connector and two ¼″ caps. These ¼″ reactors contained a volume of roughly 0.6 cm^3. In the second assembly, valve-equipped reactors were constructed from a 3/8″ port connector, one 3/8″ cap, a 3/8″ to 1/8″ reducing union, a 3.8-cm long nipple from High Pressure Equipment Company (HiP) (30-HM2-1.5) that was coned and threaded on one end only, and a two way angle valve (30-12HF2) from HiP. The valves were ordered with grafoil packing (427°C temperature rating) in place of the stock Teflon packing (232°C rating) to maximize reactor integrity at elevated temperatures and pressure. The volume of these valve-equipped 3/8″ reactors was roughly 1.8 cm^3.

Reactors were first loaded with a precisely measured amount of organic reactant and placed in a glove box for water addition. The amounts of organic reactant loaded were typically chosen to achieve an initial reactant concentration



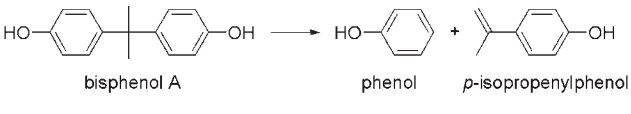
Scheme 1. Dibenzyl ether hydrolysis.



Scheme 3. Methyl benzoate hydrolysis.

of 0.2 mol/kg. Deionized water was also placed within the glove box, which was then sealed. The water was then sparged vigorously with helium gas for at least 25 min to remove dissolved atmospheric gases. Precise amounts of degassed water were loaded into each reactor using a syringe. The target amount of water loaded was chosen such that roughly 95% of the reactor volume would be occupied by the liquid phase at reaction temperature, based on the saturation density of pure liquid water.[13] For experiments using the ¼″ reactors with added CO_2, dry ice was also added to the reactors in the glove box in quantities greater than the target quantity. Gas was allowed to escape slowly from the reactor until the desired amount of CO_2 remained (determined gravimetrically), at which point the reactor was sealed. For experiments using the 3/8″ reactors with added CO_2, the loaded reactors were removed from the glove box, sealed, and attached to a CO_2 gas cylinder via a quick-connect valve. A block valve between the cylinder and reactor was then opened, allowing the reactor to be pressurized with CO_2 gas at a (nonequilibrium) CO_2 loading pressure $P_{CO_2}^{LOAD}$ of 1.4–5.5 MPa. Because the block valve was only opened long enough for the pressure in the transfer line and reactor to equilibrate (~1 s), the amount of CO_2 transferred to the reactor was assumed to be only that which occupied the vapor phase of the reactor at ambient temperature, so that dissolution of CO_2 into the liquid phase was negligible during this loading step. This assumption was applied in estimating the liquid phase pH of these reactors under HTW conditions.

Loaded and sealed reactors were placed in a preheated fluidized sand bath (Techne SBL-2) controlled to within 1°C of the reaction temperature. For the valve-equipped 3/8″ reactors, the reactors were suspended such that the 3/8″ section of the reactor was submerged in the fluidized bath, but the valve was positioned outside of the heated bath zone. This positioning was done to maximize the useful life of the valves. The ¼″ reactors were completely submerged in the sand bath. After the desired reaction time had elapsed, the reactors were removed from the sand bath and submerged in room-temperature water to quench the reaction. The reactors were then placed in a refrigerator for at least 30 min to decrease the loss of any volatile organic species upon reactor opening. Cooled reactors were then opened, and the contents recovered by transferring them to a solvent-containing flask, rinsing the reactor several times with solvent, and collecting the solvent rinses in the flask. The solvents used for DBE hydrolysis (Scheme 1), BPA cleavage, (Scheme 2), methyl benzoate hydrolysis (Scheme 3), and *o*-phthalic acid decarboxylation (Scheme 4) systems were acetone, methanol, acetone, and DMSO, respectively. In the experiments with ¼″ reactors and added CO_2, the cooled reactors were opened slowly and carefully to gradually relieve the pressure in the reactor. In the experiments with valve-equipped reactors and added CO_2, the reactors were depressurized and contents collected using a previously described technique[7,11] involving a septum-containing attachment. Samples of the flask contents were then transferred to gas chromatography (GC) or high-pressure liquid chromatography (HPLC) vials for analysis.

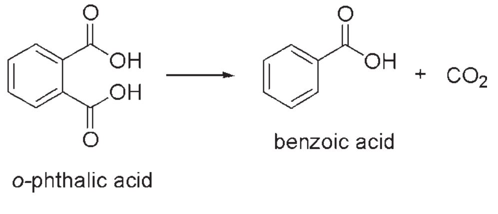


Scheme 2. Bisphenol A cleavage.

GC was performed using an Agilent 6890 with flame ionization detection and an autosampler. In all GC runs, a 50 m × 0.2 mm × 0.33 mm HP-5 capillary column was used to separate the reaction products. The temperature program generally consisted of an isothermal soak at 70°C, followed by a 70°C/min ramp up to 240°C, which was held for an additional isothermal period. The initial isothermal holding time was typically 8–10 min, and was optimized for each system to minimize the time for analysis. Injection volumes were typically 2 μL, and the split ratio was typically 25:1. Products were identified by matching retention times with those of known standards. GC was used to analyze all DBE hydrolysis and BPA cleavage reaction products, as well as methyl benzoate.

HPLC was performed using a Waters HPLC system. Products were again identified by matching retention times with those of known standards. An Alltech LC-18 column, with 4.6 mm internal diameter, 250 cm length, and 5 μm particle size, was used to separate the products. Mobile phases for all HPLC runs were filtered and degassed before use. For methanol and acetonitrile, a teflon filter (Millipore, P/N FHUP04700) was used. For aqueous solutions, a mixed cellulose ester filter (Millipore, P/N HATF04700) was used. The HPLC method used has been described previously.[14] Products were detected using a Waters photo diode array detector set at a wavelength of 254 nm. Benzoic acid and *o*-phthalic acid were analyzed via HPLC.

Calibration curves, established for each GC or HPLC run set, were used to calculate the molar concentrations of the species in the flask samples, which were then used to calculate molar yields of the reaction products. Molar yields were calculated as the ratio of moles of product formed to the



Scheme 4. *o*-Phthalic acid decarboxylation.

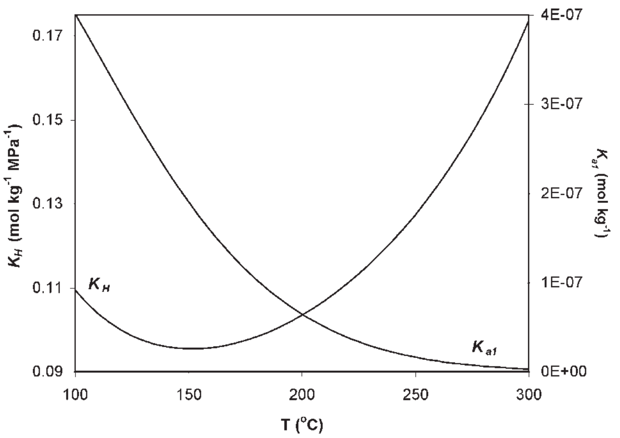


Figure 2. Solubility of CO_2 in H_2O K_H, and first ionization constant of carbonic acid K_{a1}, in H_2O at elevated temperature.

moles of reactant loaded. Aromatic ring balances, defined later for each system, were used to verify no substantial loss of reactor contents during the reaction and were typically greater than 90%. Uncertainties reported herein represent the 95% confidence interval, calculated based on at least three replicate experiments from different reactors.

