Spectroscopy of Hydrothermal Reactions 16: Kinetics of Decarboxylation/Hydrolysis of Methyl Propiolate Ester and Decarboxylation of Propiolic Acid at 150−210 °C and 275 Bar

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The coupled kinetics of decarboxylation and hydrolysis of methyl propiolate were determined in real time at 160−210 °C and 275 bar by using a titanium-cell flow-reactor equipped with sapphire windows for direct IR spectral detection. The rate constants were calculated from the formation of CO_2 and the disappearance of methyl propiolate at the natural pH of the solution. The product acid (propiolic) also decarboxylates, and its kinetics were determined at 150−200 °C and 275 bar for use in the overall model. At 180 °C, the relative rates are in the order propiolic acid decarboxylation > methyl propiolate decarboxylation > methyl propiolate hydrolysis. Hence, the hydrolysis step is rate-determining over most of the temperature range studied. Because of the instability of the propiolic acid product, the hydrolysis of methyl propiolate is not acid-catalyzed. Instead, the Arrhenius activation energy for the ester hydrolysis more closely resembles those previously reported for base catalysis.

Introduction

The need for detailed, directly measured kinetics and mechanisms of reactions at hydrothermal conditions has been stimulated by industrial and geochemical applications.[1−3] The ester group is among the more important organic functional groups which has yet to be investigated by direct spectral observation at these conditions. The well-known hydrolysis reaction of an alkyl ester (eq 1) produces the corresponding carboxylic acid and alcohol according to reaction 1.[4] The observed rate constant k_{obs} for the hydrolysis reaction strongly depends on the pH of the solution according to eq 2, where the rate constants k_0, k_a, and k_b refer to neutral, acidic, and basic solution conditions, respectively

$$RCO_2R' + H_2O \rightarrow RCO_2H + R'OH \qquad (1)$$

$$k_{obs} = k_0 + k_a[H^+] + k_b[OH^-] \qquad (2)$$

The kinetics of reaction 1 have been determined for ethyl acetate at 250−450 °C in the pressure range of 230−300 bar in an Inconel 625 tubular reactor by using postreaction analysis of the acetic acid and ethanol products.[5] Under the reaction conditions employed, these products essentially unreactive. Consequently, the experimental results obtained below the critical temperature of water are consistent with reaction 1 being acid-catalyzed by the formed acetic acid. Other studies on the hydrolysis of esters of relatively unreactive acids conducted with batch-mode hydrothermal conditions also show autocatalysis of reaction 1 by the carboxylic acid product.[6,7]

In addition to reaction 1, however, hydrothermal conditions may enable the esters of acids other than the most refractory carboxylic acids (e.g., acetic and benzoic acid) to undergo hydrolysis (reaction 1) and decarboxylation (reaction 3) simultaneously. Moreover, the carboxylic acid product of reaction 1 may decarboxylate and produce additional CO_2 by reaction 4

$$RCO_2R' \rightarrow RR' + CO_2 \qquad (3)$$

$$RCO_2H \rightarrow RH + CO_2 \qquad (4)$$

Therefore, the observed reaction of most esters at hydrothermal conditions may be influenced by competition of parallel reactions 1, 3, and 4.

In the present paper, the coupled kinetics of decarboxylation and hydrolysis of methyl propiolate were determined in real time in the temperature range of 160−210 °C at 275 bar by direct observation in an IR cell-flow reactor. To accomplish this task, we also needed the kinetics of decarboxylation of the propiolic acid product (reaction 5) in the 150−200 °C range at 275 bar. The propiolate group is particularly well suited for a detailed IR spectral study of these reactions because both the C≡C group and CO_2 intensely absorb in the band pass of the sapphire windows used in the flow cell (1800−3000 cm^{-1}). Moreover, the C≡C stretch of acetylene is IR inactive and does not interfere spectrally with the parent acid

$$HC{\equiv}CCO_2H \rightarrow HC{\equiv}CH + CO_2 \qquad (5)$$

Experimental Section

The propiolic acid ($HC{\equiv}CCO_2H$, 96% mass) and methyl propiolate ($HC{\equiv}CCO_2CH_3$, 96% mass) were obtained from Aldrich Chemical Co. Milli-Q deionized water was sparged with compressed Ar to expel CO_2 before use as the reaction medium. Because of the limited solubility of methyl propiolate at room temperature, the concentration chosen for the methyl propiolate solution was 0.25 *m*. Propiolic acid was studied at 0.5 *m* concentration.