Results and Discussion

Thermodynamics of the CO_2–H_2O system at high temperatures

The pH of CO_2-enriched HTW is dictated by the solubility of CO_2 in H_2O and by the dissociation of carbonic acid. Thus, we begin discussion of the CO_2–H_2O system at high temperatures by reviewing these quantities.

The solubility of CO_2 in H_2O can be represented by the equilibrium constant K_H, which relates (H_2CO_3*), the concentration of "carbonic acid," to P_{CO_2}, the partial pressure of CO_2:

$$K_H = \frac{(H_2CO_3{}^*)}{P_{CO_2}}. \tag{1}$$

Here, (H_2CO_3*) refers to the sum of the aqueous CO_2 and undissociated carbonic acid concentrations. Herein, curved brackets represent molal concentration, or mol/kg. In an equilibrated CO_2 solution at 25°C, H_2CO_3 comprises less than 0.3% of the undissociated CO_2 species,[15] and H_2CO_3 is not expected to be a significant species at higher temperatures.[16] Hence (H_2CO_3*) is essentially equal to the aqueous concentration of CO_2.

We calculated K_H based on the Henry's constant H[16] as described previously.[10] Figure 2 displays the effect of temperature on K_H from 100 to 300°C. The figure shows that a minimum in CO_2 solubility exists near 150°C. This minimum in solubility at moderate temperatures is typical of gases in HTW.[6] Figure 2 reveals that an increase in temperature in the HTW region favors the dissolution of CO_2 into solution. To understand the impact of temperature on pH, however, dissociation of the ionic species must also be considered.

The first dissociation of carbonic acid in an aqueous medium can be represented by the following equation:

$$H_2CO_3{}^* \rightarrow H^+ + HCO_3^- \qquad K_{a1} = \frac{(H^+)(HCO_3^-)}{(H_2CO_3{}^*)} \tag{2}$$

where K_{a1} is the first dissociation constant of carbonic acid. The bicarbonate anion may also dissociate to form the carbonate anion. CO_2-enriched HTW, however, which contains only dissolved CO_2, will be acidic and exhibit pH < pK_{a1} (pK_{a1} = −log K_{a1}). Hence, the concentration of the carbonate anion in CO_2-enriched HTW will be negligible. We thus focus on K_{a1} for the present discussion.

Patterson and coworkers provide a model for K_{a1} at the saturation pressure of H_2O at infinite dilution.[17] Figure 2, which displays K_{a1} as calculated from their model, shows that carbonic acid becomes a weaker acid as temperature increases. For example, K_{a1} is equal to 6.5×10^{-8} mol/kg at 200°C, and only 3.2×10^{-9} mol/kg at 300°C. This behavior is not surprising, given the decrease in dielectric constant that occurs as the temperature of liquid water increases. Thus, although CO_2 becomes increasingly soluble as temperature increases, carbonic acid is less acidic at higher temperatures. Hence, for a given amount of added CO_2, the pH of HTW solutions increases as temperature increases.[10]

Pressure penalty associated with CO_2-enriched HTW

In our previous article,[10] we estimated the pH of CO_2-enriched HTW for a two-phase system at a given total carbonate loading and for a given liquid phase volume fraction. This estimate is useful for determining the amount of CO_2 required to achieve a given pH in a batch reactor. An obvious consequence of adding CO_2 to HTW is an increase in system pressure. Here, we seek to explore this pressure penalty as related to the pH achieved by adding CO_2. Analysis done in this manner presents a practical inspection of the CO_2–H_2O system, as operating pressure is an important design specification required for process definition and plant design.

We begin by examining the CO_2 partial pressure required to achieve a given pH. The CO_2 partial pressure will be similar to, but not exactly equal to, the increase in process operating pressure resulting from CO_2 addition, because of the nonideality of the system. We address the actual increase in process operating pressure in subsequent sections.

In the CO_2–H_2O system, a charge balance provides the following relation:

$$(H^+) = (OH^-) + (HCO_3^-) + 2(CO_3^{2-}). \tag{3}$$

Translating this relation in terms of the previously defined equilibrium constants, and recognizing the fact that the carbonate ion concentration will be negligible compared with the other species concentrations, leads to the following expression for H^+ concentration:

$$(H^+) = \frac{K_W}{(H^+)} + \frac{K_{a1}K_HP_{CO_2}}{(H^+)}. \tag{4}$$

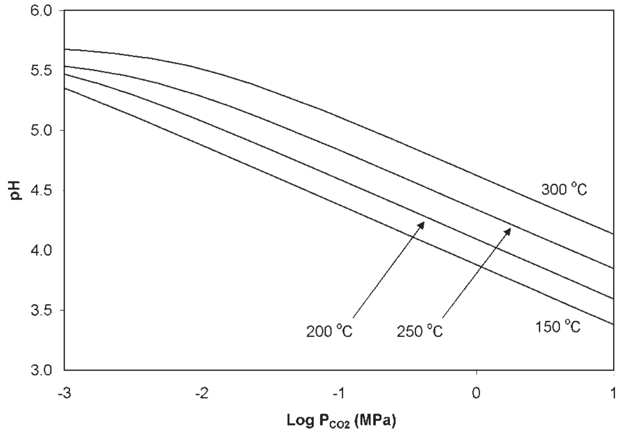


Figure 3. Estimated pH of CO_2-enriched HTW as a function of CO_2 partial pressure.

Solving Eq. 4 for H^+ leads to the final equation used to relate CO_2 partial pressure to H^+ concentration:

$$(H^+) = (K_W + K_{a1}K_H P_{CO_2})^{1/2}. \tag{5}$$

We estimated the pH of CO_2-enriched HTW under varying P_{CO_2} and temperature using Eq. 5. K_W was calculated using the relation provided by Marshall and Franck,[18] K_{a1} was calculated from the Patterson et al. model,[17] and K_H was calculated based on H.[16]

Figure 3 shows the estimated pH for CO_2-enriched HTW. Herein, we define pH as $-\log\,(H^+)$, where the units of (H^+) are mol/kg. The figure shows that the pH is significantly affected by added CO_2, even at modest partial pressures. At low P_{CO_2} (<0.01 MPa), the pH transitions from a K_W-controlled region where

$$(H^+) = K_W{}^{1/2} \tag{6}$$

to a CO_2-controlled region where

$$(H^+) = (K_{a1}K_H P_{CO_2})^{1/2}. \tag{7}$$

The curves show a nonuniform trend with temperature at low P_{CO_2} because the temperature dependence of K_W (K_W-controlled region) is different from the temperature dependence of K_{a1} and K_H (CO_2-controlled region). At higher P_{CO_2} (>0.01 MPa), the pH becomes linearly dependent on $\log P_{CO_2}$. Inspection of Eq. 7 reveals that a two order of magnitude increase in P_{CO_2} is required to decrease the pH by one unit for $P_{CO_2} > 0.01$ MPa. Compared with the pH of neutral HTW, addition of CO_2 at 10 MPa partial pressure leads to a decrease in pH by 2.4–1.6 units over the temperature range of 150–300°C.

Figure 3 also demonstrates the temperature dependence of the pH for a given CO_2 partial pressure. The figure indicates that CO_2-enriched HTW becomes less acidic with increasing temperature for a constant CO_2 partial pressure. As temperature increases, CO_2 becomes more soluble, but H_2CO_3* becomes less acidic. Evidently, the temperature dependence of K_{a1} is more significant than the temperature dependence of K_H for determining the overall temperature dependence of the pH of carbonated HTW solutions. This behavior suggests that CO_2 addition to HTW will be most effective for promoting acid catalysis at lower temperatures (150–200°C).