The flow reactor constructed with sapphire windows, and a Ti body has been described in detail elsewhere.[8−10] The following specifications of flow reactor were employed in the present study: temperature = 150−200 °C (propiolic acid) and

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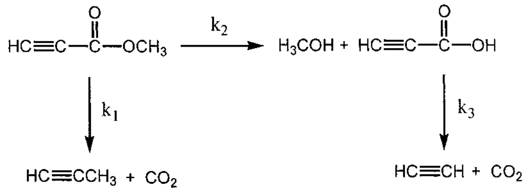
SCHEME 1



160−210 °C (methyl propiolate); pressure = 275 ± 1 bar; cell volume = 0.0819 cm^3; flow rate = 0.1−1.0 ± 0.5% mL/min; and residence time = 4.4−44.5 s.

A Nicolet 560 Magna FTIR spectrometer equipped with an MCT-A detector was used to collect transmission IR spectra at 4 cm^{-1}. The total collection time of the summed 32 spectra at each reaction condition was approximately 10 s. All of the spectra were normalized against the background spectra of pure water recorded at the same conditions. In these experiments, the asymmetric stretch of aqueous CO_2 at 2343 cm^{-1} and C≡C stretch of propiolic acid (2215 cm^{-1}) and methyl propiolate (2217 cm^{-1}) are available for calculating the kinetics of decarboxylation and hydrolysis. The absorption area of CO_2 was converted into concentration by using the Beer−Lambert Law and the previous determination of molar absorptivity of aqueous CO_2.[11] The concentrations of the acid and the ester were determined from the intensity of the alkyne stretching mode at the initial conditions. The weighted least-squares regression[12] was performed on the resulting concentration data, in which the statistical weight was set to be $1/\sigma^2$, where σ was the standard deviation of the variables.

In addition to the real-time flow kinetics experiments, batch mode experiments of hydrothermolysis of methyl propiolate were performed to identify the reactions, to help find the starting temperature for flow kinetic experiments, and to check for precipitate that might plug the flow reactor. A titanium tube with an internal volume of 12 cm^3 was sealed with the same solutions prepared for flow reactor and heated in a sand bath at a set temperature and time. The solution volume was chosen so that only the liquid phase existed at the reaction conditions. The Ti tube was then removed, immersed in a cool water bath to quench reaction, and opened. The solutions were analyzed by IR spectroscopy. It is difficult, however, to detect all of the peaks from the expected products by IR spectroscopy due to the facts that (1) the decomposed products have low concentrations, (2) the methyl propiolate evaporates, and (3) the IR radiation is intensely absorbed by water. The gases from Ti tube were collected in a gas-sampling bag and analyzed with a HP 5890 gas chromatograph with a mass selector. The expected products of methyl propiolate were confirmed to be CO_2, CH_3OH, propyne, and acetylene.

Results and Discussion

Scheme 1 shows the competitive decarboxylation and hydrolysis pathways of methyl propiolate described in this paper. This scheme is based partly on observations in Figure 1, where the peak at 2343 cm^{-1} results from CO_2 dissolved in aqueous solution and the peak at 2117 cm^{-1} is the C≡C stretch of methyl propiolate. There is no obvious shift for the peak at 2117 cm^{-1} during the reaction. The spectra did not show the C≡C absorptions of the expected propyne and propiolic acid products because the concentration is too low in the case of propyne and the C≡C absorption overlaps methyl propiolate in the case of propiolic acid. The C≡C stretch of the acetylene product from decarboxylation of propiolic acid is IR-inactive. As noted above, the GC-MS analysis showed the existence of propyne, acetylene, CH_3OH, and CO_2. Because two sources of CO_2 exist, however, it is necessary to determine the kinetics of reaction 5 as a separate study. Hence, we discuss the kinetics of propiolic acid in reaction 5 (k_3) first, followed by the hydrothermolysis of methyl propiolate (k_1 and k_2).