We point out that the increases in system pressure, when compared with HTW at its saturation pressure, required to achieve the P_{CO_2} displayed in Figure 3 are not equal to the value of P_{CO_2}, because of the nonideal behavior of the CO_2–H_2O system. Rather, the required increase in system pressure is greater than the value of P_{CO_2}. Calculation of the actual system pressure P can be achieved using empirical equations for the bubble- and dew-point curves of the CO_2–H_2O system provided by Blencoe.[19] Using these equations to calculate P and P_{CO_2}, we observe that P_{CO_2} accounts for only 86 and 71% of the increase in system pressure at 200 and 300°C, respectively, at pressure increases of up to 10 MPa. Hence, the increase in process operating pressure, $\Delta P_{\text{process}}$, that occurs as the result of CO_2 addition, will be slightly greater than P_{CO_2}. Because the actual increase in operating pressure is an important consequence of employing CO_2 to accelerate acid-catalyzed reactions, we continue discussion of CO_2-enriched HTW in terms of $\Delta P_{\text{process}}$.

Effect of added CO_2 on rate of reaction

To understand the potential effect of added CO_2 on the rates of acid-catalyzed reactions in HTW, we examined the increase in rate that would result from CO_2 addition for an acid-catalyzed reaction that is first order in both H^+ and reactant A. For reactions of this type, the rate of reaction r is represented as

$$r = k(H^+)(A) \tag{8}$$

where k is the second-order rate constant. In pure HTW, $(H^+) = K_W^{1/2}$ so that the rate of reaction r_{HTW} in pure HTW is equal to

$$r_{\text{HTW}} = kK_W^{1/2}(A). \tag{9}$$

In CO_2-enriched HTW with $(H^+) = (H^+)_{CO_2+\text{HTW}}$, the rate of reaction $r_{CO_2+\text{HTW}}$ is equal to

$$r_{CO_2+\text{HTW}} = k(H^+)_{CO_2+\text{HTW}}(A). \tag{10}$$

Hence, the increase in rate of reaction, or rate increase factor (RIF), achieved by adding CO_2 to HTW can be calculated as the ratio of $r_{CO_2+\text{HTW}}$ to r_{HTW}

$$\text{RIF} = \frac{r_{CO_2+\text{HTW}}}{r_{\text{HTW}}} = \frac{(H^+)_{CO_2+\text{HTW}}}{K_W^{1/2}}. \tag{11}$$

In this development, we seek to understand the effect of $\Delta P_{\text{process}}$ on the RIF. To calculate $(H^+)_{CO_2+\text{HTW}}$ as a function of $\Delta P_{\text{process}}$, we applied Blencoe's empirical equations for the bubble point of CO_2–H_2O mixtures to calculate the mole fraction of CO_2 in the liquid phase, $X^L_{CO_2}$, as a function of $\Delta P_{\text{process}} = P - P^{H_2O}_{\text{sat}}$. We then calculated ($H_2CO_3$*) from $X^L_{CO_2}$ as

$$(H_2CO_3{}^*) = X^L_{CO_2}C_T \tag{12}$$

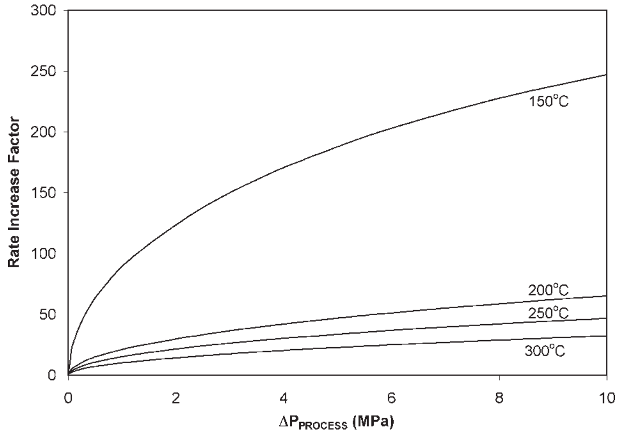


Figure 4. Effect of CO_2 addition, quantified in terms of the resulting increase in process operating pressure, on estimated rate increase factor for CO_2-enriched HTW.

where C_T is the total molal concentration of the liquid phase. $(H^+)_{CO_2+HTW}$ can then be calculated from $(H_2CO_3{}^*)$ as

$$(H^+) = (K_W + K_{a1}(H_2CO_3{}^*))^{1/2}. \qquad (13)$$

We point out that Eq. 13 allows the pH to be calculated on the basis of $\Delta P_{process}$, which can be related to $(H_2CO_3{}^*)$ as discussed earlier, whereas Eq. 5 allows the pH to be calculated on the basis of P_{CO_2}.

We calculated the RIF for an acid-catalyzed reaction, with H^+ order equal to one, in HTW with added CO_2 at 150–300°C and up to $\Delta P_{process} = 10$ MPa using Eq. 11. Figure 4 displays the results of these calculations. The figure suggests that the rate of reaction for an acid-catalyzed reaction in HTW can be significantly increased through the addition of CO_2, provided that the reaction is first order in H^+. At a $\Delta P_{process}$ of 10 MPa, the RIF varied from 247 at 150°C to 33 at 300°C. Decreasing $\Delta P_{process}$ to 1 MPa decreases the RIFs only moderately to 89 at 150°C and 10 at 300°C. Further, at only 0.1 MPa increase in process pressure, RIFs remain significant, ranging from 29 at 150°C to 3.4 at 300°C. Hence, significant rate increases may be possible with only modest CO_2 partial pressures for some acid-catalyzed reactions in HTW.

Figure 4 also demonstrates the temperature dependence of the potential rate increase with added CO_2. Lower temperatures favor larger rate increases. The RIF decreases substantially as temperature increases from 150 to 300°C, but it is still significant at the higher temperature.

The significant change in the effectiveness of CO_2 addition with temperature is explained by the relatively large change in K_{a1} that occurs from 150 to 300°C, in contrast with the smaller changes that occur in K_W and K_H over the same range. Substitution of Eq. 7 into Eq. 11 shows that the RIF can be calculated as

$$\mathrm{RIF} = \left(\frac{K_{a1}K_H}{K_W}\right)^{1/2} P_{CO_2}^{1/2}. \qquad (14)$$

Table 1 lists the values of K_W, K_{a1}, and K_H at 150, 200, 250, and 300°C. As the temperature increases from 150 to 300°C, K_{a1} decreases by almost two orders of magnitude, whereas K_W and K_H do not change significantly. Thus, the ratio $K_{a1}K_H/K_W$ decreases over this temperature range, and the RIF decreases accordingly.

The increase in rate of reaction calculated in Figure 4 applies to an acid-catalyzed reaction that is first order in H^+. Many classical acid-catalyzed reactions are first order in H^+ at lower (near-ambient) temperatures. However, some reactions in HTW may not be first order in H^+ over the range of pH that is practically accessible with added CO_2.[7,8] If an acid-catalyzed reaction in HTW exhibits an apparent reaction order less than unity at near-neutral pH, then the reaction rate will be less sensitive to added CO_2 than is calculated using Eq. 11. Hence, the RIF calculated using Eq. 11 and shown in Figure 4 provides a best-case estimate of the rate increases possible with added CO_2. The actual increase in reaction rate resulting from CO_2 addition may be lower than these calculated values, depending on the sensitivity of the specific reaction to changes in pH.