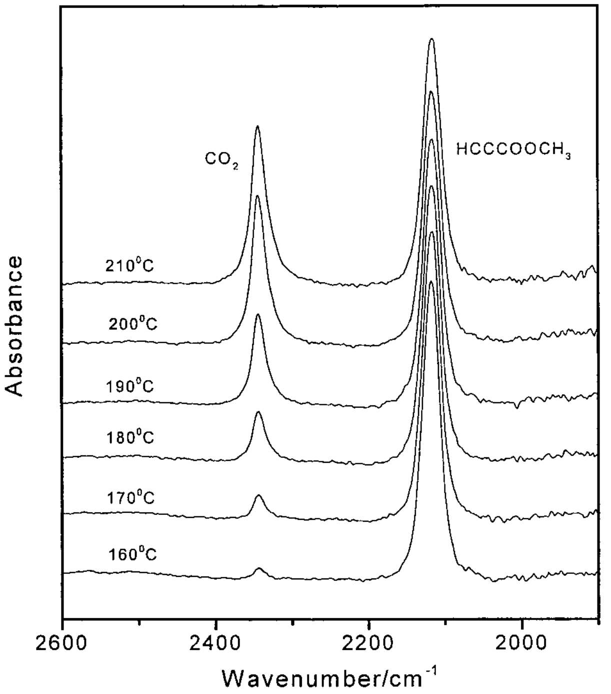


Figure 1. Transmission IR spectra reflecting the decarboxylation and hydrolysis of 0.25 *m* methyl propiolate 44 s into the reaction as a function of temperature at 275 bar.

Decarboxylation of Propiolic Acid. The IR spectra of 0.5 *m* propiolic acid at different temperatures and the residence time of 44 s are shown in Figure 2. Decarboxylation of propiolic acid occurs according to reaction 5, which was confirmed by these IR spectra. Propiolic acid is a moderately strong acid (pK_1 = 1.88 at 25 °C),[13] which necessitates that its ionization (reaction 6) be taken into account

$$HC\equiv CCO_2H + H_2O \overset{K_1}{\rightleftharpoons} HC\equiv CCO_2^- + H_3O^+ \tag{6}$$

About 5% of the acid is ionized at 275 bar and 160 °C based on an iso-Coulombic analysis.[14] Thus, the total CO_2 concentration released by the decarboxylation process comes from both the neutral propiolic acid and its anion. In the calculations here, the acid−base equilibria are always maintained because the equilibration rate is very fast compared with the decarboxylation rate. In acidic solution, the mass balance and the charge balance (eqs 7 and 8) together provide [H$^+$] at each temperature and residence time

$$[HC\equiv CCO_2H]_0 = [HC\equiv CCO_2H]_t + [HC\equiv CCO_2^-]_t + [CO_2]_t \tag{7}$$

$$[H^+] = [OH^-] + [HC\equiv CCO_2^-] \tag{8}$$

The CO_2 hydrolysis equilibrium (vide infra) can be ignored at the pH of the solution (1.5 at 25 °C) determined by the pK_a of propiolic acid. Therefore, eq 9 results

$$\ln([HC\equiv CCO_2H])_t = \ln([HC\equiv CCO_2H]_0 - [CO_2]_t) - \ln(1 + K_{a1}/[H^+]) \tag{9}$$

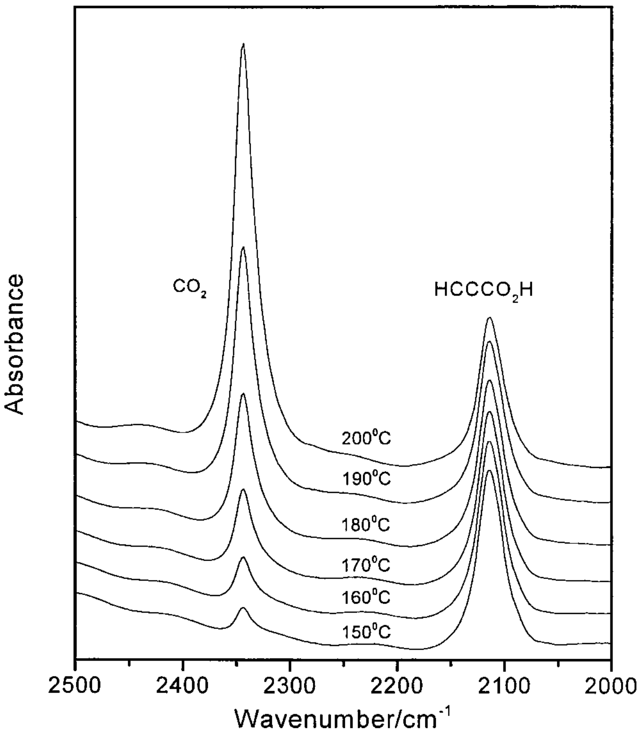


Figure 2. Transmission IR spectra showing the decarboxylation of 0.5 *m* propiolic acid as a function of temperature 44 s into the reaction at 275 bar.

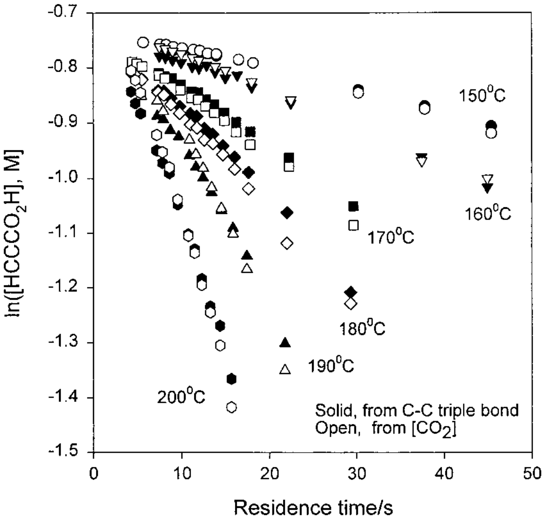


Figure 3. The pseudo first-order rate plots for decarboxylation of 0.5 *m* propiolic acid at 275 bar as measured by the change in the intensity of CO_2 and the alkyne group.

Moreover, the experimental concentration of propiolic acid is available from the IR absorption area of the C≡C band so that eq 9 is overdetermined.

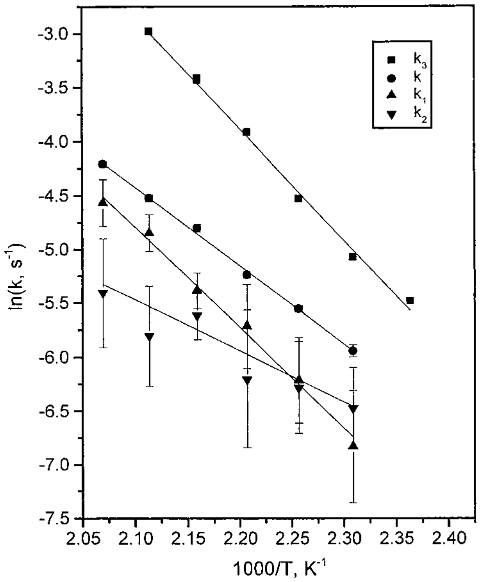


Figure 4. Arrhenius plots for the decarboxylation of propiolic acid (k_3) and the decarboxylation (k_1) and hydrolysis (k_2) of 0.25 *m* methyl propiolate at 275 bar.

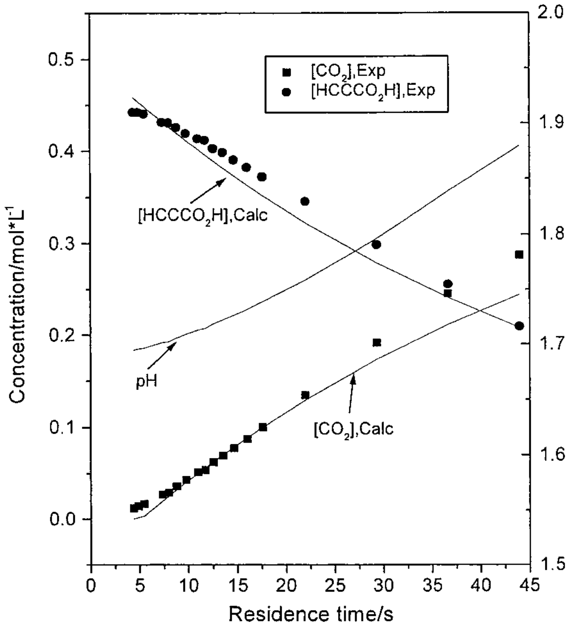


Figure 5. Experimental and calculated species concentration profiles for the decarboxylation of propiolic acid at 180 °C and 275 bar.