Effect of added CO_2 on conversion

To visualize the potential effect of CO_2 addition on acid-catalyzed reactions in HTW, we calculated batch reactor conversion vs. time profiles for RIFs ranging from 1 to 100. We performed these calculations for an irreversible, first order reaction using Eq. 15:

$$X = 1 = e^{-\mathrm{RIF}k_0 t} \qquad (15)$$

where X is the conversion and k_0t is the dimensionless reaction time. Figure 5 presents the results of these calculations.

We discuss Figure 5 in terms of the rate increases calculated in Figure 4. For $\Delta P_{Process}$ of 1–10 MPa, and over the temperature range of 200–350°C, we calculated RIFs of roughly 10–100. Figure 5 shows that the conversion can be substantially increased by achieving RIFs in the range 10–100. The increases in conversion are most significant at early times, where the unaccelerated reaction exhibits low conversion. For example, at $k_0t = 2$, the conversion increased from about 2% for the unaccelerated reaction (RIF = 1) to about 19% at a RIF = 10 and to almost 65% at RIF = 100. Significant increases in conversion are also possible at lower values of RIF, as the conversion increased from about 9% for the unaccelerated reaction to about 18 and 39% for RIF = 2 and 5, respectively, at $k_0t = 10$.

Thus, the combined results of Figures 4 and 5 indicate that the addition of CO_2 to HTW at 150–300°C should be effective for achieving significant reaction rate increases for acid-

Table 1. Comparison of K_{a1}, K_W, and K_H at 150, 200, 250, and 300°C

T (°C)	K_W 10^{-12} (mol/kg)^2	K_{a1} (mol/kg)	K_H [mol/(kg MPa)]	K_{a1} K_H/K_W (MPa^{-1})
150	2.3	1.9×10^{-7}	0.09	7500
200	5.1	6.5×10^{-8}	0.10	1200
250	6.4	1.7×10^{-8}	0.12	320
300	3.9	3.2×10^{-9}	0.17	140

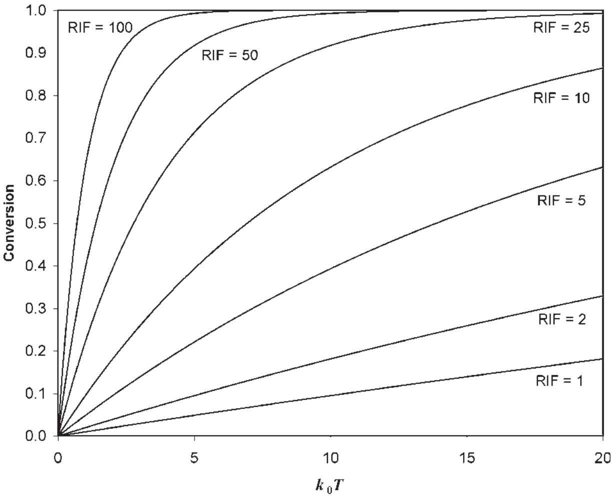


Figure 5. Effect of RIF on conversion profile of first-order, irreversible, isothermal reaction.

RIF is the rate increase factor, defined by Eq. 11.

catalyzed reactions that are first order in H^+. The largest increases will be achieved at lower temperatures.

CO_2-addition vs. increased temperature: operating pressure comparison

In this work, CO_2 is added to HTW for the purpose of achieving increased reaction rates at a given temperature. An obvious second method of achieving increased reaction rates is to increase the reaction temperature, without adding CO_2. In both cases, the system pressure will be higher as a result of the change, as the saturation pressure of H_2O increases with temperature. From a process design standpoint, lower pressures will of course be preferred. A prudent comparison to make, then, is to consider which method is more effective for a given increase in pressure. We explore this question in this section, and compare anticipated RIFs for CO_2-enriched HTW with those obtained by increasing the temperature of HTW.

We begin by calculating the RIF that may be achieved by either adding CO_2 to the system or increasing the temperature of the system. In both cases, we consider operation at saturation conditions, so that a minimal vapor phase is maintained above the reacting liquid phase. For the CO_2-enriched HTW case, we calculate the RIF according to Eq. 11, with (H^+) calculated according to Eq. 13. For the HTW-only case, we again assume an acid-catalyzed reaction first order in both H^+ and reactant A, with Arrhenius temperature dependence, so that

$$\mathrm{RIF}_{\mathrm{HTW}} = \frac{k(T)[(\mathrm{H}^+)(T)](\mathrm{A})}{k(T_0)[(\mathrm{H}^+)(T_0)](\mathrm{A})} = \left(\frac{K_\mathrm{W}(T)}{K_\mathrm{W}(T_0)}\right)^{1/2} \exp\left[-\frac{E_\mathrm{a}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \tag{16}$$

where $k(T)$ is the rate constant at temperature T, $K_W(T)$ is the ion product of water at temperature T, E_a is the activation energy, and T_0 is the base case temperature. In this analysis, $T > T_0$, and $\mathrm{RIF}_{\mathrm{HTW}}$ compares the rate of reaction in "increased-temperature" HTW at temperature T with that in HTW at temperature T_0. We calculated $\mathrm{RIF}_{\mathrm{HTW}}$ considering an activation energy range of 15–35 kcal/mol. A brief survey of the literature[7,20–24] covering more than 10 classically acid-catalyzed reactions conducted in HTW suggests that the activation energies of most acid-catalyzed reactions in HTW fall in this range.

Figure 6 demonstrates the effect of $\Delta P_{\mathrm{process}}$ on the RIF for the two cases. In CO_2-enriched HTW, increasing $\Delta P_{\mathrm{process}}$ via CO_2 addition leads to the expected result of increased RIF, at all $\Delta P_{\mathrm{process}}$ up to 10 MPa. The effect of increased pressure on the RIF for increased-temperature HTW, however, is less obvious. The reaction rate in increased-temperature HTW will be affected by the change in temperature that occurs for a given $\Delta P_{\mathrm{process}}$ and by the change in K_W that occurs as the temperature changes. At lower temperatures, the primary effect of increased pressure is the Arrhenius response of the reaction rate constant to the increased temperature. For example, at $T_0 = 200°C$ the RIF increases essentially monotonically for each investigated activation energy as pressure increases. At higher temperatures, however, the sensitivity of K_W to temperature becomes significant, and K_W decreases with increasing temperature. For reactions at these temperatures with low activation energy, the reaction rate can actually decrease with increased temperature, as demonstrated by the RIF at $T_0 = 300°C$. This behavior is dictated both by the decrease in K_W that occurs at temperatures above 250°C and by the vapor pressure curve of H_2O, which increases in pressure at a greater rate as the temperature approaches the critical temperature. For example, at 200°C, the saturation temperature increases roughly 3°C per 0.1 MPa of pressure increase. At 300°C, this rate is less than 1°C per 0.1 MPa of pressure increase. Thus, even in the absence of the ion product effect, a given reaction in HTW will not increase in rate as quickly with increased saturation pressure at 300°C as it will at 200°C.

The results in Figure 6 show that CO_2 addition is competitive with increased-temperature water at 200°C, superior for most reactions at 250°C, and far superior for all reactions at 300°C. At 200°C, increased-temperature water becomes competitive with CO_2 addition at $\Delta P_{\mathrm{process}} = 2-4$ MPa; at higher temperatures, CO_2 addition provides greater rate enhancements than increased temperature at all $\Delta P_{\mathrm{process}}$ up to 8–10 MPa. This analysis indicates that for the model acid-catalyzed reaction, which is first order in H^+, CO_2 addition is more effective than increased temperature for practically reasonable pressure increases (up to about 2 MPa) over all practical activation energies (up to 35 kcal/mol). By choosing CO_2 addition to achieve a given reaction rate, a much lower pressure penalty is paid, and no temperature penalty is required.