TABLE 1: Rate Constants and Arrhenius Parameters for the Decarboxylation and Hydrolysis of Methylpropiolate and for the Decarboxylation of Propiolic Acid at 275 Bar

temp/°C	$k_1 \times 10^3$/s^{-1}	$k_2 \times 10^3$/s^{-1}	$k_3 \times 10^3$/s^{-1}
150			4.14 ± 0.12
160	1.08 ± 0.57	1.55 ± 0.59	6.28 ± 0.16
170	2.00 ± 0.79	1.87 ± 0.80	10.81 ± 0.29
180	3.30 ± 1.28	2.20 ± 1.29	19.96 ± 0.62
190	4.58 ± 0.75	3.61 ± 0.81	32.68 ± 1.32
200	7.86 ± 1.35	3.01 ± 1.39	50.95 ±1.70
210	10.38 ± 2.24	4.55 ± 2.28	
E_a/kJ·mol^{-1}	77.64 ± 4.25	39.15 ± 7.95	86.00 ± 2.95
ln(A, s^{-1})	14.82 ± 1.09	4.41 ± 2.09	18.87 ± 0.80
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	−133	−220	−99

The variations of logarithm of acid concentration with residence time based on the C≡C stretch and CO_2 formation are displayed in Figure 3. The linearity of these rate plots indicates that the decarboxylation of propiolic acid is a first-order or pseudo first-order process. Figure 4 is the Arrhenius plot for the average of the CO_2 and acid rates. The calculated rate constants and Arrhenius parameters are given in Table 1, in which k_3 is the rate constant, E_a is the Arrhenius activation energy, ln A is the natural logarithm of the preexponential factor, and $\Delta S^{\ddagger}$ is the activation entropy calculated at the middle of the temperature range. The concentration profiles of the species in Figure 5 compares the calculated and observed values at 180 °C. The pH rises slightly during the reaction due to the loss of the acid as a result of decarboxylation.

The mechanism of decarboxylation of propiolic acid in aqueous solution is consistent with nucleophilic attack by H_2O

at the carbonyl carbon leading to the observed pseudo first-order rate constants.[10] This kind of bimolecular mechanism accounts for the negative activation entropy. Typical values for bimolecular reactions[15] are in the range of approximately −125 to −60 J K^{-1} mol^{-1}.

Methyl Propiolate Kinetics. The hydrolysis of esters in neutral pH solution follows first-order kinetics at room temperature. Base hydrolysis dominates at hydrothermal conditions in buffered solutions at pH = 5−8,[16] whereas the hydrolysis of esters of refactory acids in the batch mode indicates that the product carboxylic acids are autocatalytic.[5−7] It is reasonable to envision that the hydrolysis kinetics of esters is first-order or pseudo first-order at the conditions of the present study because (1) the experiments were conducted in a flow reactor so that the species are together in solution for only short time, (2) the dissociation constants (and hence the activity) of carboxylic acids generally decrease with increasing temperature, and (3) the decarboxylation rate of propiolic acid determined above is faster than the hydrolysis rate of methyl propiolate discussed below, which means that the steady-state concentration of propiolic acid in the solution is small.

The decarboxylation of methyl propiolate is expected to follow first-order or pseudo first-order kinetics on the basis of the decarboxylation processes of carboxylic acids at hydrothermal conditions.[10,17] Accordingly, the rate expressions 10−12 are subject to the mass balance and the

$$\frac{d[\mathrm{HCCCOOCH_3}]}{dt} = -(k_1 + k_2)[\mathrm{HCCCOOCH_3}] \quad (10)$$

$$\frac{d[\mathrm{HCCCO_2H}]}{dt} = k_2[\mathrm{HCCCOOCH_3}] - k_3[\mathrm{HCCCO_2H}] \quad (11)$$

$$\frac{d[\mathrm{CO_2}]_\mathrm{T}}{dt} = k_1[\mathrm{HCCCOOCH_3}] + k_3[\mathrm{HCCCO_2H}] \quad (12)$$