Experimental investigation of acid-catalyzed reactions in CO_2-enriched HTW

We conducted an experimental survey to examine the effect of CO_2 addition on DBE hydrolysis, BPA cleavage, and methyl benzoate hydrolysis. Each of these reactions may proceed via acid catalysis, and may be enhanced by the addition of mineral acid. Their investigation in CO_2-enriched

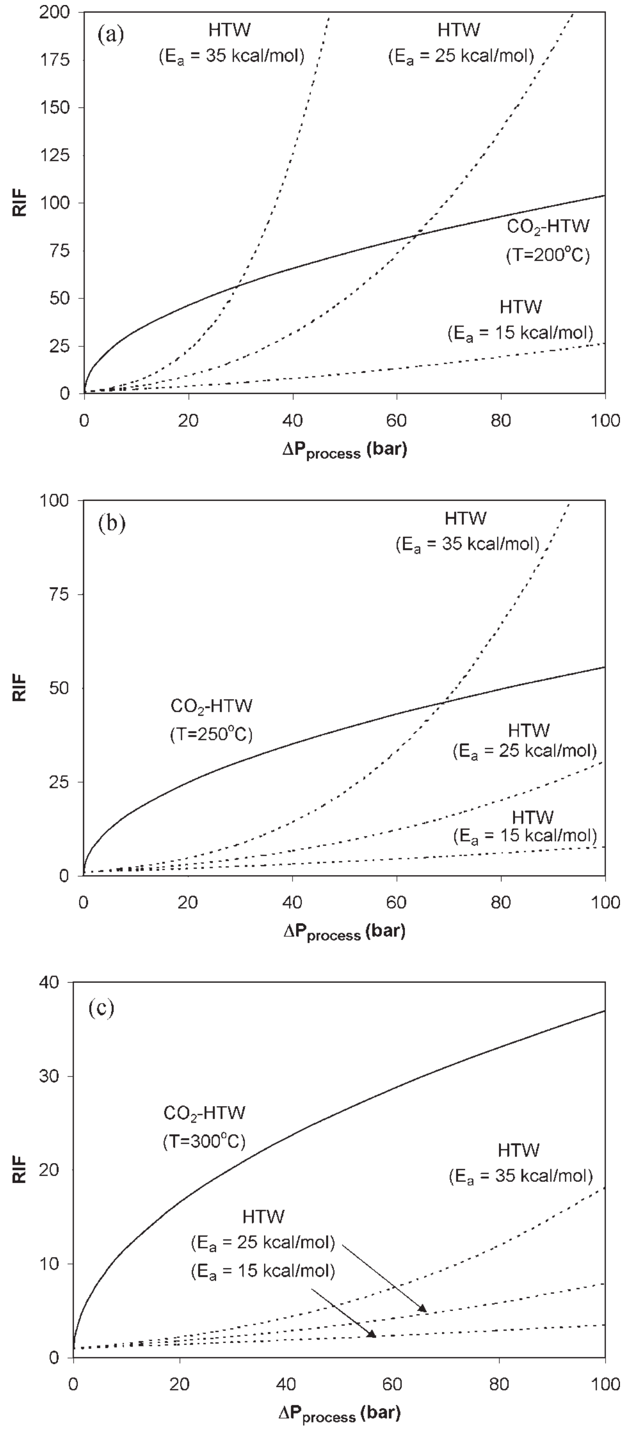


Figure 6. RIF as a function of $\Delta P_{\text{process}}$ for CO_2-enriched HTW at constant temperature (CO_2-HTW) and for increased-temperature HTW (HTW).

(a) $T_0 = 200°\text{C}$ ($P^{\text{sat}}_{H_2O} = 1.6\,\text{MPa}$). In HTW at $\Delta P_{\text{process}} = 10$ MPa ($P^{\text{sat}}_{H_2O} = 11.6\,\text{MPa}$), $T = 322°\text{C}$. (b) $T_0 = 250°\text{C}$ ($P^{\text{sat}}_{H_2O} = 4.0\,\text{MPa}$). In HTW at $\Delta P_{\text{process}} = 10$ MPa ($P^{\text{sat}}_{H_2O} = 14.0\,\text{MPa}$), $T = 337°\text{C}$. (c) $T_0 = 300°\text{C}$ ($P^{\text{sat}}_{H_2O} = 8.6\,\text{MPa}$). In HTW at $\Delta P_{\text{process}} = 10$ MPa ($P^{\text{sat}}_{H_2O} = 18.6\,\text{MPa}$), $T = 360°\text{C}$.

HTW provides new information regarding the potential for CO_2 addition to accelerate acid-catalyzed reactions in HTW, and examines the consistency between CO_2 addition and mineral acid addition. Additionally, we examine the effect of CO_2 addition on *o*-phthalic acid decarboxylation, which has not been investigated as a function of pH in HTW previously, but which is expected to be enhanced by CO_2 addition. We discuss the results of these experiments in this section.

DBE Hydrolysis. DBE is a coal model compound that has received previous attention in HTW.[25–29] Hydrolysis of DBE occurs in HTW without catalyst, and leads to the formation of benzyl alcohol. DBE can also cleave thermally to yield toluene and benzaldehyde at higher temperatures. Comisar et al.[8] examined the effect of added mineral acid on DBE hydrolysis in HTW at 250°C. They found that a pH of 3–4 was required to achieve significant increases in the pseudo-first-order reaction rate. Hence, sufficient quantities of added CO_2 should also accelerate the reaction.

We conducted DBE hydrolysis in HTW with and without added CO_2 using valve-equipped tubing bomb reactors. To minimize the potential for pyrolysis, which becomes significant at temperatures above 300°C,[26,28] we examined the reaction at 250°C. The ring balance, defined as

$$\text{Ring balance}_{\text{DBE}} = \frac{n_{\text{Benzyl Alcohol}} + 2 \times n_{\text{Dibenzyl Ether}}}{2 \times n_{\text{Dibenzyl Ether},0}} \qquad (17)$$

where n_i is the number of moles of species i recovered from the reactor and $n_{i,0}$ is the number of moles of species i initially loaded to the reactor, varied from (87 ± 5)% to (93 ± 9)% for these experiments. Benzyl alcohol was the only product of the reaction, and no toluene or benzaldehyde was detected in any of the experiments.

Figure 7 shows the effect of varying $P^{\text{LOAD}}_{CO_2}$ on the molar yield of benzyl alcohol obtained from DBE hydrolysis in HTW at 250°C and 60 min reaction time. The product yield increased from (16 ± 11)% in HTW without CO_2 to (54 ± 27)% with a CO_2 loading pressure of 5.5 MPa. Thus, the

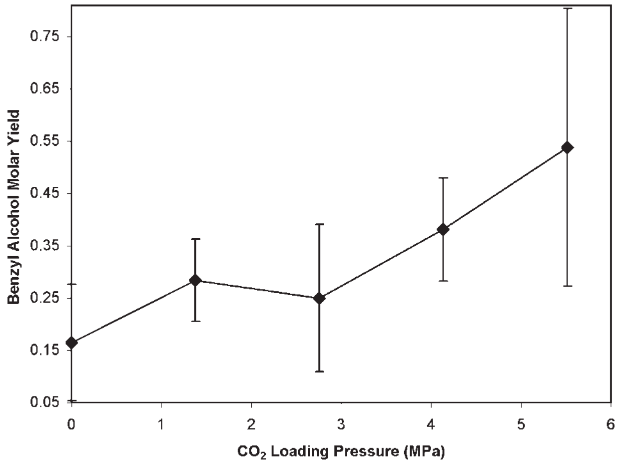


Figure 7. Effect of CO_2 loading pressure on benzyl alcohol molar yield in HTW at 250°C and 60 min of reaction time.