initial conditions 13−16

$$[\mathrm{HCCCOOCH_3}]_0 = [\mathrm{HCCCOOCH_3}] + [\mathrm{CO_2}]_\mathrm{T} + [\mathrm{HCCCO_2H}] \quad (13)$$

$$[\mathrm{HCCCOOCH_3}] = 0.25\ m \quad (14)$$

$$[\mathrm{CO_2}]_{\mathrm{T},0} = 0\ m \quad (15)$$

$$[\mathrm{HCCCO_2H}]_0 = 0\ m \quad (16)$$

To calculate the total concentration of CO_2 released ($[CO_2]_T$) from decarboxylation of the propiolic acid, it may be necessary to include the fact that CO_2 exists in equilibrium (eqs 17 and 18) if the pH of the solution reaches more basic conditions[17]

$$\mathrm{CO_2} + \mathrm{H_2O} \overset{K_{a1}}{\rightleftharpoons} \mathrm{H_3O^+} + \mathrm{HCO_3^-} \quad (17)$$

$$\mathrm{HCO_3^-} + \mathrm{H_2O} \overset{K_{a2}}{\rightleftharpoons} \mathrm{H_3O^+} + \mathrm{CO_3^{2-}} \quad (18)$$

In this case, the mass balance for the total CO_2 concentration is given by eqs 19 and 20

$$[\mathrm{CO_2}]_\mathrm{T} = [\mathrm{CO_2}]_\mathrm{free} + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}] \quad (19)$$

$$= [\mathrm{CO_2}]_\mathrm{free}\left(1 + \frac{\mathrm{K_{a1}}}{[\mathrm{H^+}]} + \frac{\mathrm{K_{a1}K_{a2}}}{[\mathrm{H^+}]^2}\right) \quad (20)$$

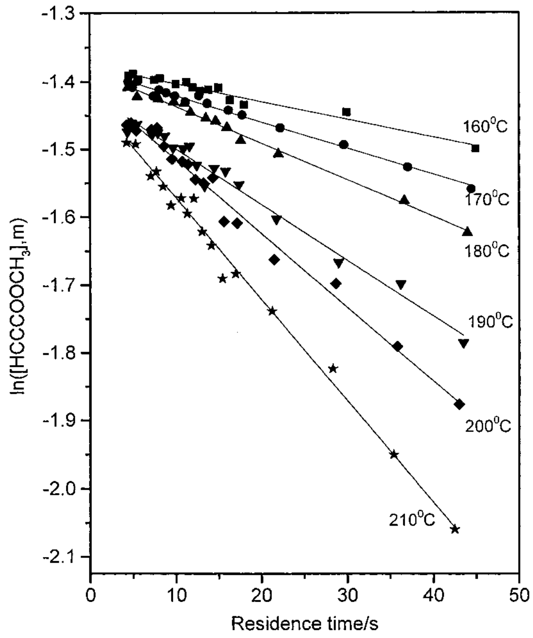


Figure 6. Pseudo-first-order rate plots for the coupled decarboxylation and hydrolysis of 0.25 *m* methyl propiolate at 275 bar.

where $[CO_2]_{free}$ is the concentration determined from the area of the asymmetric stretching mode. In the high-temperature and pressure hydrothermal solutions, the released CO_2 is completely dissolved, and no gaseous CO_2 was present, which would have been apparent by the appearance of its P and R rotational branches. According to eq 20, the observed concentration of CO_2 strongly depends on the pH of the solution. The equilibrium constants K_{a1} and K_{a2} at higher temperatures can calculated by using the iso-Coulombic extrapolation.[14] The ionization constants and specific volume of water at the temperatures of this work are needed for the iso-Coulombic extrapolation and are available.[19,20] However, the dissociation of propiolic acid is not taken into account because of its very small concentration and its decreasing dissociation constant as the temperature is raised (as calculated from iso-Coulombic extrapolation of the equilibrium constant at room temperature).[13] These approximations are entirely reasonable within the precision of these experiments.