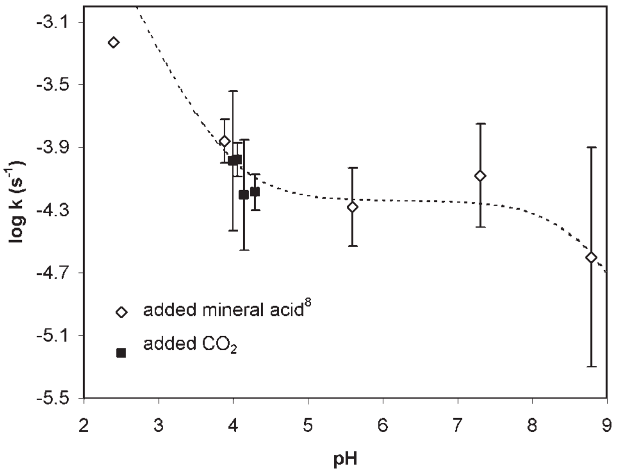


Figure 8. Comparison of pseudo-first-order rate constant for DBE hydrolysis in CO_2-enriched HTW with that in HTW with added mineral acid.[8]

addition of CO_2 was effective for increasing the rate of DBE hydrolysis in HTW.

Comisar et al.[8] report log k vs. pH data for DBE hydrolysis at 250°C, based on experiments with added mineral acid. To compare the results of the current experiments with the previous work, we estimated the pH according to Hunter and Savage[10] and calculated the value of log k for each experiment with added CO_2. Figure 8 shows the pseudo-first-order rate constants with added CO_2 plotted along with the previous data obtained with mineral acid. The experimental results obtained with added CO_2 agree well with those obtained with added mineral acid. This comparison demonstrates good consistency between added CO_2 and added mineral acid for increased rates of acid-catalyzed reactions in HTW, and suggests that CO_2 addition can serve as an environmentally benign alternative to mineral acid addition for promoting acid catalysis in HTW.

BPA Cleavage. The cleavage of BPA provides the least difficult route for synthesizing *p*-isopropenylphenol,[30] and is carried out industrially using a solid base catalyst.[31] The reaction occurs in HTW without catalyst, and may proceed via acid catalysis, base catalysis, or water catalysis.[23] Addition of sufficient quantities of mineral acid leads to acceleration of the cleavage reaction in HTW.[23] Hence, sufficient quantities of CO_2 should also lead to accelerated cleavage rates in HTW. We examined the effect of added CO_2 on BPA cleavage in HTW using tubing bomb reactors.

Figure 9 demonstrates the effect of added CO_2 on the hydrothermal cleavage of BPA at 225, 250, and 275°C. As shown in the figure, the conversion of BPA was not significantly affected by the addition of CO_2 at any of the examined temperatures. This observation is consistent with previous results concerning the effect of added mineral acid on the pseudo-first-order rate constant for BPA cleavage,[23] which demonstrate that BPA cleavage is essentially independent of pH until a sufficiently low value is reached. In the current experiments, the pH achieved with added CO_2 was not low enough to reach the pH-dependent region.

The conversion expected at 250°C and 30 min with 25 mg of added CO_2 (pH = 3.9) can be estimated using rate constants provided by Hunter and Savage,[23] which were obtained from experiments with added mineral acid. At this pH, the pseudo-first-order rate constant k for BPA cleavage is expected to be 2.0×10^{-4} s^{-1}. Using this rate constant, we calculate the conversion expected for this first-order reaction at 250°C and 30 min with 25 mg of added CO_2 to be 30%. This estimated conversion compares quite well with the experimental value of (33 ± 1)%, and further demonstrates consistency between the effects of added mineral acid and added CO_2 on the rates of acid-catalyzed reactions in HTW.

Methyl Benzoate Hydrolysis. Ester hydrolysis in HTW has been the subject of several studies.[22,32–34] Proposed ester hydrolysis mechanisms in HTW have included acid catalysis and direct attack by water,[32,34] although base catalysis is also possible.[35,36] The generation of carboxylic acids during ester hydrolysis can lead to autocatalysis, in which the generated acid provides additional protons for the reaction.[33,34] Thus, increased acidity provided by CO_2 should also promote the hydrolysis reaction. We examined the effect of added CO_2 on methyl benzoate hydrolysis in HTW using tubing bomb and valve-equipped tubing bomb batch reactors.

Figure 10 shows the results of the methyl benzoate hydrolysis experiments in HTW and in HTW with added CO_2 at 250 and 300°C. We observed only benzoic acid, methanol, and methyl benzoate as products of these experiments. The ring balance, calculated as

$$\text{Ring balance}_{\text{MB}} = \frac{n_{\text{Benzoic Acid}} + n_{\text{Methyl Benzote}}}{n_{\text{Methyl Benzoate,0}}} \tag{18}$$

ranged from (92 ± 6)% to (104 ± 5)%. At 250°C and 30 min, the methyl benzoate conversion was (44 ± 8)% in HTW and (48 ± 6)% in HTW $+CO_2$ (20 mg CO_2 added). At 300°C and 15 min, the methyl benzoate conversion was (72 ± 6)% in HTW and (75 ± 14)% in HTW + CO_2 ($P_{CO_2}^{\text{LOAD}}$ = 4.1 MPa). These results show that the added CO_2 had no significant effect on the reaction. To demonstrate that the reaction had not reached equilibrium at 250°C, we examined the reaction at 250°C for 60 min. At this longer batch

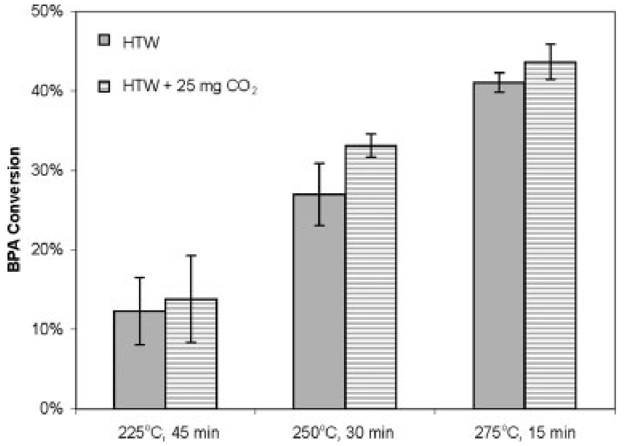


Figure 9. Comparison of BPA conversion in pure and CO_2-enriched HTW.

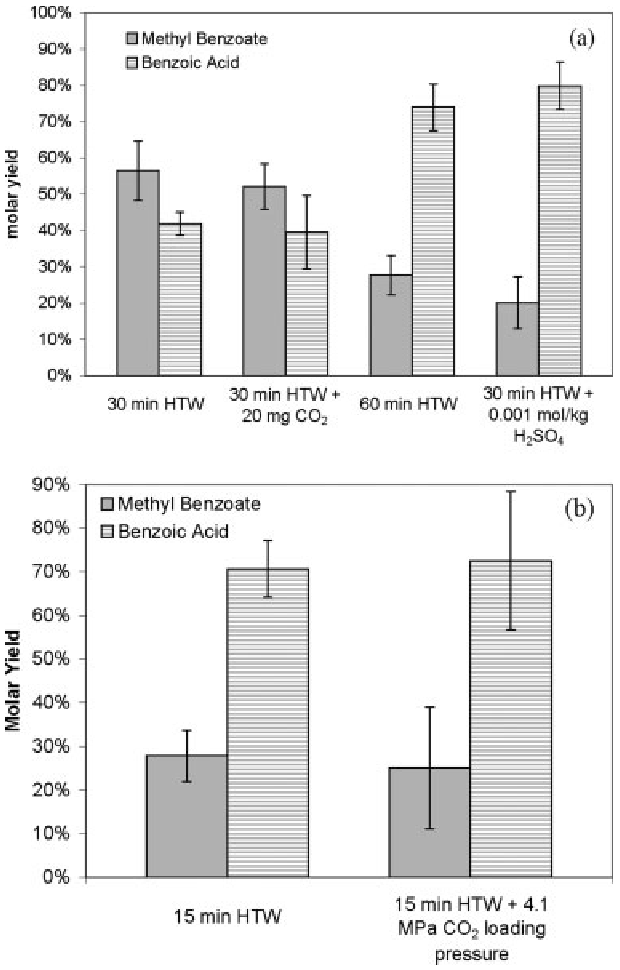


Figure 10. Molar yields of methyl benzoate and benzoic acid from methyl benzoate hydrolysis in HTW and CO_2-enriched HTW.

(a) 250°C. (b) 300°C.

holding time, the conversion was (72 ± 5)%, as compared with only (44 ± 8)% in the 30-min experiment. A longer reaction time thus led to a higher methyl benzoate conversion, whereas CO_2 addition did not have a significant effect on the conversion. Hence, CO_2 was not effective as an additive for increasing the rate of methyl benzoate hydrolysis in HTW at the examined loading.

The lack of effect of CO_2 addition on methyl benzoate hydrolysis can be explained in terms of a minimum pH that must be reached before the reaction becomes dependent on pH. Comisar et al.[8] demonstrated that a pH below 3 must be achieved to reach the pH-dependent region of methyl benzoate hydrolysis in HTW at 200–300°C. We estimated the pH in the present 250 and 300°C experiments to be 3.9 and 4.3, respectively. Thus, as in the BPA cleavage system, the amount of CO_2 added was not expected to achieve increased reaction rates.

To demonstrate that added mineral acid can increase the rate of methyl benzoate hydrolysis in HTW, we conducted an experiment at 250°C and 30 min with added H_2SO_4 at initial concentration of 1 mmol/kg. The results of this experiment are shown in Figure 10. With the added mineral acid, the conversion of methyl benzoate increased from (44 ± 8)% to (80 ± 7)%. These results suggest that increased rates of methyl benzoate hydrolysis should be accessible with amounts of CO_2 greater than those added in the present experiments.

o-Phthalic Acid Decarboxylation. The decarboxylation of aromatic carboxylic acids has received some previous attention in HTW.[9,37] These acids decarboxylate without catalyst in HTW. No mechanism has been proposed for the hydrothermal reaction, however aromatic carboxylic acids decarboxylate via an acid-catalyzed elimination mechanism in strong acid solutions.[38,39] The reaction may be autocatalytic in HTW, as the CO_2 evolved will form carbonic acid and increase the acidity of the medium. Dunn et al.[37] found that an autocatalytic kinetic model was consistent with the decarboxylation of terephthalic acid and trimellitic anhydride in HTW. Further, Aleman et al.[9] observed an increase in the conversion of mesitoic acid to mesitylene at 250°C and 2 h from 50 to 80% by adding CO_2 to their reactors. These results suggest that the decarboxylation of aromatic carboxylic acids should be enhanced in HTW with the addition of CO_2. We examined the influence of CO_2 on the decarboxylation of *o*-phthalic acid in HTW at 300°C using valve-equipped reactors.

Benzoic acid was the only organic reaction product formed. We calculated the aromatic ring balance for this system as

$$\text{Ring balance}_{\text{OPA}} = \frac{n_{\text{benzoic acid}} + n_{o\text{-phthalic acid}}}{n_{o\text{-phthalic acid},0}}. \qquad (19)$$

The ring balance varied from (92 ± 19)% to (102 ± 2)% for these experiments, and was typically 96–98% with an uncertainty of less than 8%.

Figure 11 shows the results for *o*-phthalic acid decarboxylation at 300°C in HTW and in HTW with added CO_2 ($P_{CO_2}^{LOAD}$ = 4.1 MPa). The yields obtained in CO_2-enriched HTW were not significantly different from those in HTW

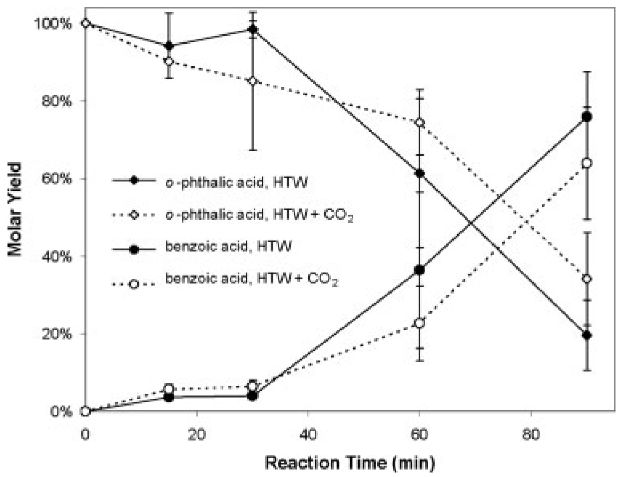


Figure 11. Molar yields of *o*-phthalic acid and benzoic acid in HTW and in HTW + CO_2 (CO_2 loading pressure = 4.1 MPa) at 300°C.

Table 2. Summary of Experimental Results for Acid Catalysis in CO_2-Enriched HTW

Reaction	Reference	T (°C)	CO_2 Loading	Estimated pH	Estimated P_{CO_2} (MPa)	XIF_{max} or YIF_{max}
Mesitoic acid decarboxylation	9	250	$P^{LOAD}_{CO_2} = 1$ MPa	N/A*	N/A*	1.9
Cyclohexanol dehydration	10	250–275	$C^{T}_{CO_2} = 0.3$–0.4 mol/L	4.1–4.2	2.9–3.4	2.5
p-Cresol alkylation	10	275	$C^{T}_{CO_2} = 0.6$ mol/L	4.1	5.1	2.2
Cyclohexene hydration	11	300	$P^{LOAD}_{CO_2} = 1.4$–5.5 MPa	4.3–4.6	1.4–5.8	5.0
Agar hydrolysis	12	160	$C^{T}_{CO_2} = 1.3$ mol/L	3.4	12.8	>23
Guar gum hydrolysis	12	200	$C^{T}_{CO_2} = 1.3$ mol/L	3.5	13.9	>2.3
Starch hydrolysis	12	200	$C^{T}_{CO_2} = 0.2$–2.2 mol/L	3.4–4.0	1.7–22.2	14
Xylan hydrolysis	12	200	$C^{T}_{CO_2} = 1.3$ mol/L	3.5	13.9	>3.2
Butanediol dehydration	7	250–300	$\Delta P_{Process} = 9.7$–11.2 MPa	3.8–4.1	9.7–11.2	4.0
Dibenzyl ether hydrolysis	Present work	250	$P^{LOAD}_{CO_2} = 1.4$–5.5 MPa	4.0–4.3	1.3–5.1	3.3
Bisphenol A cleavage	Present work	225–275	$C^{T}_{CO_2} = 1.0$ mol/L	3.7–4.0	8.5–9.8	No increase
Methyl benzoate hydrolysis	Present work	250–300	$C^{T}_{CO_2} = 0.8$ mol/L, $P^{LOAD}_{CO_2} = 4.1$ MPa	3.9–4.3	4.3–7.4	No increase
o-Phthalic acid decarboxylation	Present work	300	$P^{LOAD}_{CO_2} = 4.1$ MPa	4.3	4.3	No increase

*N/A indicates insufficient experimental information available to estimate pH or P_{CO_2}. $C^{T}_{CO_2}$ is the total carbonate loading, defined as the total number of moles of CO_2 loaded to the reactor divided by the total reactor volume.

alone. In this case, there was no measurable effect on the reaction with CO_2 addition. These results differ from those of Aleman et al.,[9] who observed a significant increase in the rate of decarboxylation of mesitoic acid with the addition of only 10 bar CO_2 at 20°C.