To obtain the rate constants, we need to calculate the solution pH at each temperature and residence time. At each temperature and residence time, the mass balance

$$[\mathrm{H^+}] = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{OH^-}] \quad (21)$$

eqs 13 and 20 provide the running pH by the solution of eq 21. Finally, we obtain the integrated rate expressions 22−24

$$[\mathrm{HCCCOOCH_3}] = [\mathrm{HCCCOOCH_3}]_0 e^{-(k_1+k_2)t} \quad (22)$$

$$[\mathrm{CO_2}]_\mathrm{T} = [\mathrm{HCCCOOCH_3}]_0\left(1 + \frac{k_1 - k_3}{k_3 - k}e^{-kt} + \frac{k - k_1}{k_3 - k}e^{-k_3 t}\right) \quad (23)$$

$$[\mathrm{HCCCO_2H}] = [\mathrm{HCCCOOCH_3}]_0 \frac{k_2}{k_3 - k}(e^{-kt} - e^{-k_3 t}) \quad (24)$$

Here, $k = k_1 + k_2$, and k_3 is the rate constant of decarboxylation of propiolic acid determined in the preceding section.

Figure 6 is rate plot for methyl propiolate, which indicates the validity of the assumption of a first-order rate expression for the decarboxylation and hydrolysis. The calculated rate

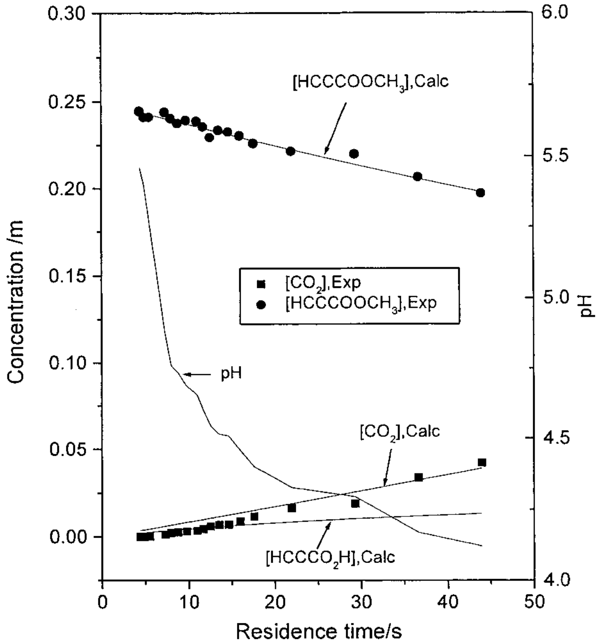


Figure 7. Experimental and modeled concentration profiles for decarboxylation and hydrolysis of 0.25 *m* methyl propiolate at 180 °C and 275 bar.

constants and Arrhenius parameters are listed in Table 1. The k_1 is rate constant of decarboxylation of methyl propiolate, and k_2 is rate constant of hydrolysis of methyl propiolate. The Arrhenius plots are shown in Figure 4. The calculated and observed concentration profiles of species at different residence times at 180 °C and 275 bar are displayed in Figure 7. The pH of the solution decreased during the reaction primarily because of the release of propiolic acid. The rates of hydroylsis obtained in our work are about an order of magnitude faster than those reported for other aliphatic esters in the pH range of 5−8.[16]

Mechanistic Conclusions

Over most of the temperature range studied, the relative rates of the three stages of hydrothermolysis of methyl propiolate are decarboxylation of propiolic acid > decarboxylation of methyl propiolate > hydrolysis of methyl propiolate. Thus, the hydrolysis step is rate-determining. Because propiolic acid decarboxylation is the most rapid of these reactions, the steady-state concentration of propionic acid is low, and thus, acid catalysis of the hydrolysis reaction is a minor factor. This result contrasts with hydrolysis of esters of more refractory acids,[5−7] such as acetic and benzoic acid. Instead, the obtained activation energy for hydrolysis of methyl propiolate (39 ± 8 kJ/mol) resembles previously reported values for base hydrolysis of aliphatic esters at hydrothermal conditions (38−49 kJ/mol).[16] At the same time, the activation energy for decarboxylation of methyl propiolate is comparable to that of propiolic acid, which is an indication that possibly a similar decarboxylation mechanism exists for methyl propiolate and propiolic acid which possibly involves nucleophilic attack by H_2O on the carbon atom of the carboxylate group.

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