The apparent disagreement between these results can be attributed to the complex acid–base equilibria and kinetics that exist in aqueous decarboxylation systems. In these systems, the pH will be determined not only by the added CO_2, but also by the dissociation of the carboxylic acid species present. Hence, the pH in CO_2-enriched HTW may not be fully dictated by the added CO_2, but may be instead influenced by the carboxylic acids. Moreover, the formation of CO_2 or depletion of carboxylic acid species during the reaction may affect the pH of the solution. In fact, Gunawardena and Brill[40] report an increase in pH during reaction for the decarboxylation of malonic acid in HTW at 140–240°C. Additionally, the carboxylate anion and carboxylic acid species may react at different rates, and either species may decarboxylate faster than the other.[40] Hence, the effect of CO_2 addition on the rate of decarboxylation in HTW is not as straightforward as in the other examined systems. A detailed study is required to decouple the effects of acid–base equilibria and acid–anion kinetics on the rate, and to fully assess the potential for CO_2 addition to accelerate decarboxylation reactions.

Review of reactions in CO_2-enriched HTW

In this section, we summarize the experimental results published to date for reactions in CO_2-enriched HTW. Previous experimental studies examined the effect of CO_2 addition on decarboxylation,[9] dehydration,[7,10] hydration,[11] alkylation,[10] and hydrolysis[12] reactions in HTW. These results are summarized along with the present results in Table 2. We estimated the pH at reaction conditions when possible according to the method described in Hunter and Savage[10] except for the butanediol dehydration system. In this case, P_{CO_2} was estimated from the measured experimental pressure, and the pH calculated according to Eq. 5. Additionally, we estimated the CO_2 partial pressure from each calculated pH based on a rearranged form of Eq. 7:

$$P_{CO_2} = \frac{(H^+)^2}{K_{a1}K_H}. \qquad (20)$$

To offer a meaningful comparison of the results achieved with added CO_2, we define the conversion increase factor (XIF) and yield increase factor (YIF) as the ratio of conversion (or yield) in CO_2-enriched HTW at time t to that obtained in HTW at the same time. We then list in Table 2 the maximum XIF or YIF observed experimentally for each reaction.

Table 2 shows that CO_2 addition is effective in some systems for achieving significant increases in conversion or product yield, whereas CO_2 addition has no effect on rate in other systems. When CO_2 was effective for increasing the reaction rate, an increase in conversion or product yield by a factor of 2–5 was typically achieved. The largest two YIFs achieved were 23 and 14, which were achieved for polysaccharide hydrolysis at 160 and 200°C, respectively. It is interesting to note that these high rate enhancements occurred at the lowest temperatures investigated. This fact is consistent with the curves shown in Figure 4 and with the analysis discussed herein, which concluded that the largest rate enhancements should occur at lower temperatures in HTW.

For those systems in which CO_2 addition showed little effect, it is likely that catalysis by H^+ is not the sole mechanism operative under HTW conditions. Rather, other mechanisms such as base catalysis or water catalysis likely contribute significantly to the reaction.[7,8,23] However, with sufficient quantities of added CO_2, accelerated rates of reaction should be possible, as these systems typically demonstrate an increase in rate constant at sufficiently low pH.[7,8,23] For these systems, however, the practical application of CO_2 as a rate-enhancing additive may be limited.

We point out that the results listed in Table 2 do not represent optimized results for each system, but rather represent the results achieved based on adding arbitrarily selected amounts of CO_2 to reactions in HTW at arbitrarily selected temperatures. We expect that further exploration of the systems in which CO_2 addition accelerated the reaction can reveal greater rate increases, particularly at lower temperatures.

Summary and Conclusions

In HTW at 150–300°C, the addition of CO_2 to HTW will lead to significant increases in the reaction rate for an acid-catalyzed reaction that is first order in H^+. Increases in process operating pressure, achieved by adding CO_2, of 0.1–1 MPa are sufficient for achieving significant rate increases, but these rate increases can be roughly tripled at pressure increases of 10 MPa. CO_2 addition is expected to achieve the greatest increases in reaction rate, when compared with the rate in HTW alone, at lower temperatures (150–200°C), as calculated RIFs decreased with increasing temperature at temperatures up to 300°C. For acid-catalyzed reactions in HTW, CO_2 partial pressure can hence serve as an additional process variable for the design engineer to manipulate.

Increased rates of acid-catalyzed reactions can be achieved via increased temperature as well as by added CO_2. In HTW, an increase in operating pressure, or pressure penalty, is required for both methods. In general, CO_2 addition carries a lower pressure penalty than increasing temperature. At 300°C and up to 10 MPa added pressure (via increased H_2O vapor pressure resulting from increased temperature or via added CO_2), CO_2 addition is more effective than increasing the temperature for activation energies of up to 35 kcal/mol. Hence, for acid-catalyzed reactions in HTW that are first order in H^+, CO_2 addition can be a more environmentally benign and more industrially attractive method of rate enhancement than increased temperature, as a much lower pressure penalty is required for a given increase in reaction rate, and without any temperature penalty.

The benefits of added CO_2 for reactions in HTW that are first order in H^+ are clear, but finding such a reaction in HTW proved difficult. The effect of CO_2 addition on product yield and conversion in HTW was examined for DBE hydrolysis, BPA cleavage, methyl benzoate hydrolysis, and *o*-phthalic acid decarboxylation. Of these systems, only DBE hydrolysis showed an increase in product yield in each experiment with added CO_2. The lack of effect of added CO_2 in the other systems can be attributed to the occurrence of mechanisms other than classical acid catalysis in HTW, such as base catalysis or water catalysis, and is consistent with previously reported rate constant vs. pH information. However, the current experiments demonstrate that reaction rates achieved via CO_2 addition are consistent with those achieved with added mineral acid. Hence, CO_2 addition may be an environmentally benign alternative to mineral acid addition for achieving increased rates of acid-catalyzed reactions in HTW.

Experimental results to date demonstrate that increases in product yield and conversion are possible via CO_2 addition for some reactions in HTW. Product yield and conversion have generally increased by a factor of 2–5 with added CO_2, although in the best case reported to date the product yield increased by a factor of 23 at 160°C.

The most promising reaction, suitable for the application of CO_2-enriched HTW, will be one that is first order in H^+ at 150–200°C. For such reactions, significant rate increases will be achieved with minimal increases (0.1–0.5 MPa) in operating pressure. As the effects of pH and CO_2 addition on the rates of acid-catalyzed reactions in HTW are inherently linked, future work should focus on elucidating the effect of pH on the kinetics and mechanism of these reactions. Information obtained regarding the fundamental influence of pH on these reactions will facilitate a comprehensive assessment of the potential for CO_2-enriched HTW to serve as an environmentally benign alternative to traditional acid catalysis.

Acknowledgments

